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FERROELECTRICITY AND FERROELECTRIC MATERIALS

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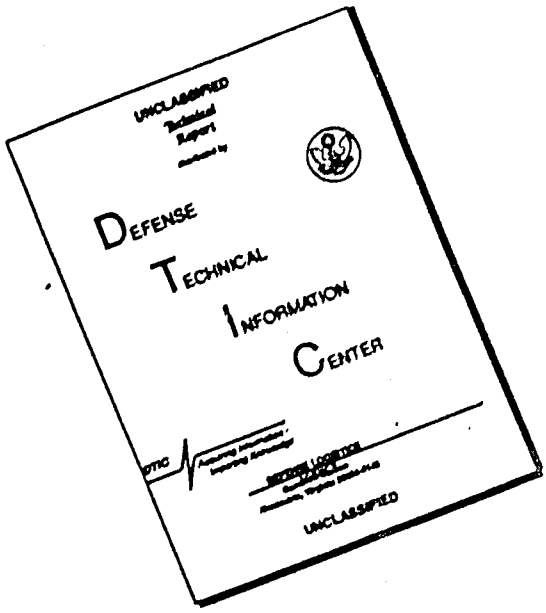

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Surveys of Foreign Scientific and Technical Literature

FERROELECTRICITY AND FERROELECTRIC MATERIALS

Work Assignment Number 72

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FOREWORD

This report, prepared in response to ATD Work Assignment No. 72, is a compilation of abstracts of articles dealing with the phenomenon of ferroelectricity and the properties of ferroelectric materials. All sources cited are available at either the Aerospace Technology Division of the Library of Congress or in the collections of the Library itself. Full translations of some of the source materials used in this report may be available from other agencies or commercially.

INTRODUCTION

This report reviews Soviet work on ferroelectricity and ferroelectric materials. The materials were selected from Soviet open-literature sources published during the period 1964–1967, with the exception of two sources: The Proceedings of the International Conference on Ferroelectricity (Prague, 1966) and the Materials of the Fifth Conference on the Problems of Ferroelectricity and the Physics of Inorganic Dielectrics (Dnepropetrovsk, 25 August - 1 September 1966) published in Akademiya Nauk SSSR, Izvestiya, Seriya fizicheskaya, v. 30, no. 7 and no. 11, 1967. The first source is available in English. The second was received in the Library of Congress too late to be included in this work and, because of its great volume (94 papers), would warrant a special study.

The report is divided into six sections, according to main groups of ferroelectrics:

I. Rochelle Salt and Related Compounds
II. Tri-glycine Sulfate (TGS) and Related compounds
III. Potassium Di-hydrogen Phosphate (KDP) and Isomorphous Crystals
IV. Barium Titanate and Other Perovskite Type Oxides
V. Miscellaneous Complex Oxides and Other Materials
VI. Methods and Instruments.

The report concludes with an alphabetic Author Index.

I. ROCHELLE SALT AND RELATED COMPOUNDS

1. Anistratov, A. T., and K. S. Aleksandrov. Electrooptical properties of Rochelle salt. Kristallografiya, v. 12, no. 3, 1967, 459-464.

Experimental investigations were carried out to refine the available data concerning the distinction of the linear (morphic) electrooptic effect from the quadratic and to establish the character of temperature dependences of these coefficients within the range covering the phase transition points of Rochelle salt. The dynamic method described earlier by Anistratov and others (AN SSSR, Izvestiya. Seriya fizicheskaya, v. 29, no. 6, 1965, 973; Kristallografiya, v. 11, no. 2, 1966, 255; Pribory i tekhnika eksperimenta, no. 3, 1965, 193) was used in the determination of the experimental data. Formulas describing the relationships between the measurement data, and both the linear and the quadratic coefficients were obtained, which make it possible to form certain general conclusions concerning the behavior of these coefficients as functions of temperature and of the applied constant and alternating fields along the ferroelectric axis with light propagating along the Y and Z axes. The authors thank I. S. Zheludev and L. A. Shuvalov for their attention.

2. Anistratov, A. T. Anomalous linear electrooptic effect in Rochelle salt. Kristallografiya, v. 11, no. 5, 1966, 823-825.

The author investigated the temperature dependence of the linear electrooptic effect in the vicinity of the Curie point by measuring simultaneously the dielectric constant of the free crystal and the coefficient of linear electrooptic effect r_{41} under identical conditions. The quantity actually investigated was $\rho_{41} = \partial\Delta a_{23}/\partial P_1$, where Δa_{23} is the increment of the polarization constant and P_1 is the polarization; the reason for investigating this quantity is that it is expected to have no anomaly in the transition region. The measurements were made on X-cut single-crystal Rochelle salt in the temperature interval +18 - 29°C in monochromatic light (546 nm) by a procedure described earlier (Izv AN SSSR, Ser. fiz., v. 29, no. 6, 973, 1965). The balance indicator was an oscilloscope. The measurements of ρ_{41} and of the dielectric constant were made simultaneously by applying to the sample a constant polarizing field ranging from 265 to 2000 v/cm. The resultant plot of ρ_{41} against the temperature shows that at large electric fields (2000 v/cm), much larger than the coercive fields, the value of ρ_{41} is independent of the temperature and of the polarizing field. However, when the polarizing fields are comparable to the coercive fields (265—700 v/cm), the deviation from constancy increases as a result of measurement errors

and losses due to the domain structure. An estimate of $-4.4 \pm 0.2 \times 10^{-8}$ cgs esu is obtained for ρ_{41}. The part of the effect induced by the inverse piezoeffect is estimated at -0.6×10^{-8} cgs esu. The spontaneous rotation of the optical axes of the free crystal is estimated at $2\phi \approx 3.1°$, in agreement with other work. It is therefore concluded that the electrooptic coefficient of Rochelle salt does not change on going through the upper Curie point and is not connected with dielectric anomalies.

3. Gerken, V. A., V. I. Pakhomov, A. S. Sonin, Ye. I. Marchenko, and V. N. Nepomnyashchaya. Ferroelectricity in tetramethylammonium triiodomercurate. Kristallografiya, v. 12, no. 4, 1967, 607-611.

Experimental investigations were carried out on some dielectric properties and the structure of the $[N(CH_3)_4]$ HgI_3 crystals. The permittivity along the ferroelectric axis, measured at 500 kc as a function of temperature, was 5.2 at room temperature and rose moderately with increasing temperatures, reaching a value of 8 at 100°C. An interesting feature of the hysteresis loops was observed. In distinction from the majority of ferroelectrics, a linear ratio between the polarization and the applied field intensity exists at subcritical field strengths (in this case 2.5 kv/cm). With stronger fields, a non-saturated loop with predominant increase along the vertical is formed, while the coercive field grows very little. Its magnitude (3.9 kv/cm at room temperature) was nearly independent of temperature, dropping a little before melting. The spontaneous polarization grew from 2.8 to 7.0 μk/cm within the same temperature range. The structure and the mechanism of polarization reversal are explained on the basis of the model of the molecule of $[N(CH_3)_4]$ HgI_3 proposed earlier by Pakhomov and Gerken (AN SSSR, Izv. Ser. fiz., v. 29, 1965, 901). A slight change of atom coordinates in this structure leads to formation of nearly tetrahedral HgI_3^- ions distinct from the pyramidal ions of, for instance, $HgBr_3^-$. Polarization reversal, connected with mirror-image transition of the anions, leads to considerable displacements of the heavy atoms of the molecule. This might be also the cause for a critical field intensity value needed to effect the polarization reversal. On the basis of these properties, the authors assume that a distinct class of ferroelectrics can be outlined. The domain structure and its changes under the field action present an interesting area for further investigations.

4. Gordeyeva, N. V., and A. V. Shubnikov. Enlargement of Rochelle salt grains in their own solutions under the action of temperature fluctuations. Kristallografiya, v. 12, no. 2, 1967, 186-190.

Experiments were carried out to establish the conditions for self-enlargement of Rochelle salt crystals in their own solutions. A special device described by Parvov (Kristallografiya, v. 11, 1966, 3) was used for the experiments. The experiment could be conducted without interruption, and test tubes could be removed and inspected. Rochelle salt was used for the experiments because of its steep solubility gradient with respect to temperature. The effect of controlled cyclic temperature fluctuations (0.6—0.7°C amplitude and 1.3-hour period) on the process of growth was established as the supply of the necessary initiating energy to incite the growth of crystals. Specimens of about 1 cm^3 could be grown from powder within a period of 3 to 4 months.

5. Gorelik, V. S., I. S. Zheludev, and M. M. Sushchinskiy. Study of the Raman spectrum of the $NaNO_2$ single crystal near the phase transition point. Kristallografiya, v. 11, no. 4, 1966, 604-609.

This is a continuation of an earlier study (Kristallografiya, v. 10, no. 3, 1965, 335) and deals with the behavior of most lines of the Raman spectrum of single-crystal $NaNO_2$ in the temperature interval from 30 to 178°C. Principal attention was paid to the small temperature range (±20°) near the phase transition point (160°C). The single crystal was a rectangular prism 3 x 7 x 10 mm, cut so that its smallest side was oriented along the ferroelectric axis z. The Raman spectra were photographed with a spectrograph, using the 4358 Å mercury line for excitation. Seven lines were registered, whose frequencies agreed essentially with those published earlier. The Raman spectrum obtained near the transition point differed noticeably from that obtained at 30°C. The low-frequency lines shifted in linear fashion, while the higher-frequency lines exhibited practically no shift. All observed lines broadened with increasing temperature, but the broadening of the low-frequency lines was larger. Some of the lines vanished with increasing temperature. A group-theoretical analysis of the spectrum for both the high- and the low-frequency parts of the spectrum is used to interpret the results. The vanishing and the intensity variations of the spectra agree with the selection rules, and the broadening is due to ordinary temperature effects connected with the increase of the interaction between the lattice oscillators themselves and the interaction between the lattice oscillators and other degrees of freedom of the crystal.

6. Krasnikova, A. Ya., V. A. Koptsik, B. A. Strukov, and Van Min. Dielectric and optical investigations of the irreversible ferroelectric phase transition in crystals of potassium. Fizika tverdogo tela, v. 9, no. 1, 1967, 116-121.

The authors carried out precision measurements of the dielectric constant, polarization, and the coercive field, and also investigations of birefringence of tetragonal potassium ferrocyanide crystals in the temperature interval -10 — -70°C. The apparatus used for the investigations is described elsewhere (PTE, no. 1, 1961, 183 and earlier). All the electric and optical properties exhibited anomalies near the ferroelectric phase transition point at -56.6°C. For the tetragonal crystals tested, the irreversible transition is accompanied by spontaneous polarization along the [101] and [101] directions, with values 1 and 0.75 microcoulomb/cm^2 respectively. It was also observed that in crystals with small angles between the optical axes irreversible transitions are observed at temperatures that increase with increasing angle between the optical axes. Comparison of the results with nuclear magnetic resonance and other tests made on these crystals leads to the conclusion that a probable connection exists between the physical properties and the fact that as a rule a potassium ferrocyanide crystal does not crystallize with any one distinct structure, but all its structural types crystallize simultaneously so that it is difficult to establish the limits governing the crystallization conditions of any particular modification.

7. Krasnikova, A. Ya., I. N. Polandov, and V. P. Mylov. Character of the behavior of the ferroelectric properties of potassium ferrocyanide. Fizika tverdogo tela, v. 8, no. 11, 1966, 3320-3323.

This is a continuation of earlier work (FTT, v. 8, no. 1, 1967) dealing with the ferroelectric phase transition in potassium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$ in different crystalline modifications. The purpose of the present investigation was to determine the influence of high hydrostatic pressure on the dielectric properties of potassium ferrocyanide, in order to obtain new information on the character of the polytypical transformations observed in this crystal. A single crystal with [101] cut, grown from a solution of recrystallized salt, was tested. The dielectric characteristics were measured in the temperature range from 0 to -55°C at pressures up to 5500 kg/cm^2. The tests showed that the greatest sensitivity of the dielectric constant to pressures observed in the region of the transition to the paraelectric phase, for which the rate of change of the transition temperature with pressure is 2.3×10^{-3} deg cm^2/kg, and the rate of change of the maximum dielectric constant with pressure is 11.8×10^{-3} kg^{-1} cm^2. The temperature dependence of the dielectric constant of potassium ferrocyanide exhibited an oscillatory dependence on the temperature, with the values of the peaks and the distances between them differing with the applied pressure.

8. Romanyuk, N. A., and N. S. Pidzyraylo. Effect of hard radiation on certain optical and dielectric properties of Rochelle salt crystals. Kristallografiya, v. 9, no. 6, 1964, 870-875.

The effects of ultraviolet and x-ray radiation on the absorption spectra, the dependence of the initial dielectric constant on the temperature, and the shape of the hysteresis loop of Rochelle salt crystals were investigated in specimens cut from a single crystal. Dielectric and optical measurements were carried out on specimens of 0.5—1 mm and 0.3—10 mm thick respectively. In the case of x-ray irradiation, the investigation proved some already known rules of variation for the initial dielectric constant, the hysteresis loop, and some other features of Rochelle salt. In the case of ultraviolet irradiation, both the initial dielectric constant and the form of the hysteresis loop vary qualitatively in the same manner. A comparison of the changes caused by ultraviolet and x-ray irradiation of the crystal showed that the displacement of the Curie point due to the same relative changes in ε_{max} is considerably smaller for ultraviolet radiation, not exceeding several tenths of a degree. An investigation of the variation in the specimen's properties with the time showed that the ε_{max} changes during some definite time interval after irradiation, first departing from the initial state, then approaching the initial state. An investigation of the absorption spectra showed that definite changes in the absorption spectrum due to x-ray irradiation were observed only during a longer isothermal rest of crystals after irradiation. They resulted in a slow decrease of absorption in the investigated spectral range during four months of "rest", and the optical density decreased at most by 15% of the value reached immediately after irradiation of the specimen. Ultraviolet irradiation appeared to cause no substantial changes in the absorption spectra of Rochelle salt crystals, even when the changes in ε_{max} were considerable.

9. Starodubtsev, S. V., and Ye. V. Peshikov. Radiation changes of properties of ferroelectrics due to an internal displacement field. Fizika tverdogo tela, v. 7, no. 11, 1965, 3175-3179.

The properties of triglycine sulfate and Rochelle salt irradiated with gamma rays from a CO^{60} source at a dose rate of 0.4—0.6 Mr/sec were investigated. The comparison of the plot of the dielectric constant near the upper peak value of the Curie point E_{max} versus the external biasing field with that of E_{max} as a function of the internal space charge field showed that the effect of the biasing and space charge fields are equivalent and can be considered to be secondary effects arising as a result of irradiation. An attempt was made to explain an increase in E_{max} of Rochelle salt at small doses of x-ray and gamma irradiation. The effect of the space charge field during pulsed polarization of irradiated triglycine sulfate was also investigated.

10. Vlokh, O. G., and L. F. Lutsiv-Shumskiy. Spontaneous electro-optical effect in Rochelle salt crystals. Kristallografiya, v. 12, no. 3, 1967, 455-458.

Experimental investigations were made of the spontaneous electro-optic effect in Rochelle salt crystals. The spectral method was used and the effect was studied on the basis of the character of birefringence changes in the direction of crystallographic axes in the region of the upper Curie point as functions of temperature and the dispersion. The results showed that the birefringence in this direction is proportional to the square of spontaneous polarization, while the angle of the spontaneous turn of the optical indicatrix is proportional to the spontaneous polarization of the first degree. This means that at the transition to the polarized phase in the region of the upper Curie point, both linear and quadratic electro-optic effects take place. The linear effect is connected with the turn of the indicatrix, while the quadratic stems from the deformation of the indicatrix in the direction of original crystallographic axes. The constants of these spontaneous effects were derived from equations describing the induced linear and quadratic electro-optic effects in the paraelectric phase, replacing in them the field intensity value with that of the spontaneous polarization. Deformation of the indicatrix on account of the linear effect can occur only in the direction of new crystallographic axes effected by polarization.

11. Zheludev, I. S., and V. V. Gladkiy. The pyroelectric effect in single crystals of Rochelle salt. Kristallografiya, v. 11, no. 3, 1966, 415-418.

Pyroelectric coefficients of Rochelle salt single crystals were measured between -30° and +30°C after polarization by mechanical straining. The pyroelectric charge was measured in a Tepler thermostat by the compensation method using slow heating rates. Temperatures were measured with Cu-constantan thermocouples to 1 or 2°C beyond the Curie point. The polarization P of the strained crystals

$$P = P_{sp} \frac{S_1 - S_2}{S} + P'$$

where P_{sp} is the spontaneous polarization; P' is the elastic polarization; S_1, S_2 are cross-sectional areas of domains having unlike signs in the crystal face perpendicular to the X axis; $S_1 + S_2 = S$ (area of the sample). The variables P_{sp}, P', S_1 and S_2 depended on T and Y_z the polarizing stress. Pyroelectric coefficients (p), obtained from $p=dP/dT$, were given as a function of temperature T for values of Y_z ranging from 0 to 4100 g/cm^2. From -30° to 0°C p was positive, from 0° to 30°C—negative. Cusps occurred near the Curie temperatures (T_k = -18°C and +24°C), the exact position being dependent on Y_z. The magnitude of p was also dependent on Y_z, rising steadily to Y_z^0 which corresponded to a critical value of S_1-S_2, whereupon it decreased slightly. Close to the Curie points, p was maximum (300 CGSE units at -18°C and 340 CGSE units at +24°C) corresponding to the monodomain state in the salts, or equivalently $Y_z = Y_z^0$ = 2280 g/cm^2. Increasing Y_z to 4100 g/cm^2 lowered p insignificantly.

12. Zheludev, I. S., and N. A. Romanyuk. Dielectric properties of pressed Rochelle salt crystals. Kristallografiya, v. 11, no. 4, 1966, 610-613.

The authors report an investigation of the domain structure, the hysteresis loop, and the initial dielectric constant of Rochelle salt crystals in the region of the upper Curie temperature for different degrees of compression of the samples. The tests were made on square polished plates with 45° X-cut, measuring 10 x 10 x (0.4—0.7) mm. The samples were measured on a microscope stage in a thermostat equipped with a device for simultaneous or successive compression of the crystals in two mutually perpendicular directions. This apparatus was described in an earlier paper (Kristallografiya, v. 4, no. 5, 710-717, 1959). The dielectric constant was measured with a bridge and a hysteresis loop was by means of a Sawyer-Tower circuit. The domain structure was observed visually and photographed when necessary. The results showed that the dielectric constant decreased with increasing compression, the upper Curie point increased in the case of unilateral compression and decreased in the case of bilateral compression, and the hysteresis loops gradually contracted to lines with increasing compression. The results agree with modern theoretical notions concerning the laws governing polarization of ferroelectrics and explain the radiative changes occurring in the dielectric properties of ferroelectric materials. The results also serve as a confirmation of the frequently used "internal field" model for the explanation of the polarization of the ferroelectric.

II. TRI-GLYCINE SULFATE (TGS) AND RELATED COMPOUNDS

1. Brandt, A. A., and V. Ya. Shevchenko. Polarity reversal of triglycine sulfate crystals in linear periodic fields of 10^2—10^{-5} cps frequency. Kristallografiya, v. 10, no. 9, 1964, 292-293.

An experimental investigation was made of the coercive field values of triglycine sulfate for various polarity reversal voltages within the 10^2—10^{-5}[sic] cps frequency range. Sawtooth-shape voltage was used to exclude the effect of the voltage gradient changes which accompany the frequency change with sinusoidal waves. The measurements were made under saturation conditions at room temperature. The single-crystal specimen (5 x 5 x 0.5 mm) had etched electrodes of dispersed silver. The measurement method was described earlier by Brandt and Larionov (Voprosy radioelektroniki. Ser. 3, radiodetali i uzli, 5—6, 1960, 147). The results of the investigation show that the dependence of the magnitude of the coercive field on the electric field gradient (in the logarithmic scale) at various frequencies has two areas of linear dependence, each with a different gradient. The first area covers the 10^{-5} —10^{-3} cps range, and the other, all higher frequencies. The lower frequency range is characterized by a much higher gradient than the higher range (about six times, in terms of the tangent of the slope angle). It appears that there are two different mechanisms of ferroelectric polarization in triglycinesulfate but their character could not be established in the experiments. The measurement data show (at the 200 cps frequency) a coercive field strength of 600 v/cm, which agrees with data published by Pulvari and Kuebler (J. Appl. Phys., v. 29, no. 12, 1958, 1742).

2. Gavrilova-Podol'skaya, G. V., S. P. Gabuda, and A. G. Lundin. Nuclear magnetic resonance and ferroelectric properties of mixed sodium hydroselenite crystals. Fizika tverdogo tela, v. 9, no. 4, 1967, 1166-1170.

The ferroelectric properties and proton magnetic resonance (PMR) spectra of mixed sodium hydro- and deuteroselenite crystals of the composition $Na[H_{1-x}D_x]_3 (SeO_3)_2$, where $0 \leq x \leq 1$, were studied in the range from room temperature to -120°C. The dependence of the Curie temperature on the deuterium content (x) was found to be nonlinear, while the dependence of second moment S_2 of the PMR spectra on x was found to be linear. Theoretical analysis shows that this linear dependence proves a random substitution of protons by deuterons.

The PMR data lead to the following important conclusion: transition from the ferroelectric to the paraelectric phase is not associated with a dynamic disordering of the hydrogen bonds, as had been proposed; actually, a "static" disordering of the hydrogen bonds takes place. In the ferroelectric range, the protons occupy fixed positions at distances of ~1 Å from oxygen atoms. In the paraelectric range, the protons also occupy definite positions, but at approximately the same distance from two oxygen atoms, and possibly oscillate slightly. In conclusion, the authors thank L. I. Zherebtsova, who made the dielectric measurements, and A. I. Rostuntseva, who grew the crystals.

3. Gavrilova-Podol'skaya, G. V., S. P. Gabuda, and A. G. Lundin. Nuclear magnetic resonance in sodium tri-hydrogen selenite single crystals. Kristallografiya, v. 12, no. 1, 1967, 141.

