FERROELECTRIC TUNGSTEN BRONZE BULK CRYSTALS AND EPITAXIAL THIN FILMS FOR ELECTRO-OPTIC DEVICE APPLICATIONS

AD-A145 577

Semi-Annual Technical Report No. 3
For Period 10/1/83 through 3/31/84

JULY 1984

DARPA Order No.	4540
Program Code:	P2D10
Name of Contractor:	Rockwell International Corporation
Effective Date of Contract:	09/30/82
Contract Expiration Date:	09/29/85
Amount of Contract Dollars:	$1,051,699
Contract Number:	N00014-82-C-2466
Principal Investigators:	Dr. R.R. Neurgaonkar (805) 498-4545, Ext. 109
	Dr. L.E. Cross Pennsylvania State University (814) 865-1181

Sponsored by

Defense Advanced Research Projects Agency (DoD)
DARPA Order No. 4540
Monitored by Naval Research Laboratory
Under Contract No. N00014-82-C-2466

DTIC FILE COPY

SEP 1 7 1984

A

84   09   14   001

AD-A145577

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassifiad	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public relaase; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S) SC5340.6SA	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Rockwell Intarnational Scienca Canter	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Defense Advancad Research Projects Agency

6c. ADDRESS (City, State and ZIP Code) 1049 Camino Dos Rios Thousand Oaks, California 91360	7b. ADDRESS (City, State and ZIP Code) 1400 Wilson Boulavard Arlington, VA 22209

8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-82-C-2466

8c. ADDRESS (City, State and ZIP Code)

4555 Overlook Avenue S.W.
Washington, DC 20375

10. SOURCE OF FUNDING NOS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT NO
	DARPA Ordar No. 4540		

11. TITLE (Include Security Classification) FERROELECTRIC TUNGSTEN BRONZE BULK CRYSTALS AND EPITAXIAL THIN FILMS FOR ELECTRO-OPTIC DEVICE APPLICATIONS

12. PERSONAL AUTHOR(S)
Cross, Dr. L.E.; Oliver, J.R.; Naurgaonkar, Dr. R.R.

13a. TYPE OF REPORT Semi-Annual Tech Rpt #3	13b. TIME COVERED FROM 10/1/83 TO 3/31/84	14. DATE OF REPORT (Yr., Mo., Day) JULY 1984	15. PAGE COUNT 48

16. SUPPLEMENTARY NOTATION
Tha views and conclusions containad in this document ara thosa of tha authors and should not be interpretad as necessarily rapresenting the official policias, either axprassad or impliad, of tha Defense Advanced Research Projects Agency of tha U.S. Government.

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB GR.	SBN, PBN, PKN, BNN, SNN, Morphotropic Phasa Boundary, Tungsten Bronze, Striations, E-O Coafficient, LPE Flux, Dialectric Constant, Writing Sansitivity, Ca, Fe Dopants

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Several doped (Fe^{3+} and Ce^{3+}) and undoped SBN:60 single crystals have been grown by the Czochralski technique. Although the quality of doped crystals needs to be improved, they show a considerable enhancement in electro-optic and photorefractive properties, specifically for Ce^{3+}-doped SBN:60 crystals. The addition of these impurity species did not change the growth conditions significantly; however, striations were present and became stronger as the concentration of impurity ions increased. Undoped SBN:60 single crystals have also been grown and they are almost striation-free and exhibit excellent electro-optic properties.

Phase diagram work on the system SrV_2O_6-BaV_2O_6-$SrNb_2O_6$-$BaNb_2O_6$ has determined that SBN:75 films can be grown from flux compositions which cover a relatively limited range in the phase diagram. Work on the pseudo-binary flux systems BaV_2O_6-PBN:60 and $Pb_{1-x}Ba_xNb_2O_6$-PBN:60 for PBN film growth has resulted in the formation of the tetragonal PBN phase for one composition, a highly encouraging result.

Research has continued on the pseudo-binary morphotropic bronze systems $Ba_2NaNb_5O_{15}$-$Sr_2NaNb_5O_{15}$ (BNN-SNN) and $Pb_2KNb_5O_{15}$-$Ba_2NaNb_5O_{15}$ (PKN-BNN). Improved sintering of ceramic compositions

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassifiad
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR   EDITION OF 1 JAN 73 IS OBSOLETE.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

1.0 SUMMARY AND PROGRESS

The tungsten bronze structural family has been shown to be useful for a number of applications, including electro-optic, nonlinear optical and pyro-electric applications. The current work reports the development of optical quality $Sr_{1-x}Ba_xNb_2O_6$ (x = 0.40) for electro-optic and photorefractive device studies. Considerable progress has been made in different areas, including the growth of doped SBN:60 single crystals and LPE films, as well as electro-optic and photorefractive characterization.

Several doped (Fe^{3+} and Ce^{3+}) and undoped SBN:60 single crystals have been grown by the Czochralski technique. Although the quality of doped crys-tals needs to be improved, they show a considerable enhancement in electro-optic and photorefractive properties, specifically for Ce^{3+}-doped SBN:60 crys-tals. The addition of these impurity species did not change the growth condi-tions significantly; however, striations were present and became stronger as the concentration of impurity ions increased. Once suitable dopants and dop-ant concentrations are optimized for photorefractive studies, effort will be extended to improve the crystal quality and size. Undoped SBN:60 single crys-tals have also been grown and the quality of these crystals is consistent, i.e., they are almost striation-free and exhibit excellent electro-optic prop-erties. In order to improve the optical quality of these SBN:60 crystals, higher grade starting materials are now being used for this growth. The results of this work are promising and will be discussed in our next report.

