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SUMMARY REPORT

on

AN INVESTIGATION OF THE EFFECTS OF VERY HIGH PRESSURE AND
TEMPERATURE ON SEMICONDUCTING AND INSULATING MATERIALS

to

SOLID STATE SCIENCES DIVISION
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
WASHINGTON 25, D.C.

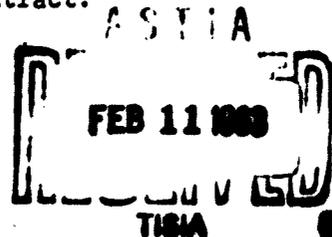
Contract No. AF49(638)-441

December 31, 1962

by

C. M. Schwartz (Principal Investigator), and A. P. Young

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INTRODUCTION

This report summarizes the results of an investigation, directed to exploration of the potentialities of ultra-high pressure as a tool in solid-state research, which was carried out under AFOSR Contract No. AF49(638)-441, beginning June 15, 1958, and extending through December 31, 1962.

At the time of the initiation of this project, the capabilities of ultra-high pressure generating apparatus in the range of 100 kb*, with simultaneous application of temperatures above 2000 C, had been reported. With such apparatus, it had been shown possible to synthesize metastable high-pressure polymorphic phases, such as diamond and borazon, and to study polymorphic transformations in electrically conducting materials, under pressure, by means of electrical resistance measurements.

As a means of further exploration of the potentialities of pressure as a research tool, this project was initiated with the following objectives:

- (1) To investigate the effect of high pressure on electrical properties of oxide semiconductors.
- (2) To investigate the effect of combined high pressure and high temperature on transformations and reactions in semiconducting and insulating oxides.

* One kilobar (kb) equals approximately 1000 atmospheres.

PRINCIPAL RESEARCH ACCOMPLISHMENTS

Effects of Pressure on Electrical Properties NiO, CoO, CuO, and Cu₂O

Pressure effects on the electrical resistivity of a semiconductor may be due to changes in carrier concentration or in carrier mobility. In broad-band semiconductors such as germanium, shifts in band gap with pressure affects the carrier concentration. The carrier mobility, which depends on scattering of nearly free carriers, is not appreciably affected by pressure.

In narrow-band semiconductors such as NiO, charge transport probably occurs by a thermally activated motion of holes self-trapped at local sites by lattice polarization. In this case pressure would be expected to decrease the carrier mobility in accord with observed pressure effects on other diffusion controlled processes.

A decrease in carrier mobility in nonstoichiometric NiO, and in CoO and CuO, which are narrow-band semiconductors, was observed in this investigation. A decrease in carrier mobility with pressure in nonstoichiometric Cu₂O was also observed, although Cu₂O is not generally regarded as a narrow-band semiconductor. However, there may be some lattice polarization of the Cu₂O lattice by charge carriers.

Publications

Effect of High Pressure on Electrical Properties of NiO, CoO, CuO, and Cu₂O,

A. P. Young, W. B. Wilson, and C. M. Schwartz, Phys. Rev., 121, 77, (1961)

Measurement of Pressure Effect on the Seebeck Coefficient of Powder Compacts,

A. P. Young, P. B. Robbins, W. B. Wilson, and C. M. Schwartz, Rev. Sci. Instr.

31, 70, (1960).

High Pressure High Temperature Mixed Oxide Phases

The effects of pressure on the electrical properties of oxides examined were not large such as Bridgman observed in some semiconductors. There was no indication from the data on electrical properties that a phase boundary was being approached. Since the oxygen lattice in many simple metal oxides is already close-packed, a phase change at high pressure is not probable. This conclusion was verified in a series of experiments at high pressure and temperature using simple oxides; no new phases were observed. Attention was then directed to pressure-induced transformation in certain mixed oxides generally selected on the basis of structural considerations, in particular, structural relationship to one form of a mixed oxide which was known to exhibit polymorphism. For example, CrTaO_4 , FeTaO_4 , CrNbO_4 , and FeNbO_4 have the rutile-type crystal structure with six-fold coordination of oxygen ions around the cations, whereas CrVO_4 and FeVO_4 do not normally have the rutile structure. Vanadium, niobium, and tantalum are each in Group VB; however, vanadium has a smaller ion radius than niobium or tantalum. It was hypothesized that the smaller ion size of vanadium was unfavorable to the development of six-fold coordination under normal pressure, but that under high pressure, the rutile-type modifications of CrVO_4 and FeVO_4 with 6-3 coordination might be formed.