The method of nuclear magnetic resonance was used to investigate the positioning of protons and the system of hydrogen bands in $NaH_3(SeO_3)_2$ single crystals. The specimen crystals were grown from an aqueous solution of the corresponding acid salt up to dimensions of 15 x 10 x 6 mm. The nuclear magnetic resonance spectra recorded at various orientations of the specimen with respect to the external magnetic field were used to compute the coordinates of the protons within the structure by the McCall method (Acta crystallogr. 12, 1959, 81). Out of three possible models of hydrogen bonds satisfying the calculation results, one came fairly close to the experimental data. In this model all oxygen atoms were linked with hydrogen bonds. The investigations of the temperature dependence of the nuclear magnetic resonance spectra showed a virtual independence of the form and width of their spectrum from the temperature up to the Curie point, where a jump in the secondary moments occurs. The band width undergoes a sudden increase with the transition from the ferroelectric to the paraelectric phase. It is concluded that the order of hydrogen bonds has a stationary character below the Curie point. The positioning of protons in the ferroelectric phase, however, requires further investigations of the moments within the range below -79°C.

4. Ivanov, N. R., and V. F. Zotov. Crystal-optical characteristics of certain monoclinic ferroelectrics. Kristallografiya, v. 11, no. 6, 1966, 924-926.

Experimental investigations were made of the crystallo-optic characteristics of several (triglycine sulfate, triglycine selenate, lithium hydro-selenite, Rochelle salt) ferroelectric materials. The frequency dependencies of the refractive index, the dispersion of the birefringence, and of the angle of optical axes, the electro-optic and thermo-optic coefficients, and the temperature dependence of the angle of optical axes were investigated and compared to some data in the literature (J. M. Dion, Acta crystallogr. 12, 1959, 259; Y. Makita, J. Phys. Soc. Japan, 20, no. 9, 1965, 1567).

5. Ivanov, N. R., and L. A. Shuvalov. Rotation of the optical indicatrix in triglycine sulfate crystals under action of the electric field E_y. Kristallografiya, v. 11, no. 5, 1966, 760-765.

Experimental investigations were carried out of the orientation of the optical indicatrix of triglycine sulfate in the electric field within the temperature range including the Curie point. Both the field and light were applied along the ferroelectric axis. At field strengths up to 15 kV/cm, the rotation of the indicatrix followed approximately the square law at temperatures not too close to the Curie point. In the ferroelectric phase, at temperatures further removed from the Curie point, the dependence was linear with a tendency to saturation at high field intensities. The investigation of the electro-optic effect showed that a sharp upward jump of the f_{52} coefficient at the phase change is caused by a dielectric anomaly. The investigations of the rotation of the optical indicatrix in weak (up to 4 kV/cm) fields, the expected but never observed quadratic loops of electro-optical hysteresis were discovered. The loop differed considerably from the usual butterfly pattern, showing peaks connected with the polarity reversal. The magnitude of the peaks and the character of the loops depended on the natural unipolarity of the crystal. In a well-annealed nonunipolar specimen, the loop approached the symmetric butterfly pattern, but retained the peaks in a reduced form. In unipolar crystals, this symmetry was distorted to a great extent, and the form of the loop was strongly affected by the field change rate. The optical indicatrices of anti-polarized domains in unipolar triglycine sulfate crystals were found to be disoriented to an extent not explainable by the electro-optic effect alone. The internal mechanical stresses stemming from impurities, imperfections and growth conditions, resulting in an elasto-optic effect appeared to contribute to the existense of peaks connected with the polarity reversal. It was assumed that the polarity reversal is accompanied by a change of the monoclinic angles and shearing oscillations of the crystal. The authors proposed a new method of investigating the domain structure in crystals in which the domains cannot be observed by the usual polarization-microscopic method.

6. Ivanov, N. R., and L. A. Shuvalov. Behavior of optical indicatrices of certain monoclinic ferroelectric crystals with change in temperature. Kristallografiya, v. 11, no. 4, 1966, 614-621.

This is a continuation of earlier work (Kristallografiya, v. 9, no. 3, 1964, 363) and it is devoted to a measurement of the rotation of the optical indicatrix in three monoclinic ferroelectric substances (triglycine sulfate triglycine selenate, lithium hydroselenite) with change in temperature. The angle of rotation was measured by two methods,

polarimetric and conoscopic (both results gave excellent agreement), but only the conoscopic method was used to measure the angle of the optical axis. All the experiments were made with the aid of a spectral polarimeter developed by the author (with A. V. Mirenskiy and G. D. Shnyrev), and prepared by the Design Office of the Crystallography Institute. The apparatus and the test procedure are described in detail. The results show that the temperature dependence of the rotation of the optical indicatrix was linear in the paraelectric and strongly nonlinear in the ferroelectric phase in the case of triglycine sulfate and selenate. The Curie points found from these plots were 48.2 and 22.9C for the sulfate and selenate, respectively. With decreasing temperature, the relation again becomes linear. In the case of lithium hydrosenite, the dependence was linear in the entire range of temperatures. The results are interpreted on the basis of the thermo-optical and spontaneous electro-optical and elasto-optical effects. It is shown that the obtained results lead to several general conclusions and estimates.

7. Ivanov, R., L. A. Shuvalov, and L. D. Kislovskiy. On the structural mechanism of the electro-optical and thermo-optical effects in ferroelectric crystals of the triglycinsulfate type. IN: Akademiya nauk SSSR. Doklady, v, 171, no. 5, 1966, 1092-1095.

Theoretical and experimental investigations were made of the important part played by the deformation of SO_4^{2-} or SeO_4^{2-} ions in the occurrence of spontaneous polarization in monoclinic triglycinsulfate or triglycinselenate crystals. The deformation resulting from the displacement of nitrogen atoms can be measured by directional changes of the maximum polarizability,i.e., by shifts of the indicatrix of the crystal. Measurements were performed of the shifts of the optical indicatrix in the paraelectric phase at a temperature close to the melting temperature of the crystals. These shifts showed up as breaks on the ϕ (T) dependence curves, which are explained as indicating the presence in both crystals of several characteristic temperatures above the Curie point, at which the rupture of bonds takes place. It is suggested that the results can be extrapolated to other crystals of the same type. Thus, for example, one can calculate that the melting temperature of triglycinfluoberyllate is 230—235°C.

8. Kislovskiy, L. D., and Ye. K. Galanov. The nature of the molecular mechanism of phase transition in ferroelectrics which are isomorphous with crystals of triglycinesulfate. IN: Akademiya nauk SSSR. Doklady, v. 170, no. 2, 1966, 327-328.

An experimental investigation was made of the molecular mechanism of the transition to the ferroelectric phase of crystals which are iso-

morphous with triglycine sulfate (TGS). The measurements were made to check the accepted view that the shift of the 1150 cm^{-1} band is connected with strain oscillations of the NH_3^+ (I) group. Since the spectrum of the triglycine selenate (TGSe) displays, at the phase transition, a change connected with the oscillations of the SeO_4^{2-} ion (or SO_4^{2-} in case of TGS), there is some indication of deformation of these rigid ions. A comparison was made between the sequence of the Curie temperatures of an isomorphous series and its sequence of rigidity criteria, which must be, at least in the first approximation, proportional to the energy difference in the electron configurations corresponding to the change of symmetry at the phase transition, which are in turn dependent on the rigidity of the electron shell and are characterized by the ionization energies of sulfur and selenium, respectively. The calculations showed that the steps in Curie points from one material to another roughly corresponded to the steps in respective ionization energies. This assumption would also explain the effect of deuteration on the shift of the Curie point in TGS, since the investigations showed a shift of bands connected with the oscillations of the SO_4^{2-} ion towards the shorter wavelengths, which is equivalent to an increase in rigidity and to a rise in the Curie point. The authors assume that the consideration of the possibility of transition of electron configuration into a state of different symmetry in certain quasisymmetric ions characteristic of ferroelectrics may furnish a new approach to the solution of the problem of the phase transition mechanism, applicable also to other ferroelectrics.

9. Koldobskaya, M. F., V. A. Meleshina, I. S. Rez, Z. A. Mironova, I. V. Gavrilova, and G. M. Safonov. Changes in the homogeneity of properties within the volume of triglycine sulfate crystals depending on the conditions of growth. Kristallografiya, v. 11, no. 5, 1966, 785-793.

Experimental investigations were made to establish the effect of conditions of growth of triglycine sulfate crystals on the homogeneity of their ferroelectric properties from point to point within their volume. The lack of symmetry of polarization with respect to the sign of the applied field, the saturation of the spontaneous polarization below the maximum, and the lack of polarization stability in time, were the inhomogeneities to be reduced by appropriate conditions of growth. By variations in temperature, rate of growth, and number of recrystallizations, a number of specimens with varying property characteristics were obtained. The experiments showed that the best homogeneity was achieved in crystals grown at a constant temperature above the phase transition point. It is concluded that it is possible to control the static domain structure and the uniformity of hysteresis characteristics within the crystal volume and thereby to establish a preference of the most homogeneous zones in the triglycine sulfate crystals. The article contains data on the changes of the density of dislocations accompanying changes in the domain patterns on occurrence of the anomalous polarization phenomena.

10. Kremenchugskiy, L. S., and V. B. Samoylov. Investigation of the pyroelectric effect in triglycine sulfate crystals. Kristallografiya, v. 12, no. 6, 1967, 1077-1079.

Measurements were made of the temperature dependence of the pyroelectric coefficients of triglycine sulfate single crystals at varying magnitudes of the applied electric field strength. The method originally proposed by Chynoweth(Phys. Rev., v. 117, no. 5, 1960, 1235) was used. The experimental setup was described earlier by Artyukhovskaya, the authors and others (AN SSSR. Izvestiya. Seriya fizicheskaya, v. 29, no. 11, 1965, 2110). The results of the measurements under opposite field polarities applied alternately, plotted against the temperature within the 45 to 52°C range, showed at positive fields typical single-domain characteristics with a spread at high fields and an insignificant (0.2—0.3°C) shift of the maxima of the coefficient toward higher temperatures. For reversed fields, a sharp drop of the coefficient in fields below 300 V/cm was observed when approaching the phase transition. It was possible to choose the field strength to keep the coefficient through the transition at a magnitude below that at room temperature. The drop apparently is caused by a rearrangement of the domain structure. The measurements also confirmed the shift of the maximum of the pyroelectric coefficient toward lower temperatures with respect to the maximum of the permittivity in very weak fields, as reported by Gavrilova and Koptsik (Kristallografiya, v. 10, no. 3, 1965, 346; AN SSSR. Izvestiya. Seriya fizicheskaya, v. 29, no. 11, 1965, 1959).

11. Leonidova, G. G., N. P. Netesova, and T. R. Volk. Study of the ferroelectric phase transition in triglycine sulfate at pressures up to 10 kbar. Fizika tverdogo tela, v. 9, no. 2, 1967, 593-595.

An equilibrium p-T diagram of the ferroelectric transition in triglycine sulfate up to a pressure of 10 kbar was plotted. The permittivity ε and spontaneous polarization P_s were measured against pressure at constant temperature. The pressure of transition was determined from the intersection of $\frac{1}{\varepsilon}(p)$ functions in the ferroelectric and paraelectric regions. It is shown that the transition point is that which corresponds to the maximum value of the permittivity, measured in weak fields. The measurements confirmed the nonlinearity of the phase transition diagram of triglycine sulfate. The data are described by the quadratic equation $T_c = 49.52 + 2.85 \times 10^{-3}\, p - 0.58 \times 10^{-7}\, p^2$, where T_c is the temperature (°C) and p is the pressure (kg/cm^2). From the functions $\frac{1}{\varepsilon}(p)$ in the paraelectric region and $P_s^2(p)$ in the ferroelectric region, the expansion coefficients A and B of the Devonshire-Landau equation for the thermodynamic potential ($\phi = \phi_0 + A(T-T_0)P^2 + BP^4 + \ldots$) were obtained. The change of these coefficients confirms the hypothesis of the Landau-Ginzburg

theory concerning the change in the character of the phase transition as one moves into the high-pressure region on the phase diagram.

12. Mylov, V. P., I. N. Polandov, and B. A. Strukov. Change of the dielectric properties of triglycine fluoberyllate subjected to hydrostatic pressure. Fizika tverdogo tela, v. 9, no. 10, 1967, 3012-3014.

Experimental investigations were made of the ferroelectric properties of triglycine fluoberyllate (TGFB) under high pressures. Measurements of permittivity were conducted under varying hydrostatic pressures up to 8000 kg/cm^2. It was established that the permittivity at Curie point decreased down to 50% of its value at atmospheric pressure as the pressure increased to maximum. The Curie point at the same time shifted toward higher temperatures at a rate of 2.5×10^{-3} degrees per atmosphere, up to 4000 kg/cm^2, at which point ferroelectric transition occurs and the shift continues at a reduced rate of 1.8×10^{-3} degrees per atmosphere. The measurements of the temperature dependence of the spontaneous polarization within the same pressure range showed a shift of the polarization point toward higher temperatures as the pressure increased, but without a change in the character of the dependence.

13. Shuvalov, L. A., and A. M. Shirokov. The characteristics of the amplitude dependence of internal friction in single-crystal ferroelectrics. Akademiya nauk SSSR. Doklady, v. 154, no. 5, 1964, 1075-1077.

An experimental study has been made of some features of the internal friction in single crystals of Rochelle salt and triglycine sulfate with various types of the Weiss domain structure. The bar-shaped samples, measuring about 30 x 4 x 2 mm, were tested in a constant-temperature retort. As it was very difficult to measure the deformation amplitude of the samples, the experimental curves were plotted according to the current passed through the crystal by mechanical resonance oscillations. The behavior of the logarithmic damping decrement was studied while the current going through the sample was changed from 0.02 to 2 milliamperes. The results of the above tests justify the following two basic conclusions: 1) the intensive internal friction in some of the Rochelle salt samples within the ferroelectric temperature region is determined by a variety of Weiss domain processes. It is possible that large deformation amplitudes produce volumetric deformations which change the nature of the internal friction. 2) It may be assumed that the amplitude dependence of the internal friction in the case of relatively small deformations will be observed in the ferroelectric region of the Rochelle salt crystals in which the reorientation of the Weiss domains may occur under the effect of homogeneous mechanical stresses.

14. Sonin, A. S., and A. S. Vasilevskaya. Electro-optical properties of triglycine sulfate. IV. Deuterated triglycine sulfate. Kristallografiya, v. 12, no. 3, 1967, 451-454.

Experimental investigations were made of TGS single crystals in an electric field directed along the ferroelectric axis (Y), with applied light propagating along the X, Y and Z axes. The investigation was carried out on mechanically free specimens under static conditions. The experiment was described earlier by the authors (Kristallografiya, v. 11, 1966, 49 and v. 12, 1967, 2). The temperature measurements were taken on the 5350 Å wavelength; the dispersion of electro-optical coefficients were determined near the Curie point. The induced birefringence as a function of the electric field strength, at all three directions of applied light, were linear within the whole range of temperatures for the transverse (axes X and Z) effect, while for the longitudinal effect linearity was observed only near the Curie point. The refractive indexes as functions of temperature obeyed the Curie-Weiss law above as well as below the Curie point. The Curie-Weiss constants for TGS and DTGS, however, differed substantially in the region below the Curie point. The electron and electron-ion polarization processes proved to be important for electro-optical properties of both the TGS and DTGS crystals. On the whole, the experiments showed that the exchange of hydrogen for deuterium in this case as in the case of potassium di-hydrogen phosphate (T. R. Sliker and S. R. Burlage. J. Appl. Phys., v. 34, 1963, 1837) does not substantially effect the polarizability of TGS.

15. Strukov, B. A. Electrocaloric effect in triglycine sulfate single crystals. Kristallografiya, v. 11, no. 6, 1966, 892-895.

Experimental investigations were made of the electrocaloric effect on TGS single crystals. An adiabatic vacuum calorimeter was used to eliminate certain inaccuracies involved in the hysteresis loop method due to nonlinearity of induced polarization. The arrangement made it possible to record the temperature change of the crystal as a function of electric field strength as well as that of the polarization induced by that field. Polarization as a function of the electric field showed a clear nonlinearity in the ferroelectric phase. The temperature dependence of the magnitudes of the electrocaloric constant deduced from the measured temperature of the crystal as a function of the field strength, as well as the pyroelectric constant calculated from these data, showed a sharp maximum at the phase transition under the zero field, which maximum flattened out as the field strength increased. The temperature gradient plotted against the square of polarization resulted in a straight line for any given temperature and, as expected, all lines for temperatures above the Curie point coincided. The temperature dependence of the square of spontaneous polarization was plotted from these data, which showed that at the phase transition point, the spontaneous polarization is

close to the value of the square root from the difference between the Curie temperature and the temperature of the crystal. It was concluded that the anomalous temperature dependence of the heat capacity near the phase transition point in TGS is connected with the behavior of spontaneous polarization which remains "normal" up to the transition point.

16. Strukov, B. A., and K. A. Minayeva. Some features of pulsed repolarization of naturally unipolar crystals of triglycin sulfate. Fizika tverdogo tela, v. 7, no. 12, 1965, 3579-3581.

The purpose of the investigation was to determine the influence of natural unipolarity of triglycin sulfate on the spontaneous depolarization, namely the transition of the crystal from the single-domain into the multiple domain state. This is a continuation of a similar investigation performed by the authors earlier on NH_4HSO_4 crystals (FTT, v. 6, 76, 1964). The natural unipolarity of the investigated crystals ranged from zero to 100 V/cm. Particular attention was paid to the temperature interval near the phase transition point where this phenomenon is observed, since it is in this range that the crystal loses its ability to store information. A total of 30 samples was tested by the standard procedure. The results show that application to the crystal of a definite sequence of electric voltage pulses in a certain temperature interval below the Curie point gives rise to a regular change in the areas under the current pulses. The crystals possessing internal unipolarity lose their ability of storing information far below the phase transition point. The spontaneous realignment of the domain structure at a certain temperature below the Curie point leads apparently to additional anomaly in the specific heat, the paraelectric coefficients, and a few other properties of the triglycin sulfate crystals. The temperature of total depolarization decreases linearly with increasing internal unipolarity of the sample.

17. Strukov, B. A., K. A. Minayeva, and Ye. N. Rodicheva. Reverse polarization characteristics of acid ammonium sulfate. Fixika tverdogo tela, v. 6, no. 1, 1964, 76-79.

The authors made this study because of lack of information in the literature on pulsing polarity reversals in $(NH_4)HSO_4$. In the temperature interval from -2.5 to -119°C this mineral has a rectangular dielectric hysteresis loop in a relatively small coercive field (on the order of 200—600 v/cm). This property makes the mineral of considerable practical importance. The characteristics of the polarity reversal were measured under carefully controlled stabilized temperature. These tests were made in the range from -20 to -100°C. The samples (10 x 10 x 40 mm) were given rectangular pulses, the amplitudes and durations of which ranged from 0 to 120 v and 10 to 1200

microseconds respectively. The build-up time of the pulse did not exceed 0.1 microsecond. The frequency of pulse repetition was 250 cycles. The authors have shown that, as with other ferroelectric crystals, the W. Merz model (Phys. Rev., 95, 690, 1954) may be used for the pulsing reversals of polarization. Near the points of ferroelectric phase transition (-2.5 and -119°C) spontaneous depolarization was detected in the samples.

18. Tambovtsev, D. A. Problem of asymmetry in pulse repolarization of triglycine sulfate ferroelectric crystals. Kristallografiya, v. 9, no. 4, 1964, 511-515.

An experimental study is made of the asymmetry of pulse repolarization of triglycine sulfate ferroelectric crystals when unequally spaced square pulses are fed to the crystals with a voltage which depends on the strength of the electrical field and the distance between pulses of opposite polarity. It is shown that the asymmetry of pulse repolarization is closely connected with definite processes which take place in the intervals between pulses being transmitted in layers of the crystal close to the electrodes. These are processes which lead to a change in the conditions of formation of the nuclei of new domains.

19. Tukhtasunov, I. T., V. A. Shamburov, and I. S. Zheludev. Electro-optical effect in triglycine sulfate crystals at room temperature. Kristallografiya, v. 12, no. 2, 1967, 302-306.

Experimental investigations were made to observe and evaluate the electro-optic effect in the domains of triglycine sulfate (TGS) crystals. To observe the electro-optic effect, which must exist in these crystals below the Curie point due to the characteristics of their symmetry, a high degree of optical uniformity of the specimens is required. For these experiments, a number of plates cut along the X, Y, and Z axes were investigated to find two with some surface area capable at a conoscopic pattern. These areas were used for the preparation of two specimens in the form of rectangular parallelepipeds with the following dimensions along the X, Y, and Z axes: 6 x 4.66 x 6.4 mm and 6.25 x 7.61 x 5.4 mm. The specimens, furnished with electrodes, were immersed in dehydrated silicone oil in a parallel-walled glass container, which was placed at the intersection of crosswise polarizers. A sodium lamp beam was focused on the crystal behind which a lens (focal length 250 mm) projected the image on a screen or a photo-plate. A diaphragm, instead of the lens, was used with a photomultiplier for transmittivity measurements. The experiments were made at room temperature with the field directed along the axis of spontaneous polarization and the light directed along the main axes of the indicatrix ellipsoid. Under these conditions, the electro-

optic effect was observed in the form of a pattern of four sets of light and dark hyberbolic stripes on two crossed axes. These patterns changed the sequence of light and dark when the direction of light was changed from one axis to another. A similar effect was achieved by changing the electric field strength (in this experiment, from zero to 15 kV). The reversal of the field polarity did not change the character of the pattern evolutions. The transmittivity measurements undertaken for quantitative evaluation of the observed electro-optic effect also revealed the hysteresis phenomenon common to ferroelectrics with electro-optic properties. A change of transmittivity was observed in the direction of the main axes of the indicatrix ellipsoid, and its value was measured at the position of the crystal where two other axes made 45° angle with the direction of oscillations in the crossed polarizers. An analysis of the measurements showed that the electro-optic effect in TGS crystals is essentially linear. An attempt was made to describe theoretically the electro-optic effect on the basis of equations derived from Nye and from Vlokh and Zheludev (Kristallografiya, v. 7, no. 4, 1962, 593 and no. 5, 730; Opticheskaya kristallografiya. Moskva. Izd-vo AN SSSR, 4, 1950), but insufficient optical uniformity of the specimens rendered the determination of the necessary coefficients somewhat difficult, and the results are only approximate.

20. Vasilevskaya, A. S., A. S. Sonin, and I. A. Slepkov. Electro-optical properties of triglycine sulfate. II. Kristallografiya, v. 11, no. 5, 1966, 749-754.