Extensive work has been performed on the flux systems required for LPE thin film growth of SBN and $Pb_{1-x}Ba_xNb_2O_6$ (PBN) bronze compositions. Phase diagram work on the system $SrV_2O_6-BaV_2O_6-SrNb_2O_6-BaNb_2O_6$ has determined that SBN:75 films can be grown from flux compositions which cover a relatively limited range in the phase diagram, and with a relatively high melting point (> 1350°C). Work on the flux system $Pb_2V_2O_7-Ba_2V_2O_7-PbNb_2O_6-BaNb_2O_6$ showed that only the rhombohedral PBN phase could be precipitated, even when quench-ing to room temperature from 1250°C. It appears that vanadium in the PBN flux

system stabilizes the rhombohedral structure over a much broader temperature range than is normally encountered for pure PBN. However, work on the pseudo-binary system BaV_2O_6-PBN:60 and $Pb_{1-x}Ba_xV_2O_6$-PBN:60 has resulted in the formation of the ferroelectric tetragonal PBN phase for one composition, and further research will be conducted on these systems based on these encouraging results.

Research has continued on the pseudo-binary morphotropic bronze systems $Ba_2NaNb_5O_{15}$-$Sr_2NaNb_5O_{15}$ (BNN-SNN) and $Pb_2KNb_5O_{15}$-$Ba_2NaNb_5O_{15}$ (PKN-BNN). Improved sintering of ceramic compositions from these systems has resulted in significantly improved dielectric properties, particularly near morphotropy. The system PKN-BNN shows particularly dramatic changes in dielectric properties near the morphotropic 0.75 PKN-0.25 BNN composition, with an abrupt discontinuity in the $\underline{b}$ and $\underline{c}$ lattice paramaters, indicating the potential for particularly enhanced piezoelectric and electro-optic properties. Single crystal growth of selected compositions from these systems will be attempted in the coming period.

2.0 DEVELOPMENT OF OPTICAL QUALITY SBN:60

2.1 Materials Growth Techniques

Since most of the bronze compositions grown in our laboratory are based on solid solution systems, it is important that suitable growth techniques be developed to produce crystals free of optical defects such as striations, scattering centers and twinning. Striations and other defects are typical problems common to solid solution crystals, and it is often difficult to suppress them completely. However, these problems can effectively be reduced such that the crystals can be useful for optical device studies. This task is difficult; hence, the selection of appropriate growth techniques is critical in the present work. At present, three different techniques have been chosen to develop SBN and other bronze crystals. They are as follows:

1. Bulk Single Crystals: Czochralski technique
2. Thin Films: Liquid phase epitaxy (LPE)
3. Strip Crystals Edge defined film-fed technique

The first two techniques are well established in our current work, and bulk crystals and films of SBN compositions have already been grown. In the present report, the growth of striation-free SBN crystals and films is discussed with the associated growth problems.

2.2 Growth Procedure

Nb_2O_5, $SrCO_3$, Fe_2O_3, CeO_2 and $BaCO_3$ fine powders have been used as starting materials and weighed out in the desired proportions, as summarized in Table 1. The batch mixture is ball-milled in acetone for 20-30 h, and then poured into a large drying dish. The dried powder is placed in a platinum reaction dish and calcined at 1000°C for 10-15 h to eliminate carbonates and any possible carbon from the pyrolytic breakdown of residual acetone. The calcined powder is then ball-milled and refired in an oxygen flow of 2 cfh at

1400°C for about 4-6 h. Phase checks and x-ray lattice constant measurements are made for each batch to ensure the use of a phase-pure bronze composition for crystal growth. A thick-walled platinum crucible of 2 x 2 in. in dimension is used for this growth, and this container holds roughly 450 g of melt composition.

Table 1

Materials for Bulk Single Crystal SBN:60 Growth

Crystal Composition	Starting Materials		Conditions and Remarks
SBN:60	a. $SrCO_3$	135.08 gms	* Congruent melting composition
	b. $BaCO_3$	115.48 gms	* Large crystals can be grown
	c. Nb_2O_5	398.73 gms	* Large electro-optic
			coefficient (r_{33})
	Total Wt.	649.26 gms	* Melts at 1510°C
	Growth Wt.	450.00 gms	* Crack-free and optical quality
SBN:60 + Fe^{3+}	a. $SrCO_3$	135.08 gms	* Dielectric and electro-optic
	b. $BaCO_3$	115.48 gms	coefficient increased
	c. Nb_2O_5	398.73 gms	* Growth of large crystals is
	d. Fe_2O_3	1.98 gms	possible.
			* Enhanced photorefractive
			properties
	Total Wt.	651.24 gms	* Crack-free crystals
	Growth Wt.	450.00 gms	
SBN:60 + Ce^{3+}	a. $SrCO_3$	135.08 gms	* Dielectric and electro-optic
	b. $BaCO_3$	115.48 gms	coefficient improved
	c. Nb_2O_5	398.73 gms	* Growth of large crystals is
	d. CeO_2	1.00 gms	possible
			* Enhanced photorefractive
			properties
	Total Wt.	650.26 gms	* Crack-free and optical quality
			crystals
	Growth Wt.	450.00 gms	