At temperatures to 1000 C and pressures from 60 to 90 kb, a rutile type CrVO_4 was found. The high pressure FeVO_4 was not rutile-type. However, analysis of the X-ray powder pattern showed it to be orthorhombic with nearly the same cell volume per molecule as the rutile-type CrVO_4 . The high pressure FeVO_4 probably also had 6-3 coordination.

AlAsO_4 in the usual form has the quartz structure, but AlSbO_4 is rutile-type. It was apparent that high pressure might transform AlAsO_4 to the rutile

modification. The AlAsO_4 did not transform at 60 kb. However, at the time of these experiments, the synthesis at 120 kb of rutile-type SiO_2 by the Russian scientists, Stishov and Popova, was announced. This suggested that higher pressure was probably required for the AlAsO_4 transformation. A rutile-type AlAsO_4 was formed at 90 kb and 900 C.

Stishovite, the rutile-type SiO_2 , was also synthesized at about 125 kb and 1000 C. Refractive indices and infrared spectra of the high pressure and normal forms of SiO_2 and AlAsO_4 were compared. Predictions of Dacheville and Roy on the effect of change in primary coordination number on refractive index and wavelength of infrared peaks were verified.

Attempts of synthesize high pressure rutile-type modifications of AlVO_4 , FeAsO_4 , and CrAsO_4 were unsuccessful. New high pressure modifications were found in these compounds; however, the crystal structures could not be identified from X-ray powder data.

The tungstates RWO_4 with small cation $\text{R} = \text{Mg, Zn, Mn, Fe, Co, and Ni}$ form an isomorphous series having the wolframite structure. The normally occurring molybdates do not have this structure. It has been possible however, to synthesize, at high pressure, all of the molybdates with the wolframite structure, which also exhibits 6:3 coordination. The coordination of the normally occurring molybdates is not known, but is probably lower than 6:3. A density increase from the normal to the high pressure form of about 16 per cent in CoMoO_4 and NiMoO_4 is indicative of an increase in coordination number.

The results of this investigation indicate that pressure can be used to increase the primary coordination number in mixed oxides. Occurrence of pairs of polymorphs with different primary coordination numbers have been rare up to the present time.

Publications

High Pressure Forms of CrVO_4 and FeVO_4 , A. P. Young and C. M. Schwartz, Acta Cryst.
In press.

Synthesis and Optical Crystallography of Stishovite, A Very High Pressure Polymorph
of SiO_2 , C. B. Sclar, A. P. Young, L. C. Carrison, and C. M. Schwartz, J. Geophys.
Res. 67, 4049 (1962).

Synthesis and Properties of a High-Pressure Rutile-Type AlAsO_4 , A. P. Young,
C. B. Sclar, and C. M. Schwartz, Zeit. fur Krist., accepted for publication.

High Pressure Synthesis of Molybdates with the Wolframite Structure, A. P. Young,
and C. M. Schwartz, to be submitted to J. Phys. and Chem Solids.

MISCELLANEOUS STUDIES

Electrical Properties of Doped Oxides

Many oxides such as NiO , which when stoichiometric and pure have a high resistance, may be made quite conducting by addition of impurities. Resistance of other oxides such as Al_2O_3 , MgO , and Cr_2O_3 have been relatively impervious to impurity additions. Attempts were made to dope Al_2O_3 with GeO_2 and to dope Cr_2O_3 with MgO and TiO_2 , both at ambient pressure and high pressure, to reduce the resistivity. If the resistivity of Al_2O_3 , MgO , or Cr_2O_3 could be reduced to the order of 100 ohm-cm, at room temperature, these materials would be useful for high temperature furnaces, particularly in the high pressure cell.