This second article in a series deals with experimental results of investigations on the longitudinal electro-optic effect in the triglycine sulfate (TGS) crystals in strong electric fields. The induced birefringence of TGS was studied as a function of temperature and the wavelength above and below the Curie (about 50°C) point with an external constant electric field and a light beam propagating in the [010] direction, along the ferroelectric axis. Details of the experiment and the underlying theoretical considerations are presented. Measurements of the field intensity dependence of the transmittivity, the birefringence, the temperature and wavelength dependence of the permanent part of the birefringence change at a given temperature were made to study the behavior of induced electron polarization. It was found that induced birefringence has a maximum at the Curie point. The effects of the domain structure of TGS, however, were not directly identified. For this, study of the birefringence along other crystallographic axes is deemed necessary.

21. Vasilevskaya, A. S., and A. S. Sonin. Electro-optical properties of triglycine sulfate. III. Kristallografiya, v. 12, no. 2, 1967, 297-301.

This third article in a series deals with experimental results of investigations of the electro-optic properties of triglycine sulfate (TGS) crystals in strong electric fields. The transverse electro-optic effect was studied with the electric field applied along the ferroelectric axis, and light propagating along the crystallographic axes X and Z. The experimental arrangement and the method used were described earlier by Vasilevskaya and others (AN SSSR. Izvestiya. Seriya fizicheskaya, v. 29, 1965, 969; Kristallografiya, no. 11, 1966, 749). The data obtained showed that the polarization non-linearity in TGS ferroelectric persists up to the optical frequencies and has a maximum at the Curie point. It was found that the non-linearity is not due to the domain structure, since the measurements were carried out in strong fields and on single-domain specimens.

22. Zheludev, I. S., and Ts. Zh. Ludupov. Differential permittivity of the triglycine sulfate single crystal. Kristallografiya, v. 11, no. 5, 1966, 771-775.

Experimental investigations were made of the permittivity of triglycine sulfate crystals in various parts of a hysteresis loop in the process of polarity reversal. The measurements were made on SHF (8×10^8c field strength < 10 V/cm) and in a low-frequency (500 to 15,000 c) external field. The permittivity value measured on SHF at various polarization stages effected by an applied low-frequency field was designated as "differential permittivity". The experimental setup is shown in a block diagram described in some detail. It was established by a series of special measurements that measuring with the SHF field did not affect the polarity reversal process as did the low-frequency field. This means that the SHF field actually measures some polarization process other than the domain-effected, which appears to depend on the frequency and the amplitude of the low-frequency polarity-reversing field as well as on the stage of polarization the crystal is passing at the moment of measurement. This other process is associated with the activation of imperfections and admixtures during the polarization reversal. Such an assumption would explain the observed facts, as an increase of the polarizing field increases the slope of the hysteresis loop corresponding to the polarization reversal, which must contribute to the activation of the impurities and the imperfections. An increase of the frequency of the polarity reversal has the same effect . The characteristics of the differential permittivity further show that the polarizability of the impurities and imperfections depends very little on the domain multiplicity. The absolute magnitude of the

permittivity gradient is also affected to some extent by heating of the crystal during polarity reversal, although in these experiments the temperature was kept practically constant. The authors note that the method of the experiment makes it possible to study more thoroughly the polarization process stemming from mechanical "liberation" as well as from the removal of the "orientation order" of impurities and imperfections.

III. POTASSIUM DI-HYDROGEN PHOSPHATE (KDP) AND ISOMORPHOUS CRYSTALS

1. Aref'yev, I. M., P. A. Bashulin, and T. V. Mikhal'tseva. Long-wave infrared transmission spectra of KH_2PO_4. Fizika tverdogo tela, v. 7, no. 8, 1965, 2413-2416.

This is a continuation of earlier work (Fizika tverdogo tela, v. 7, 407, 1965) on the temperature dependence of the low-frequency Raman spectra of KH_2PO_4 and $NH_4H_2PO_4$. The present study was undertaken to refine the results in the excitation-wavelength region, where the results were distorted by ghosts due to the diffraction gratings. The authors determined the transmission spectra of a polycrystalline sample (constituting a suspension of the powdered KH_2PO_4 crystal in paraffin) in the frequency range 20—235 cm^{-1} at room temperature. The entire band was covered with two echelettes, one with 4, the other with 2 lines/mm, and in the 160—235 section of the spectrum the 4 lines/mm echelette was used in the second order spectrum. The results are plotted in Fig. 1 and confirm the previously observed broad band at $\sim$52 cm^{-1}. The contribution of this vibration to the static dielectric constant is felt to be considerable. The temperature variation of the transmission coefficient was measured in the range 295—150°K. Although the experimental setup did not make it possible to reach the phase transition temperature (123°K), it is deduced from the shift of the absorption band ($\sim$10 cm^{-1} against the theoretical $\sim$18 cm^{-1}) that the optical oscillations of KH_2PO_4 have an anomalous ferroelectric behavior near the Curie point.

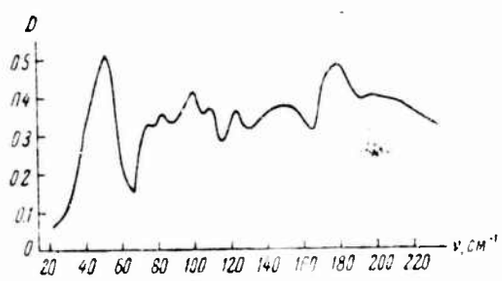


Fig. 1. Plot of optical density of KH_2PO_4

2. Ludupov, Ts. Zh. Complex dielectric permeability of deuterated potassium dihydrophosphate at superhigh frequencies. Kristallografiya, v. 11, no. 3, 1966, 468.

Complex dielectric permeability measurements were made at room temperature on deuterated potassium dihydrophosphate (DPDP) crystals in the superhigh frequency range ($f = 5 \cdot 10^8$ to $3.9 \cdot 10^{10}$ cps). In comparing the superhigh frequency results, ε_i^* was designated as the complex dielectric permeability measured at lower frequencies ($f = 8 \cdot 10^2$ cps) on an "RFT" bridge. Measurements in the decimeter range were made on a PI6A coaxial measuring line; in the centimeter and millimeter range of wavelengths the waveguide method was used. The crystal samples used had two orientations. In one case electric field measurements were taken along the X_3 axis, while in the other case the measurements perpendicular to the X_3 axis (the crystallographic X_3 axis in DPDP lies along the c axis of the crystal, and the other two axes X_1 and X_2 lie along the a and b directions).

Grinding and polishing of the samples were done in order to secure good contact with the wall of the waveguide apparatus and better clamping. All sides of the crystals were silvered by vacuum deposition. Values for ε_i and tg δ_i are given in Table 1.

№	Frequency, cps	ε_1'	tg δ_1	ε_3'	tg δ_3
1	$8 \cdot 10^2$	65	$5 \cdot 10^{-3}$	51	$3,7 \cdot 10^{-3}$
2	$5 \cdot 10^8$	70	—	47,0	—
3	10^9	62,5	$2,16 \cdot 10^{-2}$	44,2	$9,5 \cdot 10^{-2}$
4	$9,6 \cdot 10^9$	59,2	$18,2 \cdot 10^{-2}$	43	$20 \cdot 10^{-2}$
5	$3,9 \cdot 10^{10}$	34,8	$36,6 \cdot 10^{-2}$	34,4	$63,3 \cdot 10^{-2}$

Table 1. Values of ε_i' and tg δ_i for DPDP single crystals at ultrahigh frequencies

The complex dielectric permeability $\varepsilon_i^* = \varepsilon_i' + j\varepsilon_i''$, while the results give values for ε_i', tg $\delta_i = \varepsilon_i''/\varepsilon_i'$ and tg $\delta_i = \varepsilon_i''/\varepsilon_i'$.

3. Mnatsakanyan, A. V., L. A. Shuvalov, I. S. Zheludev, and I. V. Gavrilova. Elastic properties of RbH_2PO_4 crystals in a wide temperature range.

Measurements were made of the elastic properties of the rubidium di-hydrogen phosphate (RDP) crystals within a wide temperature range including the Curie point. The specimen stock was grown from aqueous solutions at an initial temperature of about 50°C within 30—40 days. Specimens in the form of bars (25 x 4 x 2 mm) and plates (10 x 10 x 1.5 mm) were cut in various directions with respect to a chosen axis. For measurements of pliability, the resonance method was used at zero field. The Curie point of the investigated crystals was, according to earlier measurements by Shuvalov and the author (AN SSSR, Izvestiya. Seriya fizicheskaya, v. 25, 1965, 1800) set at 147°K. The temperature dependence of elastic pliabilities showed a sharp anomaly at about -125°C (i.e. the Curie point) similar to potassium phosphates, with more pronounced maxima of pliabilities (s^E_{66}, s^E_{245}) connected with the ferroelectric polarization, and also in some cases stronger secondary anomalies occurring at about 40--50° below the Curie point. The latter are characterized by a faster drop of pliability due to "freezing" of domains at those temperatures.

4. Sirotin, Yu. I. Group theory investigation of the antiferroelectric phase transition in ammonium di-hydrogenphosphate. (Paper read at the International Conference on Crystallography, Moscow, 1966). Kristallografiya, v. 12, no. 2, 1967, 208-214.

A theoretical investigation has been made of the antiferroelectric phase transition in ammonium di-hydrogenphosphate ($NH_4H_2PO_4$) by the group theory method, to determine the general transformational properties of the parameter characteristics of the antiferroelectric phase transition. The treatment proceeds from the structure of the para-electric phase and the change of translational symmetry connected with the transition from the para-electric phase into the antiferromagnetic. The vector functions describing the displacement and polarization of ions are derived from an earlier work by the author and V. A. Koptsik (Akademiya nauk SSSR, Doklady, v. 151, 1963, 328) and applied with certain modifications, to show the interrelations of structural changes with the change of the symmetry of macroscopic properties. The analysis also makes it possible to determine and describe the four types of domains formed in the process of phase transition. The boundaries between the domains are considered as special defects in packaging, but their experimental identification (possibly by methods of electron microscopy) remains a matter for further investigations. The method is applicable to antiferroelectric transitions of other materials, since all such transitions are connected with a change of the number of atoms within the elementary cell, as is the case with all known antiferroelectric transitions.

5. Sonin, A. S. Spatial symmetry and induced polarization. Fizika tverdogo tela, v. 9, no. 10, 1967, 3008-3010.

An analysis is presented of the character of symmetry element loss which accompanies the spontaneous polarization or application of an external electric field to dielectrics and ferroelectrics. The analysis is based on a comparison of the point system of the initial space groups to that of the polarized groups. The $\overline{I}4$ 2d space group of the tetragonal system of potassium di-hydrogen phosphate (KDP) ferroelectric is discussed as a sample. The behavior of particles under various polarization conditions was analyzed for all the 230 space symmetry groups and a number of general conclusions were reached. The conclusions are summarized in eight rules which make it possible to determine the behavior (arbitrary orientation, orientation according to applied field, orientation in symmetry planes, etc.) of dipole moments in various space groups, at various orientation of polarization or applied field with respect to the crystallographic axes.

6. Strukov, B. A., M. Amin, and A. S. Sonin. Heat capacity and permittivity of potassium di-deuterium phosphate crystals in the region of the ferroelectric Curie point. Fizika tverdogo tela, v. 9, no. 8, 1967, 2421-2423.

An experimental investigation was made of the temperature dependence of the heat capacity and permittivity of KD_2PO_4 single crystals. The results showed that the heat capacity at the phase transition (Curie point, -70°C) reaches a very high magnitude of about 4000 cal/mol x degree C. The "tail" of the heat capacity above the Curie point is nearly absent, and the drop of the heat capacity from its peak value to the normal for the paraelectric phase takes place within a temperature interval of only 0.1°C. This means that the close-order effect is small in comparison to that in tri-glycine sulfate-type ferroelectrics. The excess entropy was found to be 0.94 cal/mol x degree C which is higher than the figure reported by Bantle (Helv. Phys. Acta, v. 15, 1942, 373). The difference, however, can be explained by the very high heat capacity peak observed in these experiments. The temperature dependence of permittivity follows the Curie-Weiss law within the para-electric range, but its maximum (at 69.95°C) remains relatively low (about 2000), which agrees with Sliker and Burlage (J. Appl. Phys., v. 34, 1963, 1837) and other sources. The experiments prove that the measurements conducted on stress-free KD_2PO_4 crystals in the absence of an electric field yield data which agree better with theory (Bline and Svetina. Phys. Rev., v. 147, 1966, 430) than measurements taken on powder.

7. Vasilevskaya, A. S., Ye. N. Volkova, V. A. Koptsik, L. N. Rashkovich, T. A. Regul'skaya, I. S. Rez, A. S. Sonin, and V. S. Suvorov. Nonlinear optical properties of deuterized ammonium dihydrogen phosphate. Kristallografiya, v. 12, no. 3, 1967, 516-519.

Experimental studies were made of the nonlinear optical properties of a new addition to the KDP group of compounds—deuterated ammonium dihydrogen phosphate ($ND_4D_2PO_4$). The DADP salt was derived by multiple recrystallization of ammonium dihydrogen phosphate salt in heavy water. The single crystals were grown by the cooling method under agitation of the solution. The degree of deuteration reached 96±1%. The temperature of the antiferromagnetic phase transition was -33°C. The measurements of the electro-optical (r_{63}) and the piezoelectric (π_{63}) coefficient showed that the contribution of the elasto-optic effect to the overall electro-optic effect is 25%, which substantially exceeds the corresponding value in KDP crystals but is below that of ADP crystals. The refractive indexes were measured at the mercury-lamp wavelengths. From these data and the refractive index corresponding to the emission of a ruby laser, it was established that the direction of synchronism for ordinary emission and the extraordinary of the second harmonic make an angle of 47 ± 5° with the Z axis and 45° with the Y and Y axes, which coincides within the margin of error of the experiment with the angles of the ADP crystals. The measurements of the relative energy of the second harmonic of a ruby laser and the ADP single crystal showed that this energy increases about 1.5 times due to deuteration. The transmittivity of DADP, which is important for its use in light modulation and frequency doubling, is characterized by the shift of the absorption band by 0.4 μ toward longer wavelengths. This lowers the absorption magnitudes in DADP (4.5 to 5 times on the 1.4 μ wavelength).

8. Vasilevskaya, A. S., S. S. Gorbach, M. F. Koldobskaya, L. I. Kuznetsova, L. G. Lonova, T. A. Regul'skaya, I. S. Rez, Yu. P. Sobesskiy, A. S. Sonin, and V. S. Suvorov. On certain physical properties of potassium di-deuterium phosphate single crystals in the para-electric phase.

Experimental investigations were made of the nonlinear characteristics of potassium di-deuterium phosphate (DKDP) single crystals. It was found that the temperature dependence of permittivity and the loss angle (tan δ) measured along the ferroelectric axis at 50 kc frequency had sharp maxima at the Curie point (-53.1°C) which corresponded to about 98% replacement of hydrogen. The peak of the loss angle lagged about 0.4°C behind the peak of permittivity. The

same characteristics measured at various frequencies indicated a maximum permittivity at about 5×10^4 c, and a declining value of tan δ, reaching 620×10^{-3} at 1.7×10^4 c frequency. These data confirm that a relaxation-type mechanism governs these parameters. The refractive indexes of the DKDP single crystals proved to be lower than those of KDP. The direction of synchronism was determined on this basis (its angle was put at 52±5° to the axis), which is important in laser applications as the direction in which the maximum of its emission energy is transformed into its second harmonic. The experiments on a specimen cut perpendicularly to the direction of synchronism showed that the relative emission of the second harmonic in DKDP single crystals is about half of that of KDP. But the DKDP crystals are considered superior to KDP with respect to the utilization of their nonlinear properties, especially of the shift (up to about 2 μ) of the absorption band further into the infrared region. The electro-optic module ($r_{65} = 7 \times 10^{-7}$ CGSE units) proved to be only slightly dependent on the light wavelength. The deuterization also affects substantially the half-wave potential (the potential to effect a half-wave path difference), which dropped from 7.5 to 3.9 kv at 5461 A wavelength.

9. Vasilevskaya, A. S. Concerning the electro-optical properties of KDP-type crystals. Kristallografiya, v. 11, no. 5, 1966, 755-759.

To ascertain the nature of the electro-optic effects in crystals, and also for practical applications, the author investigated the electro-optic coefficients of mechanically free and clamped crystals of ammonium dihydrophosphate (ADP), potassium dihydrophosphate (KDP), deuterated potassium dihydrophosphate (DKDP) and rubidium dihydrophosphate (RDP). The values of the electro-optic coefficients and their dispersion were determined in the wavelength interval from 4000 to 7250 Å. The experimental setup and the measurement procedure are described elsewhere (Kristallografiya, v. 10, no. 3, 1965). The measurements were made on 45° Z-cuts of crystals made in the form of prisms with the long dimension in the direction of the applied load (110). Three to four samples of each crystal were tested. The piezo-optic coefficients and their wavelength dependence were different for the different crystals, but exhibited a similar variation, the difference being mostly quantitative. It is shown that the electro-optic effect of mechanically clamped crystals is 90—94% of the electro-optic effect of free crystals in the case of KDP, RDP, and DKDP, and 60—70% for ADP. It is also shown that the ratio of the contribution of electronic to electron-ion polarization to the electro-optic effect, which amounts to about 50% in the case of free crystals, is altered by application of pressure to a small degree in KDP, DKDP, and RDP, but to a larger degree in ADP. The difference is related to the presence of a different system of hydrogen bonds.

10. Zheludev, I. S. and Ts. Zh. Ludupov. Complex dielectric constant of RbH_2PO_4 in the 8×10^2—$3{,}86 \times 10^{10}$ cps frequency range. Kristallografiya, v. 10, no. 5, 1965, 704-766.

Measurements were made of the permittivity of RbH_2PO_4 single crystals on frequencies between 8×10^2 and 3.86×10^{10} cps. The measurement data for permittivity values along the axis of rotation of the ellipsoid of permittivity coinciding with the c-axis of the crystal (ε_3' in the table), for permittivity along the other two axes (ε_1'(in the table) = ε'), as well as the corresponding loss angles (tan δ), are shown in Table 1. The measurements methods used, the specimen dimensions and their positioning in the waveguide for longitudinal and transverse permittivity and loss angle (ε_3', tan δ_3) are described.

Table 1. RbH_2PO_4 permittivity and loss angles

Frequency	ε_1'	tan δ	ε_3'	tan δ
8×10^2	41.4	3.4×10^{-3}	27	4×10^{-3}
4.65×10^5	41.3	0.2×10^{-3}	26.2	*
1.5×10^7	42.0	*	26.5	0.514×10^{-3}
3.8×10^9	40.6	*	25.0	*
5.8×10^9	40.4	*	23.6	*
9.6×10^9	39.4	1.1×10^{-2}	*	*
3.86×10^{10}	36.4	3.42×10^{-2}	23.6	5.1×10^{-2}

*The data greatly deviated from the expected values due to inaccuracies of certain measurement techniques and were omitted.

IV. BARIUM TITANATE AND OTHER PEROVSKITE TYPE OXIDES

1. Bogdanov, S. V., K. V. Kiseleva, and V. A. Rassushin. Effect of bismuth additives on some physical properties of $BaTiO_3$ single crystals. Kristallografia, v. 10, no. 1, 1965, 74-80.

The effect of small concentrations of bismuth additive on the structure, dielectric properties, losses, Curie point, and the spontaneous crystallization of $BaTiO_3$ was investigated. It was shown that two ranges (from 0 to 0.16 atomic % of Bi and above 0.16 atom. %) can be separated in the concentration dependency of structural parameters T_k and P_s. The different behavior of the values in these concentration ranges is linked to different behaviors of bismuth ions in the $BaTiO_3$ lattice. In the second range, relaxation dependencies ε and $tg\delta$, related to the electron processes, were disclosed. Probable mechanisms of relaxation processes are also discussed.

2. Bokov, V. A., S. A. Kizhayev, I. Ye. Myl'nikova, and A. G. Tutov. Antiferroelectric and magnetic properties of $PbCo_{1/2}W_{1/2}O_3$. Fizika tverdogo tela, v. 6, no. 10, 1964, 3038-3044.

$PbCo_{1/2}W_{1/2}O_3$ single crystals were grown from solution in molten PbO, and their crystal structure and electric and magnetic properties were determined and compared with those of $PbMg_{1/2}W_{1/2}O_3$, which is the only known stable antiferroelectric of the $A^{2+}B^{2+}_{1/2}W_{1/2}O_3$ series of compounds. The x-ray powder patterns indicated a perovskite-type structure with a rhombic unit cell at room temperature and a cubic cell at 50°C, with ordered distribution of Co^{2+} and W^{6+} ions. The temperature dependence of the dielectric constant of large single crystals showed a maximum at 32°C, corresponding to the transition from the paraelectric (cubic) phase to the antiferroelectric (rhombic) phase. This maximum shifted toward lower temperatures on application of an increasing constant electric field. The observed double hysteresis loops in the antiferroelectric phase, i.e., at low temperatures (below -100°C) when strong electric fields are applied, was correlated with an induced transition from the antiferroelectric into the ferroelectric state. The double hysteresis loop was gradually transformed into a normal loop when temperature was decreased further to -193°C. The transition point into the ferroelectric state in the absence of a field was determined to be -260°C. "critical" field, at which the hysteresis loop disappears, was shown to decrease with decreasing temperature. The transition into the ferroelectric state in a strong electric field is possible because of a small difference in the free energies of both states. The antiferroelectric state is more stable in $PbMg_{1/2}W_{1/2}O_3$ than in $PbCo_{1/2}W_{1/2}O_3$, since no double loop was obtained in the former.

The temperature dependence of the specific magnetic susceptibility of $PbCo_{1/2}W_{1/2}O_3$ could not be correlated with the appearance of antiferroelectricity, although a deviation from the Curie-Weiss law was noted below -100°C. The absence of magnetic phase transitions was deduced, at least in the temperature range above -196°C.

3. Bursian, E. V., and N. P. Smirnova. Nonlinear capacitance of thin single crystal films of $BaTiO_3$. Fizika tverdogo tela, v. 6, no. 6, 1964, 1818-1820.