2.3   Growth of Undoped SBN:60 Crystals

As summarized in Table 2, we have grown a number of undoped SBN:60 single crystals of excellent quality by the Czochralski technique. The quality of these crystals is generally excellent and the process appears to be highly reproducible for this composition. Since the ADC system is now well established to control the striation problem more effectively, we have begun to introduce a few more changes in the current system to improve the crystal quality further.

Recently, we found that small amounts of impurities have a drastic photorefractive effect in optical waveguide applications. Current optical measurements at NRL on SBN:60 crystals indicate that the elimination of impurities should significantly improve the optical quality for waveguide applications. In view of this, higher grade starting materials have been used in the present growth experiments (Table 3). Although minor changes in thermal gradients have occurred, this batch has been used to successfully grow two new SBN:60 crystals. The quality of these crystals is significantly better, and it is expected that by controlling the thermal gradients more effectively, it should be possible to further control the optical quality in these crystals. We expect that during the next six month period, we should have a sufficient number of crystals to analyze the crystal quality and thereby further refine the growth technique.

2.4   Growth of Doped SBN:60 Crystals

Since the optical quality and performance of SBN:60 crystals continues to be improved, it is important that other factors such as speed and sensitivity be enhanced for this family of crystals. Besides the further development of striation-free crystals, we have begun to examine the effects of

Table 2
Growth of SBN Single Crystals

To NRL	Boule No.	Date Grown	Boule Wt. gm	Boule Size, cm	Dip (°C)	Pull Rate, mm/hr	Rotation rpm	Remarks, Observations
	167*	11/1/83	20	1.2 x 3.0	1492	~ 9	~ 5	Basal and vertical cracks, two deep twins, deep green color
	168*	11/4/83	30	1.2 x 4.8	1492	9-10	~ 6	Basal and vertical cracks, but no twins
	169*	11/10/83	27	1.2 x 4.0	1492	8-10	5-6	Uncracked upon cutting, green color, dopant distribution uneven
	170*	1/6/84	6	1.0 x 1.8	1492	5-10	12-15	Some twins and cracks, dark pink color, 1 1/4" x 1 1/4" crucible
	171	1/18/84	4	0.5 x 4.5	1492	4-9	10	Uncracked, pink color, good diameter control, striae closer together
	172	1/20/84	~ 6	0.6 x 5.0	1492	6-9	12-20	Uncracked, pink color, diameter control by pull rate variation
	173	1/31/84	21	1.2 x 5.0	1492	8-10	15-20	New charge, good widening cone, some cracking upon seed removal
	174	2/3/84	22	1.5 x 3.5	1491	4-10	~ 15	Crack, defects from epi join
*	175	2/7/84	25	1.4 x 3.0	1492	~ 6	15	Uncracked, reversed seed dip end, good widening cone
	176	2/9/84	31	1.5 x 3.0	1492	~ 6	8	Uncracked, straight growth
*	177	2/14/84	46	1.9 x 3.0	1490	~ 6	10	Uncracked, minor coring down c-axis
	178*	3/16/84	30	1.5 x 4.0	1490	~ 6	3-8	Minor surface twinning, deep green color
	179*	3/20/84	22	1.5 x 4.3	1488	~ 6	6-12	Uncracked, coffee color
	180	3/27/84	22	1.5 x 4.3	1488	~ 6	~ 8	Uncracked, same color as 179, tendency to twin beyond 1.5 cm diameter
	181	4/4/84	44	1.9 x 2.6	1495	~ 6	~ 8	Taken from furnace uncracked but cracks upon cutting
	182	4/17/84	37	1.6 x 3.0	1492	5-8	~ 8	Cracks upon seed removal, grew a bit off c-axis
	183	5/8/84	26	1.4 x 3.0	1488	6-8	~ 6	Uncracked, minor coring
	184	5/15/84	37	1.7 x 3.0	1490	6-8	~ 6	Seed section heavily defected (by etch pit observation) near edge. Removed uncracked from furnace

Note 1: All crystals grown in O$_2$ flow of ~ 4 S.C.F.H.
Note 2: All crystals grown were of composition Sr/Ba of 0.61/0.39.
 * Doped SBN:60 single crystals.