GeO_2 additions to Al_2O_3 and Cr_2O additions to MgO had little effect on resistivity. TiO_2 additions to Cr_2O_3 increased the resistivity. MgO additions to Cr_2O_3 decreased the resistivity but not enough so that it could be used as a heater element without providing an auxiliary heater as a starter.

The choice of pressure transmitting materials, which can be used in high pressure high temperature cells is limited by the pressure transmitting properties, stability and thermal and electrical insulating properties at high pressure and temperatures. Heater elements must be compatible with the pressure transmitting medium and also with the specimen material, if possible, since the specimen and heater are in contact or in close proximity. Platinum heaters were used generally in this investigation but they are apt to fail by local burnout at temperatures above 1400 C. Graphite heaters, which have been commonly used, do not hold up well in pyrophyllite and are not compatible with oxides.

Of the doped oxides mentioned in the literature, doped ZrO_2 and titanium doped Fe_2O_3 appear to be possible choices for high pressure heater elements. It is essential to find some nonmetallic heater elements for the extension of the useful temperature range of high-pressure equipment. Work on the heater problem is continuing in this laboratory.

Development of High Pressure Apparatus and Techniques

Some time on this contract was necessarily used in developing apparatus and techniques.

Development of a method of measuring temperature at pressure in the "belt" apparatus was necessary for analytical work in determining reactions and transformations at high pressure and temperature. This was finally accomplished by replacing one of the steel cones in the "belt" apparatus with separated strips made of deep drawing steel. Thermocouple wires could be brought out successfully under the metal strips. The relative freedom of the individual strips apparently prevented pinch-off of the thermocouple wires during flow of the gasket material under pressure.

An attempt was made to measure sample resistance in situ at high pressure and temperature. For this purpose, a heater insulated from the sample was required. Rhenium wires were used for the heater. In the small specimen holder, one of the lead wires to the sample generally came in contact with a rhenium wire and was burned out. Success of this method is dependent on the development of a scaled-up high pressure apparatus and of other materials for heater elements. With the present apparatus, a more practicable method of monitoring any reaction or phase change may be by differential thermal analysis.

Methods of improving the pressure capability of high pressure high temperature devices were investigated. This effort was culminated by the development of a device capable of 130 to 140 kb pressure at elevated temperature. Stishovite was synthesized in this apparatus.

DISCUSSION

The similarity of pressure effects on hole mobility in Cu_2O and NiO is of interest, to the extent that it may denote a similarity in the charge transport mechanism in these materials. However, while the pressure effects on electrical properties were suggestive, the interpretation may be doubtful because of the use of powder compacts and nonhydrostatic pressure. Recent developments in crystal growing and in high pressure techniques indicate that effects of hydrostatic pressure on electrical properties of metal oxide single crystals can be determined. The results of this investigation are of sufficient interest to warrant a more critical examination of hydrostatic pressure effects on single crystals. Theoretical consideration of the effect of pressure on the mobility of polarons is also needed.

It is apparent from this investigation that the structure of mixed oxides is pressure sensitive and that in some instances new high pressure phases can be

predicted by structural and chemical analogy with other existing materials. Further studies of this type should lead to a broader understanding of structural principles. Some mixed oxides are of considerable interest because of their dielectric and magnetic properties and because of their potentialities as hosts for paramagnetic ions. For instance, some of the tungstates, analogous to the high pressure molybdates, are of interest for maser application. For such applications and also for determination of their properties, single crystals of new high pressure materials will be required. It is evident that considerable attention should be given to the growth of single crystals of such materials under pressure. It is reasonably certain that the high pressure apparatus developed in this program can be scaled up and that provision can be made to obtain controllable temperature gradients for growing single crystals. High pressure may also be advantageous for controlling composition and eliminating some defects such as voids in single crystals of materials, which exist at ambient pressure.