This is a continuation of a series of papers by various authors devoted to the investigation of polarity reversal in thin films of $BaTiO_3$. The authors have extended the range of thickness of single $BaTiO_3$ crystals that may be investigated for determining the geometrical effect. They have found that nonlinear polarization is preserved as the thickness is diminished from 100 to 1 micron, but that the activation field of the nonlinear part increases proportionally to the reciprocal of the thickness. In rather strong fields the temperature dependence of the dielectric constant is preserved, as are the other features of ferroelectricity. These results confirm the view that the surface layer plays a decisive role in the mechanism of polarization. It is pointed out that complete polarization at saturation proves to be no less for thin layers than for thick, and it may even be greater. A value of 2.5 microcoulombs/cm^2 was obtained for a thickness of 6 microns and of only 2 microcoulombs/cm^2 for a thickness of 30 microns.

4. El'gard, A. M. Effect of unilateral mechanical stresses on the dielectric and piezoelectric properties of polarized ferroelectrics. Fizika tverdogo tela, v. 6, no. 8, 1964, 2502-2509.

This investigation was prompted by the fact that the effects of mechanical stresses on ferroelectric properties have not been sufficiently well studied, with the possible exception of the $BaTiO_3$ ceramic, and by the fact that recently highly effective piezoceramic materials have been developed on the basis of other ferroelectrics. The author investigated the effect of unilateral mechanical stresses on the dielectric and piezoelectric properties of polarized ceramic ferroelectrics based on barium titanate, lead metaniobate, and lead zirconate-titanate. The unilateral compression was effected with the aid of a special lever-type press. The samples were prisms (8 x 8 x 15 mm with electrodes either on the ends or on the side faces) which were always compressed along the height so that the mechanical stresses were oriented either parallel or perpendicular to the polarization direction. The variation of the dielectric constant with the

applied alternating voltage was obtained for the ferroelectrics both in the compressed state and after removal of the load. This yielded data on the reversible and irreversible variation of the piezoelectric moduli in both compression (~1200 kg/cm²) and tension (~200 kg/cm²). The differences between the various compositions are analyzed in detail. The results are interpreted on the basis of the reorientation of domains under the influence of mechanical stresses.

5. Fedotov, I. I. Sound veloctiy and the E - effect in ferroelectric ceramic cell piezoelements. Fizika tverdogo tela, v. 9, no. 8, 1967, 2419-2421.

Measurements were made of the ultrasound velocity and ΔE effect in a $Pb_{0.95}Sr_{0.05}x(Zr_{0.53}Ti_{0.47})O_3 + Nb_2O_5$ ferroelectric ceramic. The method of measurement was described earlier by Fedotov and others (Primeneniye ul'traakustiki k issledovaniyu veshchestva, Sbornik, no. 14, 1961, 269; Fizika tverdogo tela, v. 6, 1964, 602). The ultrasound velocities (with frequencies from 3 to 9 Mc) were found to vary between 4280 and 4700 m/sec in polarized specimens, and between 3940 and 3860 m/sec in the same, but depolarized specimens. The Poisson coefficient was equal to 0.33. The ΔE effect, as a function of the polarizing field intensity and the duration of its application was found to grow in a nonlinear ratio as the field intensity and its duration increased (reaching 18% increase at 30 kv/cm and 30 min duration), the main increment occurring during the first 1-2 min, and at coercive field intensities (10 to 15 kv/cm). An anomalous effect of reduction of the ΔE effect with time in a high intensity field was observed. A full cycle of applied field intensities produced a butterfly-type hysteresis loop similar to one of barium titanate (Fedotov, Fizika tverdogo tela, v. 6, 1964, 602) and that of the direct and reversed piezoeffect in the present material (Balash, Kramarov and Shpolyanskiy, Izv. AN SSSR, Ser.fiz., 29, 1965, 2086). The magnitude of the residual ΔE effect was about 90-95% from its maximum. The hysteresis loop was closed if the measurements referred to the points of the sign reversal of the ΔE effect, but remained open when plotted with reference to the zero point (designating the initial state of the specimen). This observation remained unexplained until further investigations.

6. Guyenok, Ye. P., and A. Yu. Kudzin. Dependence of polarization of single crystal $BaTiO_3 - Ta_2O_5$ on the humidity of the surrounding atmosphere. Fizika tverdogo tela, v. 8, no. 6, 1966, 1702-1707.

This is a continuation of earlier work (FTT, v. 7, 2845, 1965 and

preceding papers) on the ferroelectric properties of single crystals of barium titanate to which tantalum oxide is added. The tests were made on $BaTiO_3$ with 0.3 mol.% Ta_2O_5, grown from the solution in a potassium fluoride melt. Silver electrodes were deposited by cathode sputtering. The dielectric constant and the dielectric loss angle were measured at 1 Mc by variation of the reactance, and at audio frequencies by a bridge method. The dielectric hysteresis loops were investigated at 50 cps by the Sawyer-Tower procedure. The electric conductivity was measured with an ohmmeter. The relative humidity of the surrounding atmosphere was produced with the aid of saturated salt solutions. The results showed a strong increase in the dielectric constant and in the dielectric losses with increasing humidity, when measured in a weak field, and an increase in the crystal polarization in strong fields. The dielectric constant decreased more rapidly with increasing frequency at increased humidity than in a dry atmosphere. Although the results are strongly influenced by the surface finish of the crystals, they cannot all be interpreted as being due to an increase in the effective electrode area by absorption of moisture on the free surface. It is concluded that the effects are due to the joint action of the moisture and the surface properties of the crystals, particularly the nature of the ferroelectric domains and their wedges on the surface. A model capable of explaining qualitatively the results is briefly described.

7. Guyenok, Ye. P., and A. Yu. Kudzin. Effect of vapor from liquid polar compounds on the dielectric properties of barium titanate single crystals with various admixtures. Fizika tverdogo tela, v. 7, no. 9, 1965, 2845-2846.

Some data are given from an investigation of the effect which atmosphere has on the dielectric properties of $BaTiO_3$, both as a pure single crystal and with small additions (<1 mol %) of cobalt, nickel, manganese, tantalum, and niobium oxides. The effect of ambient moisture content on the dielectric constant of the specimens was studied. Crystals of pure barium titanate and those with impurities of cobalt, nickel, and manganese oxides showed almost no change in the dielectric constant when the relative humidity was changed from 70 to 100%. The properties of crystals with small additions ($\sim 0.3\%$) of Ta_2O_5 or Nb_2O_5 are strongly dependent on ambient humidity. For most crystals with these impurities, an increase in humidity from 70 to 100% caused an increase of 30—60 μμf, which is 25—50% of the original capacitance of the specimen. For some specimens the change was greater than 100%. The capacitance of these specimens was a function not only of water vapor in the air, but of vapor from other liquids as well. It is assumed that the experimentally observed phenomena are due to the effect of adsorbed polar molecules on the surface layer.

8. Ismailzade, I. G. X-ray diffraction study of phase transformations in bismuth ferrite. Akademiya nauk SSSR Doklady, v. 170, no. 1, 1966. 85-87.

Sintered $BiFeO_3$ bismuth ferrite has been investigated to determine the Curie points and the nature of changes occurring at temperatures of 20—850°C. The transformations occur between 20—845°C. It was concluded that a superstructure exists in the lattice of bismuth, ferrite due to the antiparallel displacement of ions in the lattice. Consequently, bismuth ferrite is antiferroelectric-antiferromagnetic. The temperature of transformation from an antipolarized to a para-electric phase was found to be 875°C.

9. Isupov, V. A., and L. T. Yemel'yanova. Antiferroelectric phase transitions in tungstates with a perovskite-type structure. Kristallografiya, v. 11, no. 5, 1966, 776-784.

Experimental investigations were made of the temperature dependence of the permittivity, dielectric losses, and thermal expansion of $PbCd_{0.5}W_{0.5}O_3$ and of the $PbMg_{0.5}W_{0.5}O_3$-$PbCd_{0.5}W_{0.5}O_3$ solid solution. Purpose of the investigations was 1) to disclose the nature of the phase transition of $PbCd_{0.5}W_{0.5}O$ and 2) to determine the effect of replacing the Mg^{2+} ions in the aforementioned solid solution with Zn^{2+}, Cu^{2+}, and Ni^{2+} ions on the temperature of the antiferroelectric phase transitions and the stability of the ferroelectric and antiferroelectric states. The measurement results showed that the permittivity of $PbCd_{0.5}W_{0.5}O_3$ as a function of temperature, has a jump at 420°C which is accompanied by a change in volume. The dependence has a flat maximum within the 130-240°C range. The permittivity jumps in both investigated materials appear to correspond to the displacive phase change. An antiferroelectric phase change occurs within the 130—240°C temperature range. It is possible that several phase transitions occur within this temperature range, which would explain the flat permittivity maximum in that interval. Replacement of the Mg ions with those of Zr and Cu causes the temperature of the antiferroelectric phase change to rise; replacement with the Ni ions has the opposite effect. The temperature dependence of the antiferroelectric phase change in the solid solution on the type of its second components appears to be connected, to a degree, with the electron polarizability of the B^{2+} ions and ion polarizability of the W^{6+} ions.

10. Isupov, V. A., and N. N. Kraynik. New antiferroelectrics with perovskite structure and rare-earth ions in octahedral lattice points. Fizika tverdogo tela, v. 6, no. 12, 1964, 3713-3715.

Three new compounds and one known antiferroelectric compound with perovskite structure were studied in the series of compounds with the general formula $Pb(B^{3+}_{0,5}B^{5+}_{0,5})O_3$, where B^{3+} is Lu or Yb and B^{5+} is Nb or Ta. The purpose of the study was to discover new compounds with ferroelectric or antiferroelectric (and possibly ferromagnetic) properties, in view of indications in the literature of the possibility of obtaining such compounds in the $Pb(B^{3+}_{0,5}B^{5+}_{0,5})O_3$ series with rare-earth ions of small dimensions in octahedral sites. The polycrystalline compounds were synthesized by sintering oxides at 960—980°C in an atmosphere of lead oxide vapors. X-ray study revealed a distorted perovskite structure in all four compounds. The dielectric constant measured with an IE-2 instrument at 500 khz was found at a maximum in the 270—300°C range. Moreover, two additional low-temperature phase transitions were detected in Yb-containing compounds by dielectric-constant and dilatometric measurements. The phase transitions were identified as antiferroelectric on the basis of the linearity of the plot of dielectric constant versus the electric field potential. All the antiferroelectrics studied have a relatively high Curie point. The Curie points of Nb and Ta compounds and those of Lu and Yb compounds are practically the same. The linear thermal expansion is smaller in the paraelectric than in the antiferroelectric phase. The antiferroelectric properties of the new compounds were compared with those of known ferroelectrics.

11. Ivanov, I. V., and N. A. Morozov. Nonlinear properties of ferroelectric ceramics in strong microwave fields. Fizika tverdogo tela, v. 7, no. 12, 1965, 3627-3630.

The authors report on experiments indicating that at temperatures below the Curie point the dielectric constant of ferroelectric materials with perovskite structure (VK ceramic) depend on the instantaneous values of the electric microwave field. The purpose of the investigation was to check whether the linear properties, the existence of which was proved experimentally above the Curie point, persist below the Curie point, and to ascertain whether these properties are due to the presence of paraelectric grains intruded in the ferroelectric ceramic below the Curie point, or to a true nonlinearity of the ferroelectric crystal. To avoid difficulties encountered with experiments on bulk samples, the authors perform the experiments on ferroelectric films of thickness smaller than 100 μ, on which electrodes were fastened by a special method. The method for testing the nonlinear properties is claimed to be original and reduces to a measurement of the first Fourier-expansion coefficient of the time-varying capacitance modulated by a harmonic voltage at 1500 Mcs. A resonance chamber tuned to 3,000 Mcs was used to measure the nonlinearity coefficient. The procedures are briefly described. The tests disclosed

that in the temperature interval from 10 to 50°C type VK-3 ferroelectrics have a nonlinearity at 1500 Mcs, as evidenced by frequency doubling. The nonlinearity coefficient differs from zero both above and below the Curie point, and has a relatively weakly pronounced maximum in the paraelectric temperature region. Since the Curie point of VK-3 is 30°C, the nonlinearity occurred in both the paraelectric and in the ferroelectric phases of this material. Tests of the nonlinearity at different frequencies demonstrated the presence of slow relaxation effects and a dependence of the hysteresis on the frequency. The latter has not been satisfactorily explained.

12. Kapyshev, A. G., V. V. Ivanova, and Yu. N. Venevtsev. Some new perovskites. Akademiya nauk SSSR, Doklady, V. 167, no.3, 1966, 564-565.

Experiments were made to synthetize new perovskite-type materials with a view to further investigate their ferroelectric and other properties. The specimens were prepared, as usual in the technology of ceramics, by solid phase reactions using carbonates and oxides of metals as starting materials. The phase composition of the specimens was controlled by x-ray techniques using RKD-57 cameras with CuKα - radiation. The parameters and distortions of cells were determined by RKD-14 x-ray cameras built at the Karpov Physicochemical Institute, with which the authors are associated. The results of the experiments were summarized in a table which is partially presented below.

No. of specimen	Compound	Initial materials	Temperature (°C) and duration of heat treatment (hour)	Parameters of elementary cell (a and c in Å)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

It is considered significant that the specimens 1 to 6, containing ions of bivalent copper, had the same type of distortion ($c/a > 1$), which is of relatively high magnitude. In specimens 1, 4 and 6 it was not less than with $PbTiO_3$ ($c/a = 1.06$). It is also obvious that the exchange of barium for strontium has only a slight effect on the tetragonality of the cells, although the magnitudes of a and c will reflect the exchange. The table includes a specimen found to have distortions ($c/a > 1$ or $\alpha < 90°$) characteristic of ferroelectrics and containing ions of high polarizability. These compounds, therefore, may have ferroelectric properties.

13. Khuchua, N. P., and V. A. Yevseyev. Investigation of n-type ferroelectrics with perovskite structure in the microwave range. Fizika tverdogo tela, v. 8, no. 1, 1966, 258-260.

To explain the noticeable dispersion of the dielectric constant at microwave frequencies, observed in ferroelectrics below the Curie temperature, the authors measured the dielectric properties of $PbMg_{1/2}W_{1/2}O_3$, $PbZrO_3$, $PbZrO_3$, and 0.98 $PbZrO_3$ -- 0.02 $CaZrO_3$ which have perovskite structure at microwave frequencies. Particular attention was paid to the frequency and temperature dependence of the dielectric constant of $PbMg_{1/2}W_{1/2}O_3$ near the phase-transition point, since this substance is a pure antiferroelectric and has no ferroelectric components. The temperature dependence of the dielectric constant were plotted at 10^3, 2×10^9, 9.4×10^9 cps. The results show that within the accuracy of ± 7 per cent the dielectric constant does not depend on the frequency up to about 10^{10} cps. The same thing holds for the other antiferroelectrics up to 2×10^9 cps. It is therefore concluded that in antiferroelectrics with perovskite structure the dielectric constant is independent of the frequency in the range 10^3 -- 10^{10} cps. This is used as an indirect confirmation of the assumption that the dispersion of dielectric constant in ferroelectrics is connected with the presence of a domain structure in the ferroelectrics. For a comparison of the loss angles for the ferroelectric and antiferroelectric crystals at microwave frequencies it is deduced that the contribution of the orientational polarization to the dielectric constant of ferroelectrics in the decimeter band is quite large.

14. Kosman, M. S., A. N. Sozina, and A. I. Alikhanov. Relaxation oscillations in dielectrics. Akademiya nauk SSSR, Doklady, v. 156, no. 4, 1964, 778-780.

The authors found in a previous work (Fizika tverdogo tela, no. 3, no. 1, 1961, 2504) that current oscillations are produced in silicon

upon application of a sufficiently high voltage. They find now a similar phenomenon in dielectrics such as polycrystalline barium titanate. The oscillations were observed with an oscilloscope on a 1-mm thick sample, with one flat and one pointed electrode; the applied voltage was about 700 v. The current pulses were not strictly periodical. Higher "frequency" corresponded to a lower amplitude. The circuit resistance greatly influenced the pattern. With 10^6 ohms, the current reached the maximum in about 10^{-6} sec; the decrease was somewhat longer. It appeared that while in the semiconductors the resistance changed during oscillations only in the layer near the surface, in the dielectric the resistance of the whole specimen changed periodically.

15. Kraynik, N. N., N. P. Khuchua, A. A. Berezhnoy, A. G. Tutov. On the nature of phase transitions in solid solutions $BiFeO_3$-$PbFe_{1/2}Nb_{1/2}O_3$. Fizika tverdogo tela, v. 7, no. 1, 1965, 132-142.

The authors investigated the dielectric properties of $BiFeO_3$ and of its solid solutions with $PbFe_{1/2}Nb_{1/2}O_3$ which is ferroelectric below 112°C and is simultaneously an electromagnet. A standard ceramic technology was used for the synthesis of the samples. The temperature dependences of the dielectric constant and of the loss angles, and the dependences of these quantities on the constant bias field, were measured with a procedure described by Khuchua with L. F. Lychkataya (Akademiya nauk SSSR, Izvestiya, Seriya fizicheskaya, v. 28, 1964, 708). The dependence of the parameters of the unit cell on the composition at room temperature was also determined. The results show that there are two regions of solid solutions, pseudocubic and rhombohedral, separated by a morphotropic boundary which lies in the composition region with 60--75% $BiFeO_3$. This agrees with other data indicating the presence of the phase boundary in this region. The dielectric constant and the loss angle exhibited anomalies in the phase transitions. A smoothed-out ferroelectric phase transition was observed in solid solutions containing not more than 65% $BiFeO_3$. Two phase transitions were observed in solid solutions with 80--90% $BiFeO_3$; both phases are more likely antiferroelectric than ferroelectric, although no final decision has been made on this question. One phase transition was observed at more than 93% $BiFeO_3$. The phase below the temperature of this transition is identical to the low-temperature electrically-ordered phase in compositions with 80--90% $BiFeO_3$. The presence of electric ordering in the high-temperature phase with such compositions has not been proved. No anomalies of the dielectric constant were observed near the Curie temperature. The temperature range was -150--800°C. A diagram was constructed of the phase transitions in this system, corresponding to the occurrence or change in the spontaneously polarized state.

16. Kudzin, A. Yu. Effect of admixtures on the properties of barium titanate. Kristallografiya, v. 9, no. 2, 1964, 295-297.

Unit cell parameters of barium titanate single crystals were measured at temperatures up to 300°C. Samples were prepared both without admixtures and with CoO, NiO, Nb_2O_5, $2NiO \cdot Nb_2O_5$, or $2NiO \cdot Ta_2O_5$. The measurements were made to show the effect of nonisomorphous admixtures on the shift of the Curie point and thus to correlate the ferroelectric properties of barium titanate-base solid solutions with their geometry. The parameters were measured with the RKE chamber and a tube with a copper anticathode. Sample temperatures were determined with an accuracy of ±2°C from the unit cell parameter of the aluminum powder added to the $BaTiO_3$ powder before compacting. A linear increase of the parameter with increasing oxide admixture content was established for all crystals studied. The parameter at the Curie point is a constant, independent of the nature or concentration of admixtures. The increase in volume of the unit cell is attributed 1) to the greater radius of Co and Ni ions compared to that of the titanate ions or 2) to the formation of vacancies in the Ba sublattice in the presence of tantalum and niobium oxide.

17. Kudzin, A. Yu., L. G. Guskina, and I. S. Petrushkevich. Stabilization of domain structure in single crystals of barium titanate. Fizika tverdogo tela, v. 6, no. 1, 1964, 92-95.

The dielectric hysteresis loops of single crystals of barium titanate containing tantalum oxide and nickel oxide are anomalous. All samples tested contained about 0.3 molecular % tantalum oxide and from 0 to 0.5 molecular % nickel oxide. Increase in nickel content led to a decrease in Curie point. Optimal conditions for growing the barium titanate were obtained with nickel oxide concentrations of 0.3-0.4 molecular %. The anomalous loops were found to be stable relative to external effects, this relation resulting from stabilization of domain structure. The rate of forming the domain structure during application and removal of the electrical field was rather large, since twin hysteresis loops were noted at frequencies up to 10 kilocycles. It is concluded that vacancies in the barium sublattice, resulting from introduction of pentavalent ions, may serve as centers for fixing the domain walls.

18. Leonidova, G. G., and T. R. Volk. Investigation of phase transition in barium titanate at high hydrostatic pressure . Fizika tverdogo tela, v. 7, no. 11, 1965, 3344-3347.

The dielectric characteristics of a $BaTiO_3$ single crystal were

studied at pressures up to 8.5 kilobars in isothermal conditions to determine the nature of phase transition in this material as related to the variation in the constants A and B of the Devonshire equation. A reduction in the absolute value of B with pressure indicated that a second order transition may be observed in conformity with the Landau-Ginzburg theory at some critical hydrostatic pressure.

19. Lezgintseva, T. N. Concerning the structure of the surface layer in single crystals of $BaTiO_3$. Fizika tverdogo tela, v. 7, no. 4, 1965, 975-980.

The author investigated the influence of crystal thickness and the influence of the electrode materials on the behavior of single-crystal barium titanate with a complicated domain structure. The crystals were grown from a melt in potassium fluoride with both chemically pure $BaTiO_3$ and with small addition of oxides of group IV elements. The electrodes were deposited by melting-in silver paste, sputtering of silver and antimony in vacuum, and sputtering a thin film of SnO_2 at 400°C. Liquid electrodes of saturated LiCl solution were also used. The crystal thickness was 0.035--1.7 mm. The results showed a tendency to an increased thickness of the surface layer with increasing crystal thickness, due to the increased concentration of the a-domains with increasing thickness. It is indicated that the previously observed large increase in the dielectric constant observed with increasing crystal thickness was due either to the edge effect or to an increase in the concentration of the a-domains with increasing crystal thickness. Making use of the large role of a-domains in the repolarization process, the author proposed a new model of the surface layer, which explains the asymmetry of the hysteresis loops of crystals provided with different electrodes.

20. Lezgintseva, T. N. Piezoelectric effect in barium titanate single crystals with complex domain structure. Fizika tverdogo tela, v. 6, no. 12, 1964, 3509-3514.