Table 3

Impurities in Starting Chemicals used for SBN:60 Crystals
(from Johnson Mathey Chemicals)

Starting Chemical	Impurity	Previous Amount	Current Amount
Nb2O5*	Ca	---	10 ppm
	Mg	---	> 1 ppm
	Ta	---	---
BaCO3	Ca	1 ppm	---
	Cu	~ 7 ppm	---
	Mg	> 1 ppm	> 1 ppm
	Na	> 1 ppm	> 1 ppm
	Pb	---	3 ppm
SrCO3	Bi	> 1 ppm	8 ppm
	Ca	> 1 ppm	---
	Cu	1-10 ppm	---
	Fe	> 1 ppm	> 1 ppm
	Na	> 1-2 ppm	> 1 ppm
	Mg	> 1 opm	< 1 ppm
	Pb	---	10 ppm

* Basically, higher grade Nb2O5 has been used.

specific impurities in these crystals. Since the change in the refractive index for a ferroelectric crystal is given by

$$\Delta n = 1/3 \ n^3 r_{ij} E_{ij} \quad , \tag{2.1}$$

where r_{ij} = electro-optic coefficient and E_{ij} = space charge field, it is clear that both the electro-optic coefficient and space charge field should be increased to develop efficient materia: for photorefractive device applications. However, for a given crystal, e.g., SBN:60, the electro-optic coefficient is constant. Hence, it is important that the space charge field should be improved using proper dopants.

Russian[1] and Japanese[2] researchers have demonstrated that the photorefractive sensitivity and response time of tungsten bronze SBN:60 ($Sr_{0.6}Ba_{0.4}Nb_2O_5$) crystals can be effectively improved by introducing proper dopants. According to their work, Ce-doped SBN:60 crystals exhibit an exceptionally high photorefractive sensitivity of 9.5×10^{-3} cm^2/J, a value that exceeds that of Fe-doped $LiNbO_3$ (4×10^{-5} cm^2/J) by more than two orders of magnitude. The response time for these crystals is marginal, but is is substantially faster than for Fe-doped $LiNbO_3$. This work is significant and provides useful direction for future investigations in order to establish the factors controlling both sensitivity and speed. A summary of the proposed impurity ions and their possible valence states and site preference is given in Table 4.

Table 4

Proposed Dopants for Photorefractive SBN
SBN and Other Bronze Crystals

Dopant	Valence State	Site Preference			
		15-Fold	12-Fold	9-Fold	6-Fold
Cerium*	Ce^{3+}, Ce^{4+}	Ce^{3+}	Ce^{3+}	Ce^{4+}	Ce^{4+}
Terbium	Tb^{3+}, Tb^{4+}	--	Tb^{3+}	Tb^{4+}	Tb^{4+}
Iron*	Fe^{3+}, Fe^{2+}	--	--	Fe^{2+}	Fe^{2+}, Fe^{3+}
Manganese	Mn^{2+}, Mn^{3+}, Mn^{4+}	--	--	Mn^{2+}	Mn^{2+}, Mn^{3+}
Titanium	Ti^{4+}, Ti^{3+}	--	--	--	Ti^{4+}, Ti^{3+}
Molybdenum	Mo^{5+}, Mo^{4+}	--	--	--	Mo^{6+}, Mo^{4+}
Niobium	Nb^{5+}, Nb^{4+}	--	--	--	Nb^{5+}, Nb^{4+}

* Used as CeO_2 and Fe_2O_3

Table 5 summarizes the crystal compositions, dopants used and growth conditions examined thus far. Both Fe and Ce-doped SBN:60 single crystals have been grown by the Czochralski technique under identical conditions used for undoped SBN:60 crystals. In this material Fe^{+3} prefers the 6-fold coordinate sites, while the Ce^{3+} is expected to occupy either 12- or 9-fold coordinated sites in the structure. Both Russian and Japanese reserachers have used Ce in this crystal, but from their work, the valance state of Ce and its site preference are not clear.[2]

Table 5

Growth Data on Doped and Undoped SBN:60 Crystals

Property	SBN:60	SBN:60 + Fe^{3+}	SBN:60 + Ce^{4+}
Symmetry	4 mm	4 mm	4 mm
Color of Crystal	Pale cream	Green Yellow (O_2)	Pink
Conc. of Dopants	---	~ 1.0 mol%	~ 0.1 mol%
Curie Temperature (°C)	72	51	70
Dielectric Constant (23°C)	$\varepsilon_{33} = 600$	$\varepsilon_{33} = 3400$	$\varepsilon_{33} = 940$
Quality	Excellent	Good	Excellent
Photorefractive Response	Good	Better	Excellent
Size (diameter)	2-3 cm	~ 1.5 cm	1.0 cm

Growth of these doped crystals has been successful, and crystals as large as 1 cm to 1.5 cm in diameter have been grown. The addition of the 3-d (Fe^{3+}) and 4-f (Ce^{3+}) cations in SBN:60 increases the thermal conductivity of the material; hence, necessary changes in the after-heater must be made to control thermal conditions in the crucible and near the solid-liquid interface. Since the concentrations of these dopants is relatively low, these changes are minor; however, it is important in the present work to further evaluate these conditions in order to develop optical quality crystals.

The Fe-doped SBN:60 crystals are deep green in color; however, this color changes to a deep yellow after annealing in an oxygen atmosphere at 1000°C. This result indicates that at elevated temperatures Nb^{5+} reduces to Nb^{4+}, which is again a tr...sition metal ion and contributes to the color of the crystal. The Ce-doped SBN:60 crystals show a pink color which persists after oxidation at 1000°C.