The author derived formulas for the piezoelectric modulus d_i in terms of a change in the permittivity ε (or polarization P) on the application of a mechanical load. The basic formula was

$$d_i = \frac{Q_i}{F} = \frac{\Delta P_i}{\sigma} = \frac{\Delta \varepsilon P}{\varepsilon \sigma}$$

where Q is the electric charge, F the applied force, and σ the applied stress(pressure). Allowance was made for the change in the domain structure (90° domain rotation) under a mechanical load by

expressing the change of the polarization ΔP in terms of a change in the a-domain concentration (m) : $\Delta P = \Delta m P_s$, where P_s is the spontaneous polarization. The formula was checked by comparison with the published values of d for $BaTiO_3$; it was used to calculate d from [illegible] values, measured by applying either effectively hydrostatic or unideractional pressures to monocrystals and ceramic samples. The value of d_{33} for monocrystals was found to be two orders of magnitude greater than for ceramic samples. To check the results of the calculations, the author herself measured d_{33} of $BaTiO_3$ single crystals containing small admixtures of oxides of tetravalent elements having laminar domain structure, by the static and quasistatic methods. The initial concentration of a-domains did not exceed 0.5. The values of d_{33} depended both on the polarization conditions and on the crystal composition. The highest values of d_{33} were obtained for crystals with an admixture of hafnium after strong (> 200°C) heating, followed by cooling in a weak constant field. The lowest piezoelectric modulus was obtained for crystals grown with an admixture of SiO_2 in which the concentration of a-domains was highest (sometimes higher than 0.5) and in which mechanical stresses were greatest. The results were in agreement with those calculated using formulas given by the author, although these formulas did not allow for the duration of action of a load on a crystal which could affect the measured values of the piezoelectric modulus. The temperature dependence of d_{33} (20-120°C) for a single crystal of $BaTiO_3$, obtained by the quasistatic method, had the characteristic maximum near the Curie point (120°C) at which the piezoelectric modulus vanished, as expected for the direct piezoelectric effect. Dynamic measurements did not give such high values of the piezoelectric modulus but agreed completely with the published values, and confirmed that at sufficiently high frequencies the domain structure changes did not occur and the effects associated with these changes did not appear.

21. Lezgintseva, T. N. Single crystals of barium titanate with a stratified domain structure. Fizika tverdogo tela, v. 6, no. 8, 1964, 2401-2404.

The author investigated single crystals of barium titanate obtained from a melt in potassium fluoride with a small amount of hafnium added. All crystals had a stratified domain structure made up of alternating a- and c-domains at 45° to the plane of the plate. Such a domain structure is stable against heating, polarization, and prolonged action of mechanical load. A formula is derived for the dielectric constant of such a crystal and the dependence of the properties of the crystals on the concentration of the a-domains is analyzed. The variation of the piezoelectric modulus of the unpolarized single crystal on a constant bias field leads to a qualitative

connection between the piezoelectric modulus and the domain structure of the crystal. The irreversible changes in the domain structure of the crystal during the course of the measurements may be the cause of the instability of the electric and mechanical properties. A qualitative agreement was obtained between the calculation results and the experimental data.

22. Matsonashvili, B.N. Electrical and optical properties of $BaTiO_3$ crystals with admixtures of iron and cobalt. Kristallografiya, v. 12, no. 6, 1967, 995-999.

Experimental investigations were made to establish certain electric and optic properties of barium titanate crystals with various percentages of admixtures of iron and cobalt. The temperature dependence of permittivity, tan δ and the electroconductivity were measured. The permittivity dependence displayed maxima of various levels which were shifted toward lower temperatures as the content of cobalt or iron admixture increased. The character of the dependence was nearly independent of the frequency (1500 Kc and 1 Mc were used). The magnitude of tan δ reached about 10^{-2} at temperatures below and (3 to 4) x 10^{-4} above the Curie point. The dependence of the Curie point on the content of admixtures was found to differ greatly from the data of other authors (Nishioka, et al., J. Phys. Soc. Japan, v. 11 1956, 180; Arnold et al., Jr. J. Chem. Phys., v. 41, no. 5, 1964, 1520). The same applied to the comparison of crystals and ceramics. In general, the Curie point was lowered 40°C per 1 at % Co and 30°C per 1 at % Fe. Many specimens with and without (i.e., not especially doped) admixtures showed a discontinuity or anomaly of electroconductivity at the Curie point. The degree of hydrogen reduction had a marked effect on the magnitude of the conductivity and its anomalies. A high degree of reduction was accompanied by a weak temperature dependence of the conductivity and eliminated the anomalies at the Curie point. The transmittivity was studied within the 0.3 to 2.0 μ wavelength range. Three minima were observed at 1.85, 1.55 and 0.7 ev. The 1.85 ev minimum was well pronounced for weakly reduced specimens, while the 1.55 ev minimum was characteristic of specimens with Fe and Co admixtures. An increase in admixture content and reduction caused a shift of the transmission band edge into the longwave region of the spectrum. The conductivity anomaly at the Curie point is explained by the scattering of carriers on the domain boundaries, due to the fact that the reduction of electrons trapped on the domain boundaries is less pronounced than the process of scattering.

23. Matsonashvili, B. N. Temperature dependence of the electric conductivity of $BaTiO_3$, both pure and with iron and cobalt impurities, reduced in hydrogen. Fizika tverdogo tela, v. 8, no. 11, 1966, 3439-42.

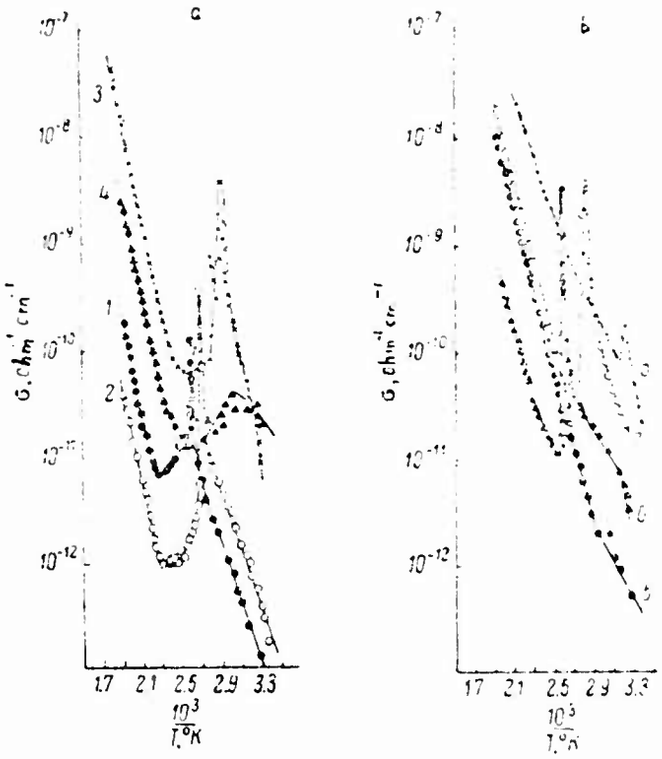
The temperature dependence was investigated at 800, 1000, and 1200°C for reduction times of 5, 4, and 2 hours respectively. Measurements of the temperature dependence were made at a constant voltage by means of two-probe and four-probe methods described by the author earlier (FTT, v. 8, 3232, 1966). In the case of weakly reduced crystals (800—1000°C) an anomaly appeared in the conductivity σ at the point where the plot of log σ vs. 1/T (T = temperature) exhibited a kink near the Curie point. In some cases the kink was observed both before and after reduction. In crystals with Fe impurities, the change in the conductivity after reduction depended strongly on the type of conductivity of the samples, increasing strongly for n-type and decreasing for p-type. In crystals with Co, the reduction increased noticeably the conductivity when the content of the cobalt was small, and decreased it when the content was large (5.0 at. %). The article reports also the effects of etching prior to measurements, the effects of heat treatment, and the average values of the activation energies for different contents of impurity, as well as the changes in the optical spectrum after reduction. No anomalies were observed in the case of strongly reduced crystals (1200°C). The results are interpreted from the point of view of the effect of the F_2-centers on the conductivity under various conditions. The conclusions agree well with optical-transmission data obtained for the crystals.

24. Matsonashvili, B. N. Temperature dependence of the electric conductivity of $BaTiO_3$ crystals, pure and with iron and cobalt impurities. Fizika tverdogo tela, v. 8, no. 11, 1966, 3232-3235.

The temperature dependence of the electric conductivity σ was studied in the 20—300°C range at a voltage of 2—15 V/cm on pure $BaTiO_3$ crystals and crystals containing 0—5 at % Fe and Co. An anomaly of σ was observed at 15—40°C in pure crystals and at 50—70°C in those containing Fe and Co; in the latter, less than in pure crystals. Such behavior of σ was due to a change in the type of conductivity associated with doping with acceptor impurities. The measured temperature dependence of σ is shown in Fig. 1. A study of optical transmission in the 0.3-2.0 μ range showed minima at 0.6 and 1.8 ev, due to the presence of F_2- and F_1- centers in all the samples (with and without impurities). Below the Curie point, the conductivity of $BaTiO_3$ crystals was due mainly to F_2-centers. Above the anomalous range, σ was chiefly determined by the thermal excitation of the dopants. A definite contribution to σ was made by the F_1-centers, especially at high temperatures.

Fig. 1.

Temperature dependence of electric conductivity of $BaTiO_3$ crystals with Fe (a) and Co (b).
Fe content, at. %: 1 - 0, 2 - 0.6, 3 - 2.0, 4 - 5.0 (crystal 4 was considerably reduced).
Co content, at. %: 5 - 0, 6 - 0.2, 7 - 2.0, 8 - 5.0.



25. Murzin, V. N., S. V. Bogdanov, and A. I. Demeshina. Dispersion relation and some microscopic characteristics of barium titanate. Fizika tverdogo tela, v. 6, no. 11, 1964, 3372-3377.

The method of W. Cochran (Adv. Phys., v. 8, 387, 1960) was used to analyze the experimental results obtained for $BaTiO_3$ and to derive in explicit form a dispersion relation for the complex dielectric constant of substances with crystal structure of the perovskite type in the cubic state. Allowance was made for the fact that in such crystals the polarization has a complex character, due to the presence of strong local electric fields and to the large contribution of the electron polarization. In the case of barium titanate a comparison of the calculations with experiments yielded estimates for the ion displacements, the total polarizability per unit crystal cell and its ionic components, the values of the local electric fields, and the ion polarizabilities of the atoms. The calculation showed that 65—80% of the total polarization of the crystal was due to electron polarization.

26. Murzin, V. N., and A. I. Demeshina. Temperature investigations of vibration in polycrystalline $BaTiO_3$ and $SrTiO_3$ over a wide spectral range. Fizika tverdogo tela, v. 6, no. 1, 1964, 182-192.

The authors have studied the transmission and reflection spectra of $BaTiO_3$ and $SrTiO_3$ in the temperature interval 45-140°C in the spectral range 2—1000 microns. Measurements on the shorter wave-lengths (2—25 microns) were made on an IKS-14 infrared spectrometer; those in the range 20—1000 microns were made on a far-infrared spectrometer; those in the range 20—1000 microns were made on a far-infrared spectrometer built in the Laboratory of Semiconductor Physics of the Physics Institute, Academy of Sciences SSSR. In addition to the known reflection band with a maximum at ~18 microns, a wide plateau segment was observed for both substances at ~22 microns. It is not well defined. Both substances have maxima at ~30 microns; $SrTiO_3$ has one at ~ 80 microns, and $BaTiO_3$ has a weak one at ~ 55 microns. These indicate the development of high permittivity because of vibration of the crystal lattice. The measurements were treated mathematically, and the spectral behavior of the actual and imaginary parts of the permittivity was determined. Observed vibration of the crystal lattice of these substances has been interpreted according to the theoretical views relative to the vibration spectrum of the perovskite crystal lattice, on the basis of group theory. Anomalous measurements of low-frequency vibration at temperatures near the phase transition are considered on the basis of recent microscopic theories of ferroelectrics. The temperature relations of the dielectric constant for the most interesting parts of the spectrum are shown in Fig. 1 on the next page. It is clear that in the region $\lambda < 1$ cm a basic change occurs in the dielectric constant for $BaTiO_3$ because of rearrangement of domains and displacement of domain boundaries. In the region $\lambda < 1$ cm, the temperature changes in the dielectric constant are due to deformation of the crystal lattice and to corresponding changes in the vibration spectrum.

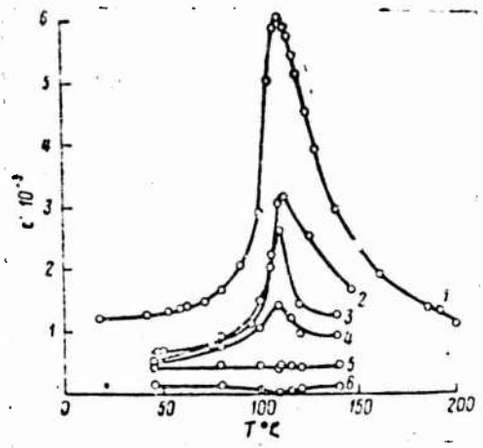


Fig. 1. Temperature behavior of dielectric constant, measured in different parts of the spectrum.

1 - f = 1 kilocycle; 2 - λ = 3.2 cm; 3-6 - for measurements in the far-infrared part of the spectrum (3 - by extrapolation $\omega \to 0$; 4 - λ = 2.5 mm; 5 - λ = 0.7 mm; 6 - λ = 0.25 mm).

27. Platonov, G. L., Yu. Ya. Tomashpol'skiy, Yu. N. Venevtsev, L. Ya. Karpov, and G. S. Zhdanov. Microelectronographic investigation of the atomic structure of tetragonal barium titanate. Kristallografiya, v. 12, no. 5, 1967, 933-935.

An experimental investigation was made of the structure of $BaTiO_3$ ferroelectric by the microelectronographic method. The investigation was undertaken to prove the effectiveness of microelectronography for the purpose, and also to resolve questions concerning the structural identity of thin films and block crystals of $BaTiO_3$. The method, comprising trial and error combined with successive approximations, is described in some detail. The resulting projection of structural potential on the coordinate force (010) of the cell is presented. Isotropic temperature adjustments were attempted for each atom, but this did not affect materially the outcome of the analysis. The displacement data obtained by the authors were compared with those reported earlier by Evans (Jr. Acta Crystallogr., v. 14, no. 10, 1961, 1019) and Frazer et al. (Phys. Rev., v. 100, 1955, 745) and found to be in fair agreement. The conclusion is drawn that, as reported earlier by Tanaka et al. (J. Phys. Soc. Japan, v. 19, no. 6, 1964, 954), the structure of barium titanate blocks and thin films obtained by thinning massive specimens are identical.

28. Polandov, I. N., and V. P. Mylov. Investigation of $Ba(TiSn)O_3$ ferroelectric ceramics under high pressures. Fizika tverdogo tela, v. 9, no. 8, 1967, 2319-2323.

Investigations were made of the dielectric properties of $Ba(TiSn)O_3$ ferroelectric ceramics with varying content (10, 12 and 16%) of Sn ions in solid solution. The measurements were taken in weak (about 5 v/cm) alternating (1000cps) electric fields within the temperature range -30 to +90°C at pressures up to 7500 kg/cm^2. It was found that the permittivity of the investigated materials within the phase transition region dropped as the pressure increased. The permittivity within the paraelectric region obeys the Curie-Weiss law at high pressures. The temperature of the ferroelectric phase transition for the investigated compounds declines linearily as the pressure rises, with a gradient of about -2.35×10^{-3} degrees per atmosphere. The tangent of the angle of dielectric losses passes a maximum at the phase transition; that maximum decreases with rising pressures. The maxima of $\tan\delta$ depending on pressure, were also observed to shift toward the lower temperatures. The heat of the ferroelectric phase transition was estimated; its amount decreased with rising pressures.

29. Polandov, I. N. Investigation of ferroelectric solid solution Ba $Ba(Ti_{0.95}Zr_{0.05})O_3$ at high pressures. Fizika tverdogo tela, v. 7, no. 6, 1965, 1874-1876.

The author describes the results of experimental investigations of the dielectric properties of the investigated solid solution in the pressure range up to 7200 kg/cm^2. The experiments were carried out with a sample 5 mm in diameter and 0.5 mm thick. The capacitance of the sample was measured at 1000 cps. The temperature dependence of the dielectric constant was measured in the temperature interval 20--120°C at various hydrostatic pressures up to 7200 kg/cm^2. The rate of temperature increase was kept constant in all experiments at 0.250° per minute. At atmospheric pressure the data obtained agreed well with those previously published. As the pressure was increased, the Curie temperature shifted towards lower temperatures continuously and the lattice symmetry changed from tetragonal to cubic; at the same time, the sample changed to the para-electric state. The dielectric constant at the Curie point decreased noticeably with increasing pressure. The sensitivity of the dielectric constant near the phase transition point to hydrostatic pressure is attributed to the influence of pressure on the main structure, indicated in an earlier paper by the author (with V. P. Mylov, FTT v. 6, 1964, 499).

30. Polandov, I. N., and V. A. Mylov. Dielectric properties of a polycrystalline solid solution of $Ba(Ti, Zr)O_3$ in the region of the phase transition at high pressures. Fizika tverdogo tela, v. 6, no. 2, 1964, 499-502.

The authors have investigated the dielectric properties of a polycrystalline solid solution of $Ba(Ti_{0.9}, Zr_{0.1})O_3$ in weak electric fields and in pressure range up to 6100 kg/cm^2. They have measured the dependence of the dielectric constant on temperature in the region of the phase transition at various pressures. These data are shown in Fig. 1. The authors found that with increasing pressure, curves showing the dependence of the dielectric constant on the temperature shifted toward low temperatures. Plotting the reciprocal of the dielectric constant as a function of temperature showed that at high pressures and in weak electric fields, the Curie-Weiss law is fulfilled. The temperature of the ferroelectric phase transition decreased linearly with application of pressure and had a coefficient of $-3.8 \cdot 10^{-3}$ degree/atm.

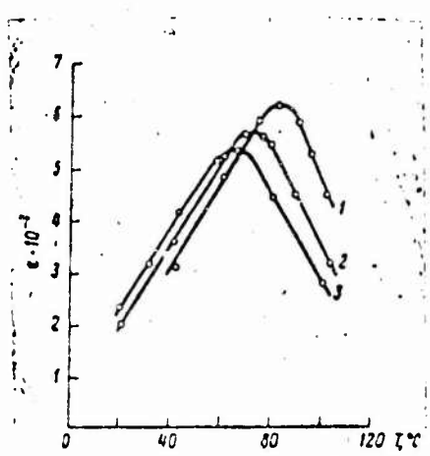


Fig. 1. Dependence of the dielectric constant of a solid solution of $Ba(Ti_{0.9}, Zr_{0.1})O_3$ on temperature at different pressures (kg/cm^2): 1 - 2000 kg/cm^2; 2 - 4300; 3 - 6100. Strength of the alternating electric field is 30 v/cm.

31. Poplavko, Yu. M., and V. G. Tsykalov. Investigation of millimeter antiferroelectric crystals. Fizika tverdogo tela, v. 9, no. 11, 1967, 3305-3310.

Experimental investigations were made of the temperature characteristics of various antiferroelectric substances on the 37 GHz frequency (8.1 mm wavelength). For purposes of comparison, low-frequency measurements were made at the frequencies from 0.5—1.1 MHz. The method of measurement was described earlier by Poplavko (Proc. Intern. Meeting on Ferroelectricity, Prague, 2, 1966, 171; Zhurnal eksperimental'noy i teoret. fiziki, v. 43, 1962, 800) B. Ya. Yazytskiy,

Table 1.

ε - dielectric constant; tan δ - loss coefficient;
T_c - transition temperature; θ - Curie temperature;
C - Curie-Weiss coefficient; TK_ε - average temperature coefficient below T_c.

	$\varepsilon_{20°C}$	$\tan\delta_{20°C}$	ε_{max}	T_c, °K	θ, °K	$C \cdot 10^{-4}$, $\frac{1}{°K}$	ε_θ	TK_ε
$PbZrO_3$	80	0.035	2500	504	425	17.5	>50	0.011
$PbZrO_3$*	58	0.05	2300	503	445	15.5	>50	0.014
$NaNbO_3$	160	0.07	1560	593	415	28	>50	0.003
$PbMg_{1/3}W_{1/3}O_3$	111	0.07	215	310	175	1.8	64	0.05
$PbCo_{1/3}W_{1/3}O_3$	~100	0.03	165	303	180	1.2	70	—
$PbYb_{1/2}Nb_{1/2}O_3$	60	0.06	270	575	295	5.8	66	0.0015
$PbYb_{1/2}Ta_{1/2}O_3$	33	0.06	110	570	445	7.3	56	0.0016
$Pb_3V_2O_8$	28	0.04	105	373	100	1.4	52	—
$BaTiO_3$	490	0.15	~6500	393	375	12.6	>50	—

* This specimen was "pulse-baked" for 20—40 min in a silicon carbide kiln at 1400°C

and Yu. M. Poplavko (Fizika tverdogo tela, v. 8, 1966, 3639), and Yazytskiy (Tez. dokl. V Vses. konf. po segnetoelektrikam. Dnepropetrovsk, Oblizdat, 1966) and involved the use of waveguide (7.2 x 3.6 mm) with specimens adapted to its dimensions. The general characteristics of the investigated materials are summarized in Table 1. The results of investigations are interpreted as confirming the applicability of the dynamic theory of ferroelectricity also to simple and compound antiferroelectric materials of the oxygen-octahedral class.

32. Poplavko, Yu. M., and B. Ya. Yazytskiy. A method of investigation of temperature characteristics of ferroelectrics on super-high frequencies. Pribory i tekhnika eksperimenta, no. 4, 1967, 144-147.

Experimental investigations were made of the permittivity and loss-angle characteristics of (Ba, Ca)TiO_3 ferroceramics as a function of temperature within the centimeter and millimeter wave range. The waveguide resonance method was used for measurements in which the resonance SHF signals' reflection coefficient from the specimen placed before the short circuit of the waveguide was observed. The wavelength in the section of the waveguide filled with the specimen shortened as its permittivity increased, and resonance occurred when the electric length of the specimen took the value of a multiple of the quarter-wavelength. The resonance occurred repeatedly when the permittivity changed with temperature and the specimen was sufficiently thick. The resonance points were determined from the maxima of the traveling wave coefficient in the system, while the magnitude of these maxima was a measure of loss angle ($\tan \delta$). The conclusions were tabulated from measurements for permittivity and loss angle as functions of temperature for frequencies of 9.4 Gc and 550 kc. The curves showed that a strong dispersion characterizes (Ba, Ca)TiO_3 ceramics. The same method applied to pure barium titanate did not indicate any dispersion above the Curie point, with permittivity reaching the value of 6400. The measurements covered the temperature range -196 to +500°C. The method is said to be suitable for automatic recording of the traveling wave coefficient.