Fracture-free and reasonably good quality crystals have been grown. Although the growth of bigger sized crystals is possible in the present set-up, the technique at present will be confined to smaller size crystals. Figure 1 shows typical Ce-doped SBN:60 single crystals grown along the c-axis. Once the initial electro-optic and photorefractive properties of these doped crystals are established, plans will be made to improve their size and quality. X-ray diffraction studies show that crystal habit for these doped crystals is similar to undoped crystals, and is based on 24 facets of four prisms: (110), (120), (100) and (130).
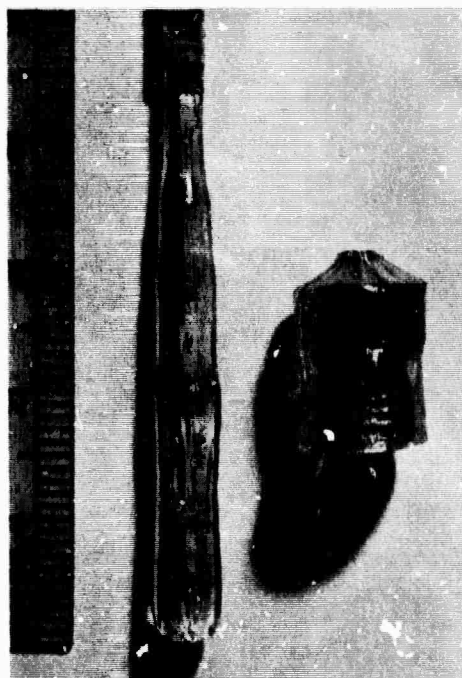

Fig. 1 Ce-doped SBN:60 crystals grown by the Czochralski method.

Optical evaluation of doped SBN:60 crystals indicates the presence of weak striations which are basically connected to the addition of Fe^{3+} and Ce^{3+} cations. It is believed that these striations can be suppressed or partially removed by controlling the thermal gradients in the crucible and near the solid-liquid interface. This task will be undertaken only when the dopant concentration is optimized. As shown in Table 5, the addition of Fe^{3+} and Ce^{3+} cations has significantly enhanced the dielectric constant, which indicates an increase in the electro-optic coefficient (r_{33}) in similar proportions. It was also found that the photorefractive sensitivity was substantially increased with dopants. These results are discussed in Section 6.0.

Based on all of these observations, we expect that by optimally controlling dopant concentrations in SBN:60 crystals, it should be possible to effectively investigate both photorefractive sensitivity and speed. During the next six months, the following experiments will be tried for photorefractive applications. The are as follows:

- Establish valance states of Fe and Ce cations in SBN:60 crystals.

- Establish optimum concentrations of Fe and Ce necessary for increased photorefractive sensitivity and speed.

- Establish the dielectric and electro-optic properties for these doped crystals and their effects on photorefractive properties.

- Develop more SBN:60 crystals with varying dopant concentrations.

3.0 LIQUID PHASE EPITAXIAL GROWTH OF BRONZE COMPOSITIONS

Large tungsten bronze single crystals are often very difficult to grow by the Czochralski method, particularly in the case of incongruently melting compositions (e.g., SBN:75) and compositions with volatile constituent ions (e.g., Pb^{2+} in $Pb_{1-x}Ba_xNb_2O_6$). In such cases, an alternative growth method is the liquid phase epitaxy (LPE) technique, which can be used to develop optical quality tungsten bronze thin films using existing bronze single crystal substrate. This technique is important not only for thin film fabrication for electro-optic, nonlinear optic and piezoelectric device applications, but also in the development of new bronze compositions for property evaluation.

The present work has focused on the development of LPE films of the tetragonal bronze compositions SBN:75 and PBN:60. Since large single crystals of SBN:50 and SBN:60 are available for use as substrate material with minimal lattice mismatch to the LPE bronze compositions, we do not anticipate any major problems in actual film growth. However, successful film growth of these selected compositions is inherently dependent on the thermodynamics of the flux systems used, with the three major requirements being (1) a sufficiently low melt temperature, (2) the absence of second phases, and (3) the maintenance of the desired bronze composition in the as-grown film. The results of our current work are discussed in the following section.

3.1 Flux Systems for SBN:75

As discussed in a previous report, we have successfully demonstrated the LPE growth of SBN:60 thin films on SBN:60 substrate using a BaV_2O_6-$Sr_{0.5}Ba_{0.5}Nb_2O_6$ flux system. However, in the case of SBN:75 thin film growth, a composition which displays the highest electro-optic and piezoelectric co-efficients in the SBN family, we did not know the proper flux recipe required in order to maintain compositional control over the as-grown film. Therefore, the present work has focused on the quaternary phase diagram for the SrO-BaO-

Nb_2O_5-V_2O_5 system in order to understand its thermodynamic behavior. Because of the extensive work required to build the entire quaternary phase diagram, our work has been restricted to possible bronze-forming flux systems such as BaV_2O_6-$Sr_{0.5}Ba_{0.5}Nb_2O_6$, SrV_2O_6-$Sr_{0.5}Ba_{0.5}Nb_2O_6$, and $(.65)$ $Sr_{1-x}Ba_xNb_2O_6$-$(.35)Sr_{0.5}Ba_{0.5}Nb_2O_6$. The ranges covered in the quaternary phase diagram with these systems are shown in Fig. 2.

A variety of flux compositions were prepared and then sintered or melted at either 1000°C or 1250°C. After leaching away the remaining vanadates with a dilute nitric acid solution, the structures of the remaining niobate solids were identified using powder x-ray diffraction measurements and analysis. The results of this work are presented in Table 6.
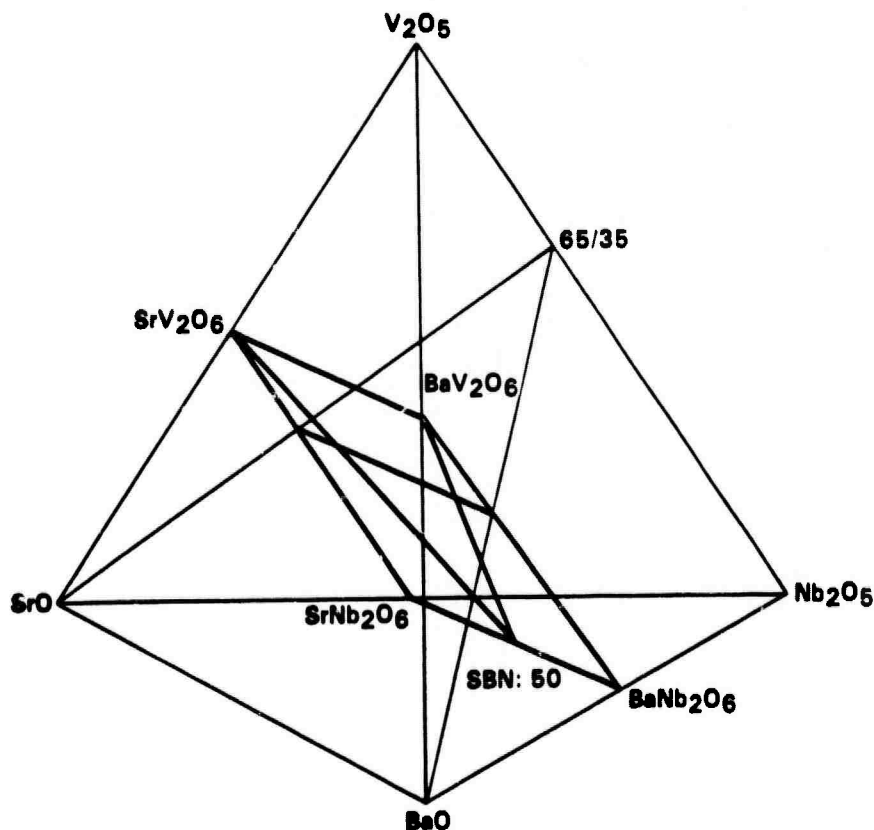

SC84-26697

Fig. 2 Quaternary phase diagram of the SrO-BaO-Nb$_2$O$_5$ system.

Table 6

LPE Fluxes for SBN

No.	Composition	Sr/Sr + Ba	Temperature (°C)	Remaining Phase
1	65% SrV_2O_6 + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.825	Melted 1000	$SrNb_2O_6$
2	65% $Sr_{0.5}Ba_{0.5}V_2O_6$ + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.50	Melted 1000	Other
3	65% $Sr_{0.3}Ba_{0.7}V_2O_6$ + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.36	Melted 1000	Other
4	65% $Sr_{0.5}Ba_{0.8}V_2O_6$ + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.305	Melted 1000	Other
5	65% $Sr_{0.1}Ba_{0.9}V_2O_6$ + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.24	Melted 1000	SBN:37
6	65% BaV_2O_6 + 35% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.175	Melted 1000	SBN:37
7	40% SrV_2O_6 + 60% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.70	Melted 1250	$SrNb_2O_6$
8	30% SrV_2O_6 + 70% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.65	Sintered 1250	SBN + $SrNb_2O_6$
9	20% SrV_2O_6 + 70% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.65	Sintered 1250	SBN:58
10	40% BaV_2O_6 + 60% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.30	Melted 1250	SBN:X
11	50% $Sr_{0.5}Ba_{0.5}V_2O_6$ + 50% $Sr_{0.5}Ba_{0.5}Nb_2O_6$	0.50	Sintered 1250	$SrNb_2O_6$