33. Poplavko, Yu. M., and V. I. Tsykalov. Dielectric constant of barium titanate in the millimeter wave range. Fizika tverdogo tela, v. 8, no. 10, 1966, 3112-3114.

Experimental investigations were made of the permittivity and the loss angle of $BaTiO_3$ and other ceramics on various wavelengths of the millimeter range. The waveguide resonance method, described by Poplavko earlier (Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 43, 1962, 800) was used. The standing wave coefficient of $BaTiO_3$ as a function of the specimen thickness was preliminarily measured at frequencies of 9.4, 26.2, and 37 Gc. The specimen was placed in a rectangular waveguide before the short-circuit with a dielectric transformer of teflon. The measurement data are shown in Table 1.

Table 1. Permittivity and loss coefficients

Frequency Gc	Waveguide cross section mm	$BaTiO_3$ (T_k=118°C ε_m = 8500)			$PbTiO_3$ (T_k=490° ε_m = 6200)			$PbZrO_3$ (T_k=235°C ε_m = 2500)		
		λ, mm	ε'	tan δ	λ, mm	ε'	tan δ	λ, mm	ε	tan δ
10^{-3}	—	—	1400	0.021	—	115	0.015	—	85	0.005
9.4	23 x 10	1.22	660	0.32	4.03	59	0.25	3.52	82	0.01
16.1	17 x 8	0.74	610	0.25	—	—	—	—	—	—
26.2	11 x 6	0.476	570	0.19	1.59	50.5	0.25	—	—	—
37	7.2 x 3.6	0.365	490	0.15	1.14	50.5	0.21	0.90	80	0.03
52.4	5.2 x 2.6	0.270	450	0.17	0.82	50	0.18	0.68	71	0.04

T_k - temperature of the phase transition; ε_m - permittivity at the phase transition; ε' and tan δ - permittivity and the loss angle measured at the room temperature (20-22°C).

The characteristics of lead ceramic compounds were measured for the first time. As seen from the table, lead zirconate has practically no dielectric dispersion even on millimeter waves. Lead titanate, on the other hand, has dispersion as pronounced as barium titanate, notwithstanding its much smaller permittivity and a farther removal from the Curie point. The data obtained for BaTiO disagree with some earlier reports (Powles and Jackson, Proc. IEE. v. 96, 1949, 383). The authors also note that the losses in $BaTiO_3$ are lower in the millimeter wave range as compared to those in the centimeter range, which shows that the mechanism of SHF dispersion in this material has a lower effect at frequencies above 10 Gc.

34. Poplavko, Yu. M. Dispersion of the dielectric constant in ferroelectrics of the barium titanate type. Fizika tverdogo tela, v. 6, no. 1, 1964, 58-64.

Investigations were made of the frequency dependence of the dielectric

constant and dielectric loss of single crystals of ceramic barium titanate. The results are summarized in Fig. 1. Measurements were made on standard apparatus in the frequency range 50-1.6·10^{10} cycles in weak electrical fields. Dispersion of the dielectric constant was observed at frequencies of 10^8-10^{10} cycles. The application of a strong steady displacement field did not noticeably shift the central region of dispersion. In the region of high-frequency dispersion the dielectric loss decreased considerably on application of the displacement field, more so than at low frequencies. The dielectric constant changed much less, however, on application of the displacement field at high frequencies than at low frequencies. It was found that the dielectric constant might be changed by a factor of 2—2.5, depending on the displacement field. The introduction of barium zirconate and barium stannate into barium titanate reduced the dielectric loss and increased the dielectric constant.

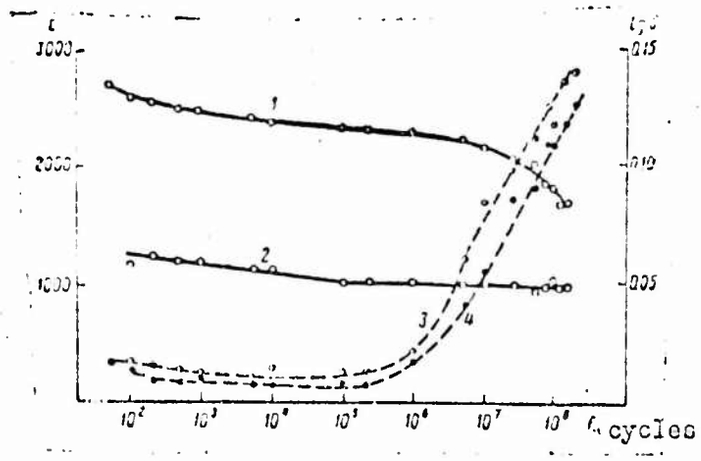


Fig. 1. Frequency dependence of dielectric constant (ε) and dielectric loss (tg δ) in a semidomain crystal of barium titanate in weak fields.
1 - dielectric constant; 2 - dielectric constant with displacement field of 10 kg/cm; 3 - tangent of dielectric loss; 4 - tangent of dielectric loss at a displacement field of 10 kv/cm.

35. Rotenberg, B. A., Yu. L. Danilyuk, Ye. I. Gindin, and V. G. Prokhvatilov. Electrophysical and microwave spectral study of barium titanate with admixtures of oxides of trivalent elements. Fizika tverdogo tela, v. 7, no. 10, 1965, 3048-3053.

The authors studied some of the electrical properties, structure, and paramagnetic resonance absorption of polycrystalline barium titanate with small admixtures of oxides of trivalent elements. Paramagnetic

resonance absorption was measured at 9320 Mc and 78°K. It was established experimentally that there are four possible types of solid solutions in $BaTiO_3$-R_2O_3 systems. 1. A solid solution of substitution in the barium ion sublattice with the formation of weakly bound electrons (donor levels)

$$Ba_{1-x}R_x^{3+}TiO_3 + xe^-$$

Solid solutions of this type have high electrical conductivity. 2. A solid solution of substitution with subtraction in the barium ion sublattice

$$Ba_{1-3/2x}\boxed{Ba}_{3/2x}R_x^{3+}TiO_3;$$

in this case, the lattice is neutral due to barium vacancies, and the specimens are dielectrics. 3. A solid solution of substitution in the titanium sublattice

$$BaTi_{1-x}R_x^{3+}O_{3-\frac{x}{2}},$$

where it is most natural to assume that electric neutrality of the lattice in the case of oxide semiconductors is due to oxygen vacancies formed during annealing, and electrical conductivity does not increase. 4. A more complex solid solution of substitution in both sublattices with the formation of oxygen vacancies and donor levels

$$(Ba_{1-y}R_y^{3+})(Ti_{1-x}R_x^{3+})O_{3-\frac{x}{2}} + ye^-.$$

An increase in electrical conductivity is possible in this case. When x = y, electric neutrality may be maintained without the formation of oxygen vacancies and donor levels according to the formula

$$\left(Ba_{1-\frac{x}{2}}R_{\frac{x}{2}}^{3+}\right)\left(Ti_{1-\frac{x}{2}}R_{\frac{x}{2}}^{3+}\right)O_3.$$

Other cases are also possible if the alloying additive has variable valence. It is shown that electrical conductivity is related to impurity concentration through changes in the type of solid solution formed during annealing of barium titanate with impurities in concentrations of 0.1-0.3 mol %. The experimental data indicate that the same types of defects are formed by reduction of the ceramic and by alloying. It is possible that these are not single-electron defects or defects of odd order in general. This hypothesis agrees with the conclusions made by other researchers.

36. Selyuk, B. V. Charge localization in a ferroelectric capacitor. Fizika tverdogo tela, v. 8, no. 12, 1966, 3500-3505.

In view of the fact that the space charge produced near the surface of a ferroelectric crystal is usually disregarded in the analysis of ferroelectric materials used in switching devices, and in view of the fact that the existence of a space charge in the transition layer between the crystal and the electrode in such a device is unavoidable, the author attempts to estimate the rate of penetration of charge through the transition layer and its influence on the behavior of the capacitor and on the rate of motion of the domain boundaries. The analysis, based on calculations for an infinite parallel-plate capacitor, showed that a considerable part of the charge in a ferroelectric capacitor is localized not on the electrode but in the transition region, and this localization remains in force up to fast switching frequencies. These switching cycles may reach 1 - 10 microseconds in duration. Consequently, in case of ferroelectric materials such as $BaTiO_3$, the charge moves from the electrodes to the surface of the crystal so rapidly, that it becomes localized not only in the electrodes but also to a considerable degree on the surface of the crystal. This localization can be either of the surface type, in a layer of the order of the lattice constant, or of the volume type, in a much thicker layer. In the latter case, there exists a ferroelectric layer whose properties differ from the rest of the ferroelectric, having anomalous properties which can greatly influence the behavior of the ferroelectric capacitor.

37. Servuli, V. A. Ye. V. Zarochentsev, and O. I. Prokopalo. Low-frequency electric oscillations in barium titanate. Fizika tverdogo tela, v. 9, no. 8, 1967, 2444-2446.

An experimental investigation was made of the nature of low-frequency oscillations in specimens of barium titanate which occur at high temperatures and are connected with the region of negative differential resistance in the current-voltage characteristic of the crystal. Condensers of pure barium titanate with an electrode area of 0.6 to 1 cm^2 and a thickness of 1-2 mm using burnt-in silver electrodes were used for measurements. In some specimens of such condensers, under simultaneous action of an strong electric field and high temperature, the expected oscillations could be observed. The temperatures were varied between 150 and 300°C and the voltages from 50 to 1000 v. The threshold temperatures and voltages proved to be interdependent. An increase of temperature or voltage increased both the amplitude and the frequency of the oscillations. The measured amplitudes reached 0.3 of the average current; the frequencies varied between 0.1 and 5 cps. The character and conditions of occurrence of the described

oscillations differ from similar oscillations described earlier (Okada, et al., Japan. J. Appl. Phys., 2, 1963, 736; ibid., 807, 812; Fridkin et al., Zhurnal eksperimental'noy i teoreticheskoy fiziki, no. 4, 1966, 461) and must have a different origin. In distinction from earlier observations (Benguigui, Proc. Intern. Meeting on Ferroelectricity II, Prague, 1966, 326) the hysteresis of the current-voltage characteristics in these experiments was repetitive, while the region of negative differential resistance was less pronounced. All threshold values of temperature and voltage fell on the hysteresis part. The authors accept the possibility of injection of carriers from the electrodes but only under the assumption that the application of a strong field and high temperature divides the specimen into layers of differing properties, namely differing current-voltage characteristics and possibly differing permittivity values. Under these conditions, the phenomenon could be qualitatively explained, but further investigations are needed to establish the exact effects of preliminary treatment of the specimens as well as conditions of the experiment on the character of the oscillations.

38. Sinyakov, Ye. V., Ye. F. Dudnik, and S. A. Flerova. Effect of mechanical pressure in the process of polarization in $BaTiO_3$ single crystals and in solid solutions of $BaTiO_3$-ZnO. Fizika tverdogo tela, v. 8, no. 10, 1966, 2848-2852.

Experimental investigations were made of the permittivity of barium titanate single crystals and its solid solution with zinc oxide as a function of temperature, applied electric field strength, and unidirectional pressure. All specimens were of uniform thickness (about 0.02 cm). Weak high-frequency fields were applied. The mechanical pressure was varied between 0 and 150 kg/cm^2, but in some cases it reached to 300 kg/cm^2. Nonlinearity and the parameters of the hysteresis loop were measured at room temperature at 60 c frequency. A special generator of bipolar pulses with the front not exceeding several nanoseconds was used for recording the polarity reversal currents. The measurement results showed that there is a narrow range of field strengths where the permittivity is independent of pressure. This range shifted toward stronger fields as the ZnO concentration (which was varied from zero to 0.66%) increased. It was also shown that in strong fields a portion of domains is excluded from the process of polarity reversal. The shift of the Curie point under pressure was found to be independent of ZnO concentration. The measurements of the polarity reversal currents in $BaTiO_3$ in strong fields at varying pressures further indicated a decrease in current as the pressure increased. The polarity reversal time increased somewhat at low pressures but declined as the pressure increased. The slight increase in polarity reversal time at low pressures is interpreted as indicating that the "clamping"

of some A-domains does not fully exclude them from the process of polarity reversal. At high pressures, however, the clamped domains are fully excluded, which leads to a decrease in current as well as in the time of polarity reversal.

39. Stolypin, Yu. Ye., and V. A. Isupov. Dielectric polarization and thermal expansion of polarized ceramic specimens of the $PbTiO_3$ - $PbZrO_3$ - $PbMg_{0.5}W_{0.5}O_3$ system. Fizika tverdogo tela, v. 9 no. 9, 1967, 2619-2624.

A series of experimental investigations was carried out on specimens of the $(1-x)$ $(0.6\ PbTiO_3 + 0.4PbMg_{0.5}W_{0.5}O_3) + xPbZrO_3$ ceramic system, where "x" takes a value between 0 and 0.70. The dependence of permittivity, the loss angle and piezoelectric characteristics on a constant electric field strength at room temperature, the deformation under action of a transverse electric field, and the thermal expansion of nonpolarized specimens and those longitudinally polarized were investigated. The permittivity was measured on 1 kc frequency. Specimens in the form of 18 mm long rods were made for measurements of thermal expansion. The polarization of rods was effected longitudinally during cooling from the Curie temperature. The measurement data made it possible to explain the dependence of physical properties of the specimens by the orientation of 180° and 90° domains, which in turn depend on the applied electric field strength. Deformation studies in a constant electric field furnished additional information on the orientation of the 90° domains. It was shown that the intense orientation of the 90° domains in the limit ($x = 0.32$) rhombohedral compound occurs at higher field strengths (about 9 kv/cm) than in the limit tetragonal compound (about 5 kv/cm). Thermal expansion studies confirmed the existence of reoriented 90° domains in the state of residual polarization. But further studies of the field-effected deformation and the temperature dependence of the parameters of the elementary cell are necessary to determine quantitatively the orientation of 90° domains.

40. Tomashpol'skiy, Yu. Ya., Yu. N. Venevtsev and, G. S. Zhdanov. X-ray investigation of the atomic structure of ferromagnetic $BiFeO_3$ Kristallografiya, v. 12, no. 2, 1967, 252-257.

An analysis was made of the atomic structure of $BiFeO_3$ single crystals, with a view to establishing the relative effectiveness of the x-ray method in comparison with the electronographic method. The measurements were taken from a single-crystal needle 0.8 mm long and 0.1 — 0.2 mm in diameter, considered, for purposes of calculations,

as a cylinder 0.15 mm in diameter. The method is described in some detail. A comparison of the ion coordinates and their distances as obtained by the x-ray method and electronographic measurements (Akademiya nauk SSSR Doklady, v. 153, no. 6, 1963, 1313; Kristallografiya, v. 9, no. 6, 1964, 846) showed that the ion shifts have the same direction and a comparable order of magnitude in both methods especially with respect to the oxygen ions. But there is a difference in the displacement of heavy ions of about 0.1 Å. This is due possibly to the difficulty in accounting for absorption and to the differing positions of the gravity centers of electron densities and Bi and Fe ion potentials. But the structural patterns derived by both methods are essentially analogous, which is said to support the assumption that the atomic structure of thin layers of ferroelectrics and ferromagnetics do not essentially deviate from the structure of blocks. Certain changes, however, are considered possible in the structure of a thin layer which might cause the physical properties of layers and blocks to differ. No indications of a "superstructure" as reported earlier by Plakhtiy, et al. (Akademiya nauk SSSR Izvestiya. Seriya fizicheskaya, v. 28, 1964, 4361) could be derived from the experimental data. It is concluded that these data confirm the earlier report by Roginskaya and others (Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 50, no. 1, 1966, 69), that $BiFeO_3$ is a ferroelectric with a compensated antiferromagnetism.

41. Tomashpol'skiy, Yu. Ya., and Yu. N. Venevtsev. Calculation of internal electric fields and their gradients in ferroelectromagnetic $BiFeO_3$. Kristallografiya, V. 12, no. 1, 1967, 24-28.

This is a continuation of earlier studies (Zhurnal eksperimentalinoy i teoreticheskoy fiziki, v. 46, 1921, 1964) of various properties of $BiFeO_3$, which combines ferroelectric and antiferromagnetic properties. The present article makes use of previously obtained data on the atomic structure of $BiFeO_3$ to calculate the polarizability of Bi and Fe ions, and from it, the internal electric fields and their gradients. A table showing these fields and gradients, as well as the spontaneous-polarization moment for different values of the polarizability and ion charges is presented, together with tables of various structural sums. The results are compared with published experimental data on resonant absorption of gamma quanta in $BiFeO_3$ and found to be in satisfactory agreement. It is deduced from this agreement that the electrostatic approach to the calculation of the properties of ferroelectricity in oxides of metals is useful and serves as additional evidence in favor of the ionic bond in these oxides.

42. Tomashpol'skiy, Yu. Ya., and Yu. N. Venevtsev. X-ray diffraction, and electric and magnetic investigations of a system comprising a ferroelectric and a ferromagnet. Kristallografiya, v.11, no.5, 1966, 731-735.

The purpose of the investigation was to check on the feasibility of synthesizing compounds which exhibit simultaneously ferroelectric anf ferromagnetic properties, which was demonstrated by the authors in earlier investigations (Fizika tvedogo tela, v. 7, no. 10, 1965, 3126). Tests were made on polycrystalline systems $BaTiO_3$ - $Sr_{0.3}La_{0.7}MnO_3$ (I) and $K_{0.5}Bi_{0.5}TiO_3$ - $Sr_{0.3}La_{0.1}MnO_3$ (II) obtained by sintering the corresponding oxides. The properties and structure of the samples were determined by x-ray analysis. The dielectric constant was measured with a bridge circuit in a weak field at 200 kcs, and the magnetic measurements were made by a procedure described elsewhere (Kristallografiya, v. 8, no. 4, 1963). The conductivity was measured with a bridge. Plots are presented of the concentration dependence of the unit-cell dimensions on the logarithm of the conductivity, the temperature dependence of the dielectric constant, and the temperature dependence of the spontaneous magnetic moment. Phase diagrams of the two systems are presented. The results show that the compounds remain ferromagnetic in almost the entire range of the concentrations, and that compounds I and II have ferroelectric properties at 87 — 95 and 90 — 97 mol %, respectively. Although the ferroelectricity and the ferromagnetism combine only at low temperatures, it is assumed that the temperature range can be extended by suitably choosing the initial components.

43. Tomashpol'skiy, Yu. Ya., and Yu. N. Venevtsev. Ferromagnetism in the Pb_2CoWO_6-$BaTiO_3$ system. Fizika tverdogo tela, v. 7, no. 10, 1965, 3126-3128.

The authors studied polycrystalline specimens of the Pb_2CoWO_6-$BaTiO_3$ system produced by sintering oxides and carbonates. Cr radiation was used for the x-ray analysis. The dielectric constant was studied as a function of temperature at 200 kc in a weak field with an accuracy of 5-10%. The magnetic susceptibility and spontaneous magnetic moment were measured. X-ray analysis showed only the cubic modification of the perovskite cell for 5-95% $BaTiO_3$ concentrations. Superstructure lines due to ordering on the Pb_2CoWO_6 side were observed on the x-ray photographs to approximately 25 mol % $BaTiO_3$, although partial ordering was apparently maintained to even higher concentrations (~40 mol % $BaTiO_3$). Curves for the dielectric constant as a function of temperature showed maxima which were characteristic for ferro- or antiferroelectrics at compositions close to the initial compounds. These maxima moved toward the low-temperature side starting with small concentrations of $BaTiO_3$ in Pb_2CoWO_6 and vice versa. No extrema were observed on ε (T) curves for compositions of 20-80 mol % $BaTiO_3$. This was apparently due to a shift in the point for ferro- or antiferroelectric transitions toward the low-temperature

side. Specimens with 5 mol % $BaTiO_3$ were used for the magnetic measurements. The curve for magnetic susceptibility as a function of temperature had a shape which is typical of ferrimagnetic materials with a poorly defined inflection at about -70°C. The phase diagram of the system showed that the antiferroelectric Curie point for Pb_2CoWO_6 and the ferroelectric Curie point for $BaTiO_3$ fell sharply in the low-temperature region and was in the temperature range below -(160—180°C) at concentrations of 15 and 85 mol.% $BaTiO_3$. Ferromagnetic solid solutions were observed in a certain region on the Pb_2CoWO_6 side with a combination of antiferroelectric and ferrimagnetic properties due to partial ordering of Co ions. An anomaly was observed in the curve for $\varepsilon(T)$ near the ferrimagnetic phase transition. This phenomenon may be due to the interrelationship between electric and magnetic dipoles.

44. Tomashpol'skiy, Yu. Ya., and Yu. N. Venevtsev. New lead-containing perovskites. Fizika tverdogo tela, v. 7, no. 2, 1965. 517-520.

New synthesized lead-containing perovskites have initial compositions of $PbSc_{2/3}W_{1/3}O_3$ (I), $PbSc_{5/9}Cr_{1/4}Nb_{1/2}O_3$ (II), $PbSc_{5/9}Nb_{1/3}W_{1/9}O_3$ (III), $PbCd_{1/3}Nb_{2/3}O_3$ (IV), and $PbCd_{4/9}Nb_{2/9}W_{1/3}O_3$ (V). Compounds I, II, and IV are absolutely new, while III and V can be regarded as combinations of known compounds. of appreciable interest, nonetheless, because they possess properties which are difficult to predict from the properties of the initial compounds. Dielectric tests of these substances were made at -170 to +530°C. X-ray diffraction tests of the substances were made by means of a precision technique described in detail elsewhere (Zavodskaya laboratoriya, no.9, 1961, 1112). The character of the distortion and the parameters of the unit cells were determined at room temperature. The presence of a superstructure due to the ordering of the ions of type B was established for compounds I—III. It is suggested that similar superstructures exist in compounds IV and V. Compound V is classified as an antiferroelectric, II is ferroelectric, while I and III display no special dielectric properties in the investigated temperature interval. Compound IV appears to be a relaxator. It is concluded that further research may disclose the presence of anomalous dielectric properties in all these compounds.

45. Tomashpol'skiy, Yu. Ya., and Yu. N. Venevtsev. X-ray diffraction and electric investigations of the system $PbCo_{1/2}W_{1/2}O_3$--$PbYb_{1/2}Nb_{1/2}O_3$. Fizika tverdogo tela, v. 6, no. 10, 1964, 2998-3003.

Earlier studies of these compounds were made on samples that were not strictly of one phase, and no determination was made of the character of distortion of the perovskite cells, whose parameters were calculated only in the cubic approximation. The purpose of the present investigation was to obtain single-phase samples and to study in greater detail their structure and properties as functions of temperature, and also to investigate solid solutions on their basis for the purpose of understanding the nature of the properties of compounds of this type, which have antiferroelectric properties. Another purpose was to obtain materials which combine antiferroelectric properties with ferrimagnetic properties. Polycrystalline samples were prepared by ceramic sintering techniques, with the phase analysis being made by x-ray methods. Electric measurements were made with ceramic tablets on which silver electrodes were deposited. High- and low-temperature measurements of the dielectric constant were made with a special circuit that permitted continuous recording of the temperature dependence of the dielectric constant. The measurements were made in a weak field (several volts per centimeter) at 200 kcs. Electric conductivity was measured only at room temperature. A phase diagram of the system of these two compounds was plotted. It was found that at temperatures below - 196°C some of the compounds combined antiferroelectric and ferrimagnetic properties. In addition, the system $PbCo_{1/2}W_{1/2}O_3$--$BiFeO_3$ was investigated and found to have two phases, of which one has strong magnetic properties (cobalt ferrite) with a magnetic transition temperature ~520°C. Tests of the system $PbCo_{1/2}W_{1/2}O_3$ have shown it to form a continuous series of solid solutions with a Curie temperature lying below room temperature in the interval of 10--20 molar per cent $BaTiO_3$.

46. Turik, A. V. Permittivity of barium titanate single crystals with a laminar domain. Fizika tverdogo tela, v. 8, no. 11, 1966, 3269-3273.

A method is proposed for calculating the permittivity of the anisotropic laminar structure of barium titanate single crystals as a function of the volume concentrations of a and c domains, which are alternating domains separated by 90-degree walls. The method is based on the fact that from the standpoint of average values of the electric field and induction, a laminar $BaTiO_3$ single crystal with a regular 90-degree structure can be described by a tensor of permittivities of rhombic symmetry. Computational formulas are derived for the components

of the tensor of permittivities at arbitrary concentrations of a and c domains. In the special case of equal concentrations, the theoretical value of the permittivity is in good agreement with the experimental data.

47. Venevtsev, Yu. N., Yu. Ye. Roginskaya, A. S. Viskov, V. V. Ivanova, Yu. Ya. Tomashpol'skiy, L. I. Shvorneva, A. G. Kapyshev, A. Yu. Teveroskiy, and G. S. Zhdanov. New lead-containing perovskite compounds of complex composition. Akademiya nauk SSSR. Doklady, no. 1, 1964, 86-88

A number of new lead-containing perovskite compounds were synthetized by introducing 2 or 3 B-type ions of varying valence into the compound. The resulting specimens were ceramics which were heat-treated in nitrogen or oxygen to insure the valence constancy of the component ions. The phase composition was checked by x-ray after each treatment. Neverthe less, only a small portion of specimen were obtained with a genuine perovskite structure, while the majority turned out to be deviations of various types. Forty-five new perovskite-type compounds were synthetized; all are listed and specified in the article. Eight specimens had somewhat deformed cells at room temperature, which is characteristic of ferro- and antiferroelectrics with Curie temperatures above 20°C. Many have cubic cells at room temperature, which indicates that their Curie points lie below that. An experimental check confirmed the rule that all lead-containing perovskite compounds have special dielectric properties. Paramagnetic ions were present in many new compounds, which were expected to cause some special magnetic properties in such specimens. Such properties were not observed at room temperature, but were identified at liquid-nitrogen temperature. On the basis of these observations and considering certain earlier data (G. H. Jonker, Physica, v. 22, 1956, 707; J. Longo and R. Ward, J.Am. Chem. Soc., v. 83, 1961, 2816) the conclusion is drawn, that six of the new compounds possess ferrimagnetic as well as special dielectric properties and five others exhibit antiferromagnetic characteristics. On the whole, 34 new perovskites are classified as ferro-, ferri- or antiferroelectrics; the rest are ferromagnetoelectrics.

48. Verbitskaya, T. N., and T. N. Burakova. Optical investigation of phase composition of barium titanate with small additions of chromium oxide. Kristallografiya, v. 12, no. 3, 1967, 436-442.

Experimental investigations were made of a large number of polycrystalline specimens of barium titanate to establish the dependence of its ferroelectric properties on the content of chromium oxide (Cr_2O_3)

varied from 0.01 to 3 mol%. The phase compostion of the specimens with differing Cr_2O_3 percentages and the character of structural changes in individual phases were determined. The investigations indicated that chronium can be introduced into the hexagonal modification of barium titanate practically without affecting the lattice parameters of the base material. It also increases the size of crystals, although the hexagonal crystals always remain much larger than grains of the perovskite type. On the whole, the studies open the possibility of obtaining ceramics on the basis of barium titanate of various modifications, from the perovskite to the hexagonal and their combinations, by appropriate additions of chromium oxide.

49. Viskov, A. S., and Yu. N. Venevtsev. Calculating the gradients of the intracrystalline field in barium titanate ferroelectric and in model crystals based on this salt. Fizika tverdogo tela, v. 8, no. 2, 1966, 416-423.

A method based on the ion model is proposed for calculating the gradients of the intracrystalline field ∇E which act on the ions in the tetragonal modification of ferroelectric barium titanate. The structural coefficients used in calculating the gradients were taken from experimental data in the literature. Curves are given showing the difference in lattice parameters $(c-a)$ as a function of temperature. The effect which temperature has on spontaneous polarization, the intracrystalline field and the gradients of the field was analyzed for the same modification of barium titanate. The gradients were studied as a function of charge and polarizability of A and B cations in ABO_3 crystals of the $BaTiO_3$ type. The proposed method yielded results which agree satisfactorily with the experimental data in the literature. The ion model was found to be highly effective for evaluating electric field intensities and gradients in ferroelectrics which are basically metal oxides. The results of this paper may be useful for interpreting experimental data on the Mossbauer effect and nuclear quadrupole resonance in isomorphic barium titanate compounds as well as in solid solutions with a perovskite structure.

50. Yazytskiy, B. Ya., and Yu. M. Poplavko. Concerning microwave dispersion in barium titanate above the Curie point. Fizika tverdogo tela, v. 8, no. 12, 1966, 3639-3641.

In view of the low accuracy of earlier investigations, the authors measured the temperature dependence of the dielectric constant of $BaTiO_3$ in the vicinity of the phase transition by using a special

waveguide resonator method developed earlier (Zhurnal eksperimental'-noy i teoreticheskoy fiziki, v. 43, 800, 1962). The only experimental data used were those obtained at resonances at multiples of one-quarter of the wavelength of the sample placed in the waveguide. This, in conjunction with exact computer calculations, made it possible to determine the dielectric constant accurate to 3%. The temperature dependence of the dielectric constant and of the dielectric losses was measured at 9.4 and at 37 GHz. (This is the first time that measurements on $BaTiO_3$ were made at such high frequency.) The results show that no dispersion takes place above the Curie point. The 37-GHz investigations have also shown that there is no dispersion in the paraelectric phase, just as there is none at lower frequencies.

51. Zheludev, I. S., Ye. V. Sidnenko, and S. I. Teplyakova. Spontaneous electrooptical effect in tetragonal $BaTiO_3$. Kristallografiya, v. 12, no. 4, 1967, 604-606.

An experimental investigation was made of the spontaneous electro-optic effect in tetragonal, single-domain $BaTiO_3$ crystal, to determine the coefficient of the linear electro-optic effect and its dispersion in the visible part of the spectrum. The results of the measurements confirmed the validity of the magnitude ($= 1.87 \times 10^{-7}$ CGSE units) of the coefficient of the linear electro-optic effect calculated earlier by Zheludev (Uspekhi fizicheskikh nauk, v. 88, no. 2, 1966, 253). The figure also agrees fairly well with the formula of Johnston and Weingart (J. Opt. Soc. America, v. 55, no. 7, 1965, 828). The conclusion of the authors about the linearity of the electro-optic effect in the tetragonal $BaTiO_3$ is said not to contradict the quadratic relationship between the birefringence and the spontaneous polarization after the transition to the ferroelectric phase accepted by some authors. The relationship here is analogous to the relationship between the piezoelectric and and electrostriction coefficients for $BaTiO_3$.

V. MISCELLANEOUS COMPLEX OXIDES AND OTHER MATERIALS

1. Dantsiger, A. Ya., and Ye. G. Fesenko. Anomalous dielectric properties of rubidium nitrate. Kristallografiya, v. 10, no. 3, 1965, 338-340.

The dielectric properties of cooled fused rubidium nitrate were investigated. The test sample was prepared by cooling it slowly (at a rate of 2 degrees per minute) in a nickel crucible from a temperature slightly above the melting point to room temperature. Measurements were taken as the crucible was cooled and during its subsequent heating. The electrodes consisted of the crucible and a nickel disk attached rigidly to a nickel wire. The special feature of this method is that the fused sample has a much greater electric strength than a crystal grown from a solution. Special measures were taken in the oscillographic investigations to eliminate parasitic capacities and leakage and to provide necessary screening. Repeated measurements showed that during cooling without an applied field the P-E relationship in high-temperature phases II and III and low-temperature phase IV is usually linear. If a field of 1.5–2 kv/cm is applied to phases II and III during cooling, double loops appear during phase IV (below 164°C) with the application of strong fields (15–25 kv/cm). These loops disappear at a temperature of 100-110°C. The double dielectric hysteresis loops below the phase transformation point IV $\rightleftarrows$ III, a sharp jump in ε at the transition point IV $\rightleftarrows$ III, the displacement of transition temperature IV $\rightleftarrows$ III in the direction of shortening phase IV, the increase in ε below the transition IV $\rightleftarrows$ III under the influence of constant bias, and a sharp minimum in the coefficient of linear expansion at the transition point IV $\rightleftarrows$ III show that in the IV phase, $RbNO_3$, has antiferroelectric properties.

2. Dantsiger, A. Ya., and I. A. Freyzon. Ferroelectric properties of $Rb_xK_{1-x}NO_3$ solid solutions. Fizika tverdogo tela, v. 7, no. 7, 1965, 2190-2194.

By means of oscillograph studies done on cooled solid solutions a ferroelectric region was mapped on the phase diagram for systems of the $Rb_xK_{1-x}NO_3$ type. The influence of additions of RbNo to KNO on the Curie temperature (T_k), the spontaneous polarization (R_{sp}), and the width of the ferroelectric region of the phase diagram were studied. Causes of the lowering of T_k and R_{sp} were also considered. Solid solutions of the $Rb_xK_{1-x}NO_3$ type were melted and cooled (2°C/min) in a specially constructed Ni crucible; R-E measurements (dielectric hysteresis) were made during the cooling. A schematic diagram of the crucible and of the experimental arrangements is given. From oscillographic measurements, a phase diagram (to 50 mol%) is drawn, mapping the region exhibiting dielectric hysteresis. This region is designated as III

in Fig. 1. Data are given for R_{sp} as a function of temperature for varying mol contents of $RbNO_3$ (0-50%); maxima from this curve are plotted along with the values for the coercive fields (E_k) as a function of content of $RbNO_3$. R_{sp} drops sharply up to about 20 mol %, after which the drop becomes more gradual; E_k increases linearly with a small slope, up to 30 mol %. Photographs are shown of the dielectric hysteresis loops, and these indicate a decrease in saturation with rise in content of $RbNO_3$. A theoretical basis is postulated for the phenomena. The lowering of T_k and R_{sp} is analyzed on the basis of cationic and anionic displacement. The atomic radii of K^+ and Rb^+ are compared, and the size difference influences the internal field. The phase transition I to III appears similar to the order-disorder type transformation. The role of the internal field appears as an ordering displacement of the NO_3^- groups, thereby lowering the internal field necessary to bring about a lower degree of order and, therefore, lowering T_k and R_{sp}.

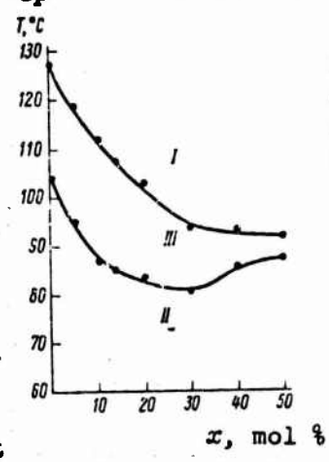


Fig. 1. Phase diagram of the system $Rb_xK_{1-x}NO_3$ (for cooling)

3. Dantsiger, A. Ya., and I. A. Freyson. Ferroelectric properties of solid solutions of the system KNO_3-KI. Fizika tverdogo tela, v. 7, no. 5, 1965, 1517-1518.

The work reported is part of the investigation of the effect of different additives on the ferroelectric properties of potassium nitrate, which was investigated by an already-described procedure (FTT v. 7, no. 7, 1965) used to study the properties of $Rb_xK_{1-x}NO_3$ solid solutions. Hysteresis loops of the melts of the investigated solid solutions, cooled in a nickel crucible, were obtained oscillographically and plots of spontaneous polarisation against the temperature were plotted from the hysteresis loops. The results have established that introduction of KI additives stabilizes the ferroelectric phase III of KNO_3, which extends in this case to room temperatures. The magnitude of the spontaneous polarisation decreases as compared with the pure KNO_3. In addition , the KI decreases somewhat the temperature of the I → III transition.

4. Grigas, I. P., and A. S. Karpus. Investigation of the anomalous dispersion of the dielectric constant of Sb_2S_3 and SbSJ crystals on SHF. Fizika tverdogo tela, v. 9, no. 10, 1967, 2887-2892.

An experimental investigation was carried out to establish the frequency dependence of the components of the dielectric constant of filamentary Sb_2S_3 and SbSJ single crystals within the 9-27 Gc frequency range. Data concerning anomalous dispersion of the permittivity and the resonance of microwaves in the above compounds were obtained. The results show that anomalous dispersion of the permittivity occurs only in stoichiometric crystals. A deviation from the stoichiometric composition results in reduction of the permittivity and disappearance of the anomalous dispersion. The temperature dependence of the anomalous permittivity dispersion was investigated in stoichiometric SbSJ crystals. It was shown that the anomalous dispersion, within the $(1.3-1.6)\times10^{10}$ cps frequency range occurs only in the paraelectric phase around the Curie point. The resonance absorption was observed at 1.5×10^{10} cps with a half-band width of $1.6.10^{9}$ cps. The experimental results confirm the theoretical assumption by some Soviet and Western authors concerning the region of long-wave optical oscillations and their temperature dependence in the presence of pronounced phase transitions. Below the transition points, the Sb atoms assume positions ensuring a constant dipole moment. The temperature dependence of the permittivity components of SbSJ in the ferroelectric phase confirms an absence of resonance absorption within the 12—17 Gc frequency range.

5. Grigas, I. P., and A. S. Karpus. Dielectric properties of Sb_2S_3 crystals . Fizika tverdogo tela, v. 9, no. 10, 1967, 2882-2886.

An experimental investigation was made of the crystallochemical characteristics of the Sb_2S_3-type lattice, and its analogy with the lattice of SbSJ and SbSBr ferroelectrics. An analysis of the structure of Sb_2S_3, and the anomalies of the temperature dependences of its dielectric constant and tan δ in directions parallel and perpendicular to the crystallographic axis, as well as consideration of dark current anomalies of SbSJ at the ferroelectric phase transition and their similarity to those in $BaTiO_3$, along with the conductivity behavior near the transition points, point to the presence of spontaneous ferroelectric polarization in this entire group of crystals. Several such phase transitions within the -30 to +70°C temperature range appear possible. An aging effect in the dielectric properties of crystals was discovered. The dielectric constant of a cooled-down crystal will diminish if the crystal is kept at room temperature for a certain length of time. The effect is considered to be connected with the possible reduction of the crystal to two phases.

6. Gulyamov, K., V. A. Lyakhovitskaya, N. A. Tikhomirova, and V. M. Fridkin. Anomalously large effect of pressure on the optical and ferroelectric properties of SbSI single crystals. Akademiya nauk SSSR. Doklady, v. 161, no. 5, 1965, 1060-1062.

Earlier investigations of the optical and ferroelectric properties of SbSI single crystals led to the conclusion that the coefficient dE_g/dp (E_g -- width of forbidden band, p -- pressure) has an anomalously large value. To check on this assumption, the authors undertook to determine dE_g/dp directly by measuring the shift of the edge of intrinsic absorption under the influence of hydrostatic pressure. The results (Fig. 1) show that single crystals SbSI have an anomalously large shift of the edge of intrinsic absorption and of the Curie point with increasing pressure. The experimental results are qualitatively in agreement with theory, and the previously observed shift of the absorption edge under the influence of an electric field can actually be related to the anomalously strong dependence of the width of the forbidden band on the pressure.

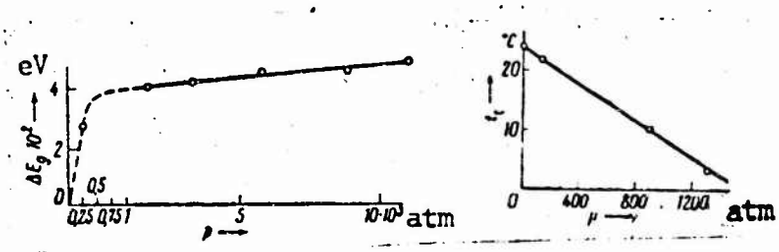


Fig. 1. Pressure variation of the width of the forbidden band (left) and of the Curie temperature (right) in single-crystal SbSI.

7. Ismailzade, I. G., V. I. Nesterenko, F. A. Mirishli, and P.G. Rustamov. X-ray and electrical investigations of the $Bi_4Ti_3O_{12}$ - $BiFeO_3$ system. Kristallografiya, v. 12, no. 3, 1967, 468-473.

Experimental investigations were made of the sturctural and electric properties of stratified ferroelectrics of the $Bi_4Ti_3O_{12}$ - $BiFeO_3$ system. The composition of the specimens covered the range from 1 mol $Bi_4Ti_3O_{12}$ to n mol $BiFeO_3$ (n = 1, 2, 5). The permittivities and the conductivity of the specimens were plotted as functions of temperature. A dielectric hysteresis loop was not observed within the range of available field intensities (about 25 kV/cm) in any of the specimens, apparently owing to a high coercive field. A detailed discussion of the results leads to the conclusion that $BiBi_4Ti_3FeO_{15}$, $Bi_2Bi_4Ti_3Fe_2O_{18}$, and $Bi_5Bi_4Ti_3Fe_5O_{27}$ have a stratified structure with

4, 5, and 8 layers in each package. They are considered the first ferroelectrics with stratified structure. The Curie temperature for the first was 750°C, and above that figure for the rest. The limits of the tolerance factor within which the stratified structure can occur, were found at 0.97 (upper limit) and 0.86.

8. Isupov, V. A. Oriented dielectric polarization of ferroceramics of the $PbNb_2O_6$ type due to reorientation of the 180- and 90-degree domains. Fizika tverdogo tela, v. 9, no. 5, 1967, 1417, 1423.

A mathematical analysis was made of the orientation of dielectric polarization due to reorientation of the 180- and 90-degree domains. The effect was studied in ferroelectric ceramics of the $PbNb_2O_6$ type as a function of electric field strength. These crystals are tetragonal in the paraelectric state and rhombohedral in the ferroelectric state. The proposed domain structure of these crystals is shown in various stages of polarization. Calculations of the initial stages of 180- degree domain reorientation were made, and equations are given for the moment vectors based on vector projections in a sphere by means of three location angles. In the calculation, the anisotropy of dielectric permeability and piezoelectric stress was ignored. Integration of the resulting differential equations gave the polarization as a function of electric field strength. Conditional equations are given in which 180- and 90-degree reorientation would occur if the 180- and 90-degree vector field exceeded the critical fields E_c' and E_c'' (E_c' for 90- and E_c'' for 180- degree reorientation). Values of the polarization ratios (P_z'/P_o, P_z''/P_o) were given as functions of the electric field ratios (E/E_c', E/E_c''), where P_z' and P_z'' are the polarizations for 90- and 180-degree reorientation, and P_o is the spontaneous polarization in the [110] direction. The plotted curves showed two regions of saturation, corresponding to the saturation of 180- and 90-degree reorientations. At the moment, no experimental data are available to check the analysis.

9. Isupov, V. A. Antiferroelectric properties of Pb_4SiO_6 lead silicate. Fizika tverdogo tela, v. 7, no. 7, 1965, 2221-2223.

An investigation of the dielectric properties of Pb_4SiO_6 was made in a study of the phase transition that occurs at about 155°C and changes the volume. Samples were made by ordinary ceramic methods from chemically pure PbO and SiO_2. Preliminary annealing was done at 600°C for 6 hours, and the material was sintered at 650°C for 6 hours. Disk-shaped samples 9 mm long and 0.7—1.5 mm thick were made for the dielectric measurements, and cylindrical samples 30 mm long were made for the dilatometric measurements. X-ray analysis assured that the

samples were single-phase with Pb_4SiO_6 composition. A graph of the results is shown in Fig. 1. The dielectric permeability goes through a maximum for the interval 155-180°C and for higher temperatures decreases steadily according to the Curie-Weiss law

$$\varepsilon_0 + \frac{C_W}{T-\theta'}$$

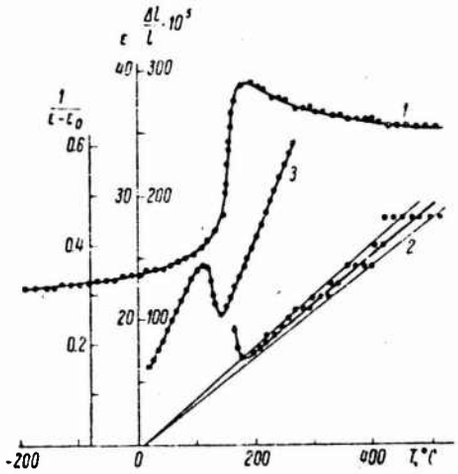


Fig. 1. Temperature dependence of dielectric permeability for 500 kilohertz (1), $1/(\varepsilon-\varepsilon_0)$ (2), and the thermal expansion $\Delta l/l$ (3) of polycrystalline samples of P_4SiO_6 lead silicate.

where $\theta' = 277°K$ and C_W is about 1000°K. These results showed that the phase transition in Pb_4SiO_6 is antiferroelectric; however, this transition differs from others in the low increase in $\varepsilon - \varepsilon_0$ and in the low value for C_W. This data are explained in terms of crystal chemistry. The cell structure and the ionic radii of cations and anions are compared with those of other antiferroelectric materials to establish a basis for these properties. Ferroelectric and antiferroelectric properties were found to be unrelated to any particular crystal structure or lattice peculiarity. However, the electronic and ionic polarizations were generally high in these materials.