Figure 3 shows the phase diagram for the system SrV_2O_6-BaV_2O_6-$SrNb_2O_6$-$BaNb_2O_6$, which is the smaller quaternary region examined here in the larger SrO-BaO-Nb_2O_5-V_2O_5 phase diagram of Fig. 2. The solid circles in Fig. 3 represent tetragonal tungsten bronze SBN phases, and the squares represent other observed phases according to the results listed in Table 6. From this work, it is seen that only in the shaded regon of Fig. 3, which includes the flux compositions No. 5, 6, 9 and 10, can single phase bronze compositions be found. The range of this bronze forming region for $Sr_{1-x}Ba_xNb_2O_6$ is $0.25 < x < 0.75$, as shown in Fig. 3.
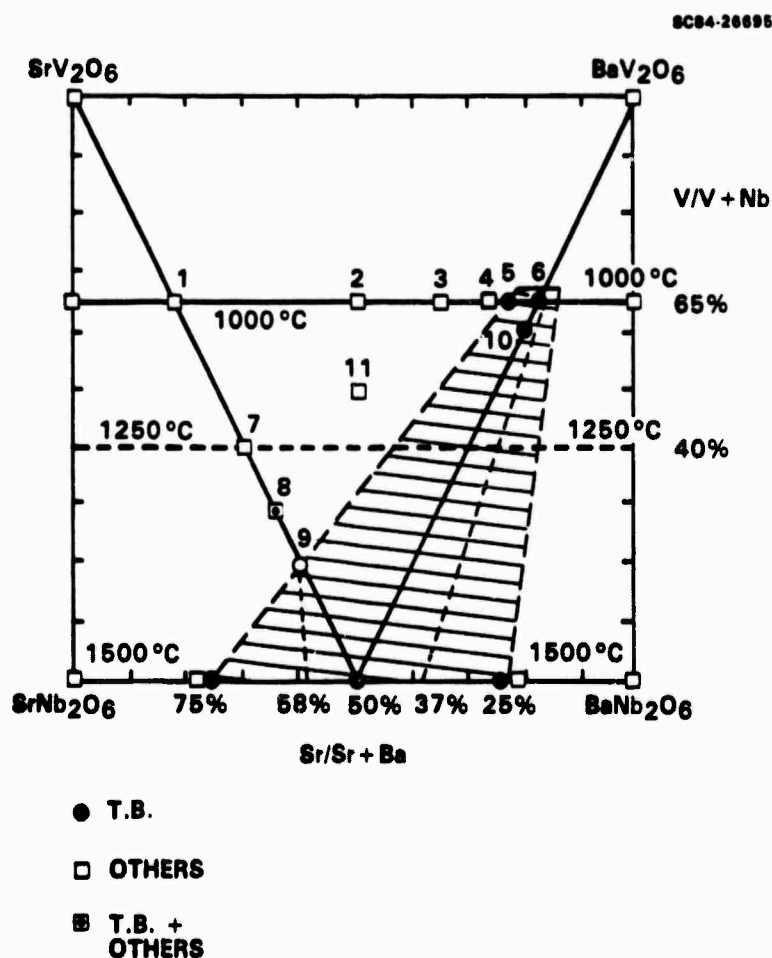
SC84-26695

Fig. 3 Quaternary phase diagram of the SrV_2O_6-BaV_2O_6-$SrNb_2O_6$-$BaNb_2O_6$ system.

At the present time, there is some uncertainty in the determination of the actual SBN compositions formed in this region. However, since we were able to establish that SBN:37 was grown from flux No. 6 and SBN:58 from flux No. 9, two tie-lines can be drawn from these flux points in the phase diagram shown in Fig. 3 (dashed lines). Hence, in order to grow LPE films with the composition $Sr_{0.75}Ba_{0.25}Nb_2O_6$, we must work in the very small region of flux compositions bounded by the SBN:58 tie-line.

Considering the melting points for various flux compositions, e.g., roughly 1000°C for $V/(V+Nb) = 0.65$, 1250°C for $V/(V+Nb) = 0.40$ and 1500°C for $V/(V+Nb) = 0$, it is clear that the LPE growth of the SBN:75 bronze composition from the $SrO-BaO-Nb_2O_5-V_2O_5$ flux system may not be particularly easy. Not only must one deal with a relatively narrow range of suitable flux compositions, but also a necessarily high flux melting point greater than 1350°C.

3.2   Flux Systems for PBN:60

As discussed previously, a V_2O_5 solvent has been initially selected for the growth of tetragonal $Pb_{0.6}Ba_{0.4}Nb_2O_6$ thin films on SBN:60 substrates. Several possible bronze-forming flux systems have been studied during the past several months, including $Pb_2V_2O_7-Pb_{0.6}Ba_{0.4}Nb_2O_6$, $BaV_2O_6-Pb_{0.6}Ba_{0.4}Nb_2O_6$ and $Pb_{2-x}Ba_xV_2O_7-Pb_{0.6}Ba_{0.4}Nb_2O_6$. Preparation and evaluation procedures were essentially the same as those for the SBN flux systems, with dilute nitric acid being used to leach out any vanadates prior to powder x-ray diffraction measurements. A summary of the fluxes examined is given in Table 7.

Figure 4 shows the phase diagram of the $Pb_2V_2O_7-Ba_2V_2O_7-PbNb_2O_6-BaNb_2O_6$ system in which the solid circles represent the ferroelectric tetragonal PBN phase, triangles represent the nonferroelectric rhombohedral phase, and squares represent the presence of other second phases. The shadowed area of Fig. 4, which includes flux systems No. 1, 2 and 5 in Table 7, is the rhombohedral phase formation region for PBN. No orthorhombic phase was ever found in this region, even when material was quenched to room temperature from 1250°C.

Table 7

LPE Fluxes for PRN

No.	Composition	Pb/Pb + Ba	Melting Temp. (°C)	Remaining Phase
1	70% $Pb_2V_2O_7$ + 30% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.93	Melted, 1000 and 1250	Rhomb. PRN
2	70% $Pb_{1.2}Ba_{0.8}V_2O_7$ + 30% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.60	Melted, 1000 and 1250	Rhomb. PRN
3	70% $Pb_{0.8}Ba_{1.2}V_2O_7$ + 30% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.50	Melted, 1000	Other
4	60% $Pb_{0.6}Ba_{1.4}V_2O_7$ + 30% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.43	Melted, 1000	Other
5	50% $Pb_2V_2O_7$ + 50% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.87	Melted, 1250	Rhomb. PBN
6	80% BaV_2O_6 + 20% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	1.12	Melted, 1000	Other
7	70% BaV_2O_6 + 30% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.18	Melted, 1000	Tet. PRN + $BaNb_2O_6$
8	50% BaV_2O_6 + 50% $Pb_{0.6}Ba_{0.4}Nb_2O_6$	0.30	Melted, 1250	Tet. PBN

Fig. 4   Quaternary phase diagram of the $Pb_2V_2O_7$-$Ba_2V_2O_7$-$PbNb_2O_6$-$BaNb_2O_6$ system.

This result is to be compared with that for normal $Pb_{1-x}Ba_xNb_2O_6$, $x < 0.6$, in which the orthorhombic phase forms when the material is quenched from 1250°C and the rhombohedral phase forms when quenched from 1000°C. It appears, then, that the presence of vanadium in the PBN flux system stabilizes the rhombohedral structure over a much broader temperature range than is normally encountered for PBN.

Since we were unable to find either tetragonal or orthorhombic bronze phases for the $Pb_2V_2O_7$-$Pb_{0.6}Ba_{0.4}Nb_2O_6$ and $Pb_{2-x}Ba_xV_2O_7$-$Pb_{0.6}Ba_{0.4}Nb_2O_6$ flux systems, we then turned our attention to the systems BaV_2O_6-$Pb_{0.6}Ba_{0.4}Nb_2O_6$ and $Pb_{1-x}Ba_xV_2O_6$-$Pb_{0.6}Ba_{0.4}Nb_2O_6$, as shown in the phase diagram in Fig. 5. Initial results in this flux system look very promising, as a ferroelectric

tetragonal PBN phase was found for flux No. 8 of Table 7, indicated by the solid circle in Fig. 5. Based on these encouraging results, future work will focus on the following:

1. Development of the BaV_2O_6-$Pb_{0.6}Ba_{0.4}Nb_2O_6$ flux system.

2. Development of the $Pb_{1-x}Ba_xV_2O_6$-$Pb_{0.6}Ba_{0.4}Nb_2O_6$ flux system.

3. Lattice parameter standards for $Pb_{1-x}Ba_xNb_2O_6$ for comparison with flux-growth phases.

With successful development of suitable PBN compositions from these flux systems, $Pb_{1-x}Ba_xNb_2O_6$ thin films will then be grown on SBN:60 substrates using the LPE technique.

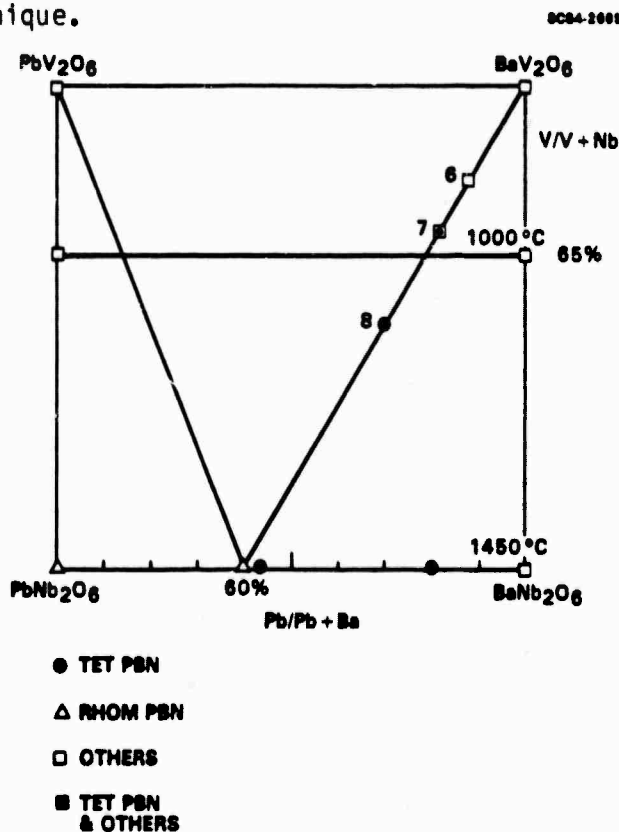Fig. 5 Phase diagram of the PbV_2O_6-BaV_2O_6/$PbNb_2O_6$-$BaNb_2O_6$ system.

4.0 NEW TUNGSTEN BRONZE SYSTEMS FOR ELECTRO-OPTIC STUDIES

Several of the more interesting tungsten bronze systems show morphotropic phase boundaries (MPB) which depend primarily on composition rather than on temperature. Ceramic or single crystal compositions adjacent to such boundaries show considerable enhancement of electro-optic, dielectric, piezoelectric, electromechanical and pyroelectric properties because of the proximity in energy of an alternate ferroelectric structure. In the present work, two such systems, $Ba_2NaNb_5O_{15}$-$Sr_2NaNb_5O_{15}$ and $Pb_2KNb_5O_{15}$-$Ba_