10. Isupov, V. A., N. N. Kraynik, I. D. Fridberg, and I. Ye. Zelenkova. Antiferromagnetic properties of ortho-vanadate. Fizika tverdogo tela, v. 7, no. 4, 1965, 1051-1056.

The dielectric properties and the thermal expansion of polycrystalline samples and single crystals of lead orthovanadate ($Pb_3V_2O_8$) were investigated. The polycrystalline samples were made by a ceramic technology, and the single crystals were grown by slow cooling. The purpose of the investigation was to clarify the reasons for the abrupt changes

in the dielectric constant and dimensions of the samples near 0 and 100°C. The test results show that lead ortho-vanadate has antiferroelectric properties. By the same token, a new type of crystal structure, admitting of the existence of both ferroelectricity and antiferroelectricity, was found, and the possibility of the existence of ferroelectric phenomena in vanadates was demonstrated. Both the antiferroelectric phase transition near 100°C and the low-temperature phase transition are first-order transitions, and are accompanied by relatively small but abrupt changes in the dielectric constant and by very large deformations. Observation of the single crystals in polarized light perpendicular to the cleavage plane disclosed the presence of a twin structure which vanished near 100°C upon heating. The high dielectric constant, its maximum near 100°C, and the absence of dielectric-hysteresis loops all lead to the conclusion that the phase transition at 100°C is antiferroelectric. At room temperature, as follows from the character of its twin structure, lead ortho-vanadate has a lower degree of symmetry than rhombohedral or hexagonal. It is concluded that the presence of antiferroelectric properties in the substance points to the necessity of producing a more general criterion for the occurrence of the ferroelectric and antiferroelectric states.

11. Kraynik, N. N., S. N. Popov, and I. Ye. Myl'nikova. Observation of nuclear quadrupole resonance signals in the ferroelectric SbSI. Fizika tverdogo tela, v. 8, no. 12, 1966, 3664-3665.

The authors observed NQR signals in SbSI crystals grown by spontaneous crystallisation from the melt. The investigation was made with an IS-2 spectrometer constructed by the design office of the Institute of Radio Engineering and Electronics, AN SSSR, using pairs of 90° and 180° pulses. In addition, the temperature dependence of the dielectric constant of the crystal was measured at 750 kHz. The transitions corresponding to the frequencies observed in the NQR signals were identified from the variation of the temperature dependence of the ratio of these frequencies. This temperature dependence indicated that the asymmetry parameter of the crystal differs from zero, as was confirmed also by x-ray data on the crystal structure. Further research is necessary for complete identification of the spectrum. In addition to the anomalies corresponding to the Curie point, small anomalies were observed at 210-230°K and also near 160°K. These anomalies occur in most crystals, and are assumed to correspond to low-temperature phase transitions.

12. Nosov, V. N. On the mechanism of the change of photoconductivity of SbSi single crystals in the region of ferroelectric phase transition. Kristallografiya, v. 12, no. 2, 1967, 359-361

Measurements were made of the temperature dependence of the quantum yield of photocurrent near the ferroelectric transition point (20°C) in SbSI single crystals using a method described earlier by Nosov and Fridkin (Fizika tverdogo tela, v. 8, no. 1, 1966) and Ryvkin (Fotoelektricheskiye yavleniya v poluprovodnikakh. Moskva, Fizmatgiz, 1963) with some modifications. The results showed that the quantum yield of photocurrent in the region of phase transition occurs in the antiphase with the lifetime of nonequilibrium carriers. Considering the fact that the product of photocurrent by the lifetime must be proportional to the concentration of nonequilibrium carriers, and plotting the calculated values of the latter against the temperature, a curve with a maximum near the Curie point results. The mobility of carriers was deduced from the measured temperature dependence of the photocurrent and other known relationships. The mobility determined in this way does not, as was expected, show any jump at the Curie point, although the gradients in paraelectric and ferroelectric phases differ. This is apparently connected with a change in the level of trapping energy at the transition point due to the drift.

13. Rinkyavichus, V. S., and M. P. Mikalkevichus. Pyroelectric effect in antimony trisulfide single crystals. Fizika tverdogo tela, v. 9, no. 10, 1967, 2997-998.

Experimental investigations were made to detect in Sb_2S_3 single crystals certain effects stemming from spontaneous polarization. The authors succeeded in measuring the pyroelectric effect in some specimens. The method used was described earlier by Grigas and others (FTT, v. 9, 1967, 1532). The cross section area of the specimen crystal was $2x10^{-4}$ cm^2, to which a constant polarizing field of 250V/cm was applied for one minute, then cooled to 77°K and thereafter heated at a constant rate of 0.6 degrees per second. A maximum of pyrocurrent was observed at 325°K. A pyroelectric signal of the same polarity was recorded during the cooling of the crystal. The same effects could be observed several times in sucession without applying the electric field. A polarization reversal by means of applying a reversed field proved possible only at temperatures above 315°K. Below that point the field affects neither the polarity nor the magnitude of the polarization (as well as pyrocurrents). Application of the field within the 315 to 323°K temperature range effected a pyroelectric signal with two maxima of opposite signs, the the maximum at lower temperature always being of opposite polarity to the polarizing field. But the two-maxima effect did not occur

at repeated measurements without renewed application of the polarizing field. This behavior of the pyroelectric signal is similar to that in well-known ferroelectrics. The special characteristic of Sb_2S_3 consists in the absence of a pronounced drop of the pyroelectric signal strength at the Curie temperature (about 325°K). An attempt was made to establish whether temperature gradients within the crystal could contribute to the flatness of the maximum. Special measurements made at different heating rates (from 0.06 to 0.6 degrees per second), however,did not affect the temperature dependence of the pyrocurrent.

14. Roytberg, M. B., E. I. Shapiro, and A. Z. Rabinovich. Pyroelectric effect and spontaneous polarization in $LiTaO_3$. Fizika tverdogo tela, v. 9, no. 12, 1967, 3613-3614

Anexperimental investigation was made of the temperature dependence of the pyroelectric effect and the spontaneous polarization in $LiTaO_3$ single crystals grown by the Chokhral'skiy method. The pyroelectric coefficients were measured by continuous charge removal and temperature change, which eliminates voltage bias. The measurement results on polydomain specimens of $LiTaO_3$ showed, first, a very low pyroelectric effect below the 200°C which can be ascribed to the "rigidity" of this ferroelectric at low temperatures. Second, the anomalies observed within the 300—350 and 400—450°C ranges are connected with the simultaneous change of macroscopic polarization and an increase of electroconductivity. A strong discharge of surface layers was observed within the region of Curie temperatures (600-660°C), which resulted in a noticeable increase of the pyrosignal above the phase transition. A slow drop of the signal to zero was observed within the 650-800°C range. A polarity reversal of the specimen after the first heat treatment did not change the sign of the pyroelectric signal, which suggest a change of the polarization vector on account of electric fields accompanying the discharge of surface layers, as is also the case, for instance, with triglycine sulfate (Chynoweth, Phys. Rev. v. 117, 1960, 5). The observed drop of pyroactivity with repeated heat treatment, which can be explained by a reduction of the degree of unipolarity, could be eliminated by aging the specimens for at least 100 hours at room temperature. The measured magnitude of spontaneous polarization of $LiTaO_3$ was estimated at 65 μcoulomb/cm^2 at 200°C.

15. Rudyak, V. M., and A. A. Bogomolov. Illumination-induced jumps in reverse polarization of the SbSI ferroelectric. Fizika tverdogo tela, v. 9, no. 11, 1967, 3336-3337.

Experimental investigations were made of the polarization spiking observed in the SbSI single crystals under a constant electric field. The method used was described earlier by the author and Kamayev

(Akademiya nauk SSSR. Izvestiya. Seriya fizicheskaya, v. 29, 1965, 937). The measurement data showed that the basic characteristics of the polarity reversal process in SbSI are the same as in better known ferroelectrics such as Rochelle salts and tri-glycine sulfate. A new effect of the appearance of similar spikings was observed when a light pulse was applied to the specimen in a constant electric field. The direction of spikes coincided with the polarity of the field. The spiking subsided after 5 to 7 seconds, and could not be repeated by renewed application of light pulses at the same field strength. The spiking could be induced again after stepping up the field strength. The application of light during the spiking process enhanced their intensity but shortened the duration of the series. The phenomenon was observed within the temperature range from -70°C to Curie point (+20°C). The authors note that the phenomenon can be induced by light beams of various wave lenghts, but it is most pronounced when effected by white light. An increase of the light beam intensity leads to an increase in the number of spikes. The phenomenon is ascribed to the augmentation of the nucleation process under the action of light.

16. Shapiro, Z. I., S. A. Fedulov, and Yu. N. Venevtsev. Curie point of ferroelectric lithium tantalate. Fizika tverdogo tela, v. 6, no. 1, 1964, 316-317.

An attempt was made to determine the dielectric properties in ceramic specimens of lithium tantalate across a broad temperature range. Experimental specimens were produced from lithium carbonate and tantalum pentoxide. They were purified by two repeated heatings (60 min each), one at 1100C and one at 1350C. X-ray analysis and subsequent calculations proved that the lattice parameters of lithium tantalate were: on hexagonal axes -- $a_H = 5.153$ Å and $c_H = 13.775$ Å; on rhombohedral axes -- $a_{Rh} = 5.470$ Å and $a_{Rh} = 56°12'$. Dielectric permeabilities were measured with a bridge MPP-300 at the frequency of 250 kilohertz. The curve of $\varepsilon = f(T)$ showed a sharp maximum at the temperature of about 665°C. Dielectric permeability at room temperature was 70, at the maximum it reached 1850. Above the Curie point the change in the dielectric permeability was calculated from the Curie-Weiss law. The specimens showed a weak piezoelectric effect. These results disprove the claim made by H. D. Megave (Acta Cryst., v. 7, 1954, 191; "Ferroelectricity in Crystals," London, 1957), to the effect that lithium tantalate forms simple pyroelectrical crystals. The authors are undertaking a study of properties exhibited by $LiTaO_3$ and $LiNbO_3$ and also of solid solutions based on these substances.

17. Suvorov, V. S., and A. S. Sonin. Nonlinear optical materials. Kristallografiya, v. 11, no. 5, 1966, 832-848.

This review consists of a brief discussion of the phenomenological theory of nonlinear polarization at optical frequencies in anisotropic media, and of the methods of detecting and studying the second harmonic and nonlinear optical properties of materials, with emphasis on single crystals. Generation of the second harmonic with the ruby laser as the input source has been studied in crystals of the KDP group (KDP, KDA, DKDP, ADP, RDP, and DADP etc.). Encouraging results in growing large single crystals of DKDP and DADP have been achieved by A. S. Vasilevskaya et al. The second harmonic conversion efficiency in the index matching direction is approximately the same for all KDP-group crystals except RDP, whose single crystals are twice as effective as KDP. Other types of crystals considered here are (Na, K) NbO_3, SiO_2, $NaClO_3$, tourmaline, TGS, $KNaC_4H_4O_6$, $NaBrO_3$, GASeH, GGSH, and GASH. Recently, a ruby laser was used to obtain second harmonic generation in certain amino acids and sugars, and in single crystals of hypuric acid (Orlov, R. Yu. Kristallografiya, v. 11, 1966, p. 463). In Orlov's case, the harmonic output power was comparable to that of KDP crystals. Further theoretical research is expected to correlate the capability to generate the second harmonic with the ferroelectric properties of crystals. Of practical importance is the search for new, more effective crystals, particularly those including structural groups characterized by a high electronic polarizability.

18. Tomashpol'skiy, Yu. Ya., Yu. N. Venevtsev, and V. N. Bezmozdrev. Ferromagnetism in ferromagnetic-ferroelectric systems. Fizika tverdogo tela, v. 7, no. 9, 1965, 2763-2767.

The $PbTiO_3$-$Sr_{0.}$ $La_{0.7}MnO_3$ system was used as a basis for studying the feasibility of producing ferromagnetics in the form of solid solutions in a ferroelectric-ferromagnetic system. The specimens were prepared by sintering MnO_2, TiO_2, $PbCO_3$, and $SrCO_3$, at 850-1350°C for 1-3.5 hours. X-ray diffraction patterns were taken and the dielectric constant, magnetic susceptibility, spontaneous magnetic moment and conductivity were measured. X-ray analysis at room temperature showed that this system forms a continuous series of solid solutions of the perovskite type. Phase transitions occur at 30 and 70% $PbTiO_3$. The experimental data indicated that the solid solutions from 70 to 100 mol% $PbTiO_3$ may have ferroelectric properties in a definite temperature range. Curves for the dielectric constant as a function of temperature in this system showed maxima which indicated phase transitions from the paraelectric to the ferroelectric state. Curves for inverse magnetic susceptibility and spontaneous magnetic moment as functions of temperature showed that the point of the magnetic phase transition decreases with an

increase in the lead titanate concentration. Extrapolation showed that the transition point lies close to absolute zero at 95 mol % $PbTiO_3$. The phase diagram for the system showed that the ferroelectric transition point falls more rapidly than that for magnetic phase transition. Thus, the system keeps its ferromagnetic properties in the 0-92 mol% range, while ferroelectric properties occur in compositions with 70-100 mol% $PbTiO_3$. The system displays both ferroelectric and ferromagnetic properties in the interval between 70 and 92% lead titanate at below room temperatures. The method proposed in this paper may be used for producing materials with various combinations of ferro- and antiferroelectric with ferro-, ferri- and antiferromagnetic properties.

19. Zvonkova, Z. V., V. Ya. Krivnov, and A. N. Khvatkina. Refinement of the atomic and molecular structure of thiourea. Kristallografiya, v. 11, no. 3, 1966, 385-388.

X-ray measurements were made of coordinates of atoms and to improve quantum-chemical calculations of bond orders and atomic charges in thiourea, using the method of successive approximations of three-dimensional atomic density. The cross sections of electron density of thiourea were calculated on the basis of experimental data obtained earlier by Zvonkova et al. (Kristallograifya, v. 3, 1958,553) and Truter shown under I and II in Table 1.

Table 1. Cross sections of thiourea electron density.

Source	Atom coordinates						
	Sulfur (y = 0.250)		Carbon (y = 0.250)		Nitrogen		
	x	z	x	z	x	y	z
I. This work	0.9966	0.1141	0.0941	0.8442	0.1324	0.1187	0.7295
II. Truter	0.9954	0.1134	0.0938	0.8269	0.1299	0.1200	0.7150

Table 1a. Corresponding interatomic distances and valence angles

	Interatomic distances (Å)		Valence angles (°)	
	S-C	C-N	S-C-N	N-C-N
I.	1.669	1.319	121.9	116.2
II.	1.752	1.300	121.4	117.3

The article dwells on comparsion of these data with earlier sources, such as papers by Dvoryankin and Vaynshteyn (Kristallografiya, v. 5, 1960, 589), Goldsmith and White (J. Chem. Phys., v. 31, 1959, 1175) and Coulson and Zauli (Molec. Phys., v. 6, 1963, 525).

VI. METHODS AND INSTRUMENTS

1. Ismailzade, I. G., and V. I. Nesterenko. Method of determining the Curie point and measuring the temperature dependence of the permittivity of ferro- and antiferroelectrics with high electroconductivity. Kristallografiya, V. 12, no. 4, 1967, 717-719

A setup is proposed for measurement of the permittivity and the Curie point of ferroelectric materials with high electroconductivity. The arrangement is to replace the conventional resonance method and in it the resonance point is indicated by the phase coincidence of the voltage on the RCL-circuit with that of the power source. An EO-7 oscilloscope was used as a visual phasometer. The method of measurement consists in manipulation of a variable capacitor in the circuit to balance the change of the capacitance increase due to the temperature rise of the specimen. The arrangement was tested on several ferroelectric and antiferroelectric materials and the Curie points measured agree closely with the data of Subbarao (J. Phys. Chem. Solids., v. 23, 1962, 665). The difference, not exceeding 3°C in these measurements, can further be reduced by using a more sensitive phasometer.

2. Ivanov, I. V., and N. A. Morozov. Method of studying the dynamic nonlinearity of ferroelectrics in superhigh frequency fields. Fizika tverdogo tela, v. 8, no. 11, 1966, 3218-3225

The paper describes an experimental method of studying the nonlinear properties of ferroelectric materials in SHF fields which makes it possible to determine the first coefficients of a series expansion of the permittivity in powers of the SHF electric field

$$\varepsilon(E, E_0) = \varepsilon(E_0)(1 + \alpha_1 E + \alpha_2 E^2 + \dots), \qquad (1)$$

where $\varepsilon(E_0)$ is the permittivity of the material studied at a given strength of the constant bias electric field and α_1, α_2... are nonlinearity coefficients, which are also functions of the bias field. The effectiveness of multiplying the frequency of the SHF signal by a factor of two or three and the capacity of the sample studied were measured. It was found that if a film configuration is given to the ferroelectric sample, the measurements can be made under continuous (not pulsed) conditions. The proposed method was used to study the nonlinear dynamic properties of a series of ferroelectrics, and the results obtained will be published separately.

3. Ivanov, N. R, L. A. Shuvalov, A. V. Mirenskiy, and G. D. Shnyrev. Polarimetric precision setup and its use for investigation of the change of rotation of the light polarization plane and the rotational electro-optical effect in ferroelectrics. Kristallografiya, v. 12, no. 2, 1967, 307-313.

A new precision polarimeter installation for measuring the rotation of the polarization plane and the optical indicatrix of low-symmetry ferroelectric crystals was developed by the Special Design Bureau of the Institute of Crystallography, Academy of Sciences SSSR. The basic principle was derived partially from Cary, Hawes, et al. (Appl. Optics, v. 3, 1964, 329) A fairly detailed description of the instrument and its operation is accompanied by a block diagram. The readings of the instrument, derived from purely geometric relationships, are independent of the intensity of light, except for oscillograph-photographic recordings. The accuracy of the measurement of the polarization plane angle is within $\pm 0.002°$ and can reach with certain measurement method, the $\pm 0.0005°$ limit. The instrument has been used for investigations of thermo-optic and spontaneous electro-optic and elasto-optic effects in tri-glycine sulfates, and ferroelectric lithium and sodium hydroselenites with the results reported by N. R. Ivanov, L. D. Kislovskiy, et al. (Kristallografiya, v. 11, 1966, 614; Zhurnal eksperimental'noy i teoreticheskoy fiziki, no. 4, 1966, 220; Proc. Int. Meeting on Ferroelectricity. Prague, v. 1, 1966, 205), and of the stimulated electro-optic effect in tri-glycine sulfate (Ivanov, N. R., et al. Kristallografiya, v. 11, 1966, 760). Some new characteristics of the dynamics of the domain structure under polarity reversal and effects of gamma-radiation will be published soon. Field-induced polarity reversal process in a number of crystal types was carried out by Shuvalov and Ivanov (Kristallografiya, v. 9, 1964, 363), on the basis of which a list of 13 crystals with their polarity reversal data are presented. A number of characteristics of the lithium hydroselenite $LiH_3(SeO_3)_2$ (electro-optic, hysteresis of optical activity, specific rotation of the polarization plane, etc.) are described.

4. Ver'tskaya, T. N., Yu. M. Poplavko, and B. Ya. Yazytskiy. Temperature characteristics of variconds in the three-centimeter wave range. Fizika tverdogo tela, v. 9, no. 11, 1967, 3344-3345.

Experimental investigations were made of the dielectric dispersion of VK-1—Vk-4 variconds on the 9.4 Gc frequency and up to temperatures of 350—400°C. The VK - type variconds are solid solutions of $BaTiO_3$ - SnO_2 with varying ratios of components. A strong dielectric dispersion was observed in the ferroelectric region (the permittivity at 9.4 Gc dropped 2-3 times in comparison with its value at 0.5 Mc). Dispersion is practically absent in the paraelectric region,

especially at a distance from the Curie point. Most interesting is the behavior of the permittivity at the Curie point, where its character strongly depends on the concentration of SnO_2, as shown in the Table 1.

Table 1. SnO_2 concentration

Material	SnO_2 content %	FREQUENCY					
		0.5 Mc			9.4 Gc		
		ε at 25°C	ε max	cx10^{-4}	ε at 25°C	ε max	cx10^{-4}
VK-4	1.5-2	900	5720	7.7	450		7.7
VK-2	6	1450	11200	7.8	570	5750	7.8
VK-1	6	1850	7900	9.0	900	4600	7.8
VK-3	11	7700	7800	7.5	2200	2250	6.9

The temperature dependence of permittivity was measured on VK-3 and VK-4 variconds as the extreme cases of solid solutions which displayed a sharp but widely spread phase transition. The temperature characteristic of VK4 exhibited no dispersion above the Curie point. In VK-2, dispersion appeared in the paraelectric phase within a temperature range of about 20°C. In VK-1 it extended to 60° and in VK-3 reached 100°C. The permittivity dispersion at the phase transition was accompanied (except in VK-4) by a shift of its temperature dependent maximum (7°C in VK-1 and VK-2; 15°C in VK-3). These relationships are characteristic for relaxation processes, which are prominent in ferroelectrics with a broad phase transition. Relaxation polarization of domains and boundaries contributed substantially to the permittivity at a spread phase transition, which led to permittivity dispersion at super high frequencies.

5. Verbitskaya, T. N., L. D. Kislovskiy, Ye. K. Galanov, and L. S. Sokolova. Barium titanate reflection filters for the far infrared region. Zhurnal prikladnoy spektroskopii, v. 7, no. 2, 1967, 276-277.

A method has been developed for preparing varicond plates of various forms and dimensions on the basis of $BaTiO_3$. The spectral

characteristics obtained follow closely those of barium titanate single-crystal plates. The method makes it possible, in principle, to produce plates with an area of up to 100x100 mm. The reflection spectra of the variconds were recorded over the 1 to 40 μm wavelength range. Their reflection coefficient was reduced to 0.5% within the 1-13 μm range and increased to 75-80% within the 30-40 μm range by working them over with M-10 corundum powder. Such ceramic varicond plates can be used as reflection filters for cutting off short-wave scattered radiation up to 13 μm is spectral instruments operating within the 30-1000 μm range.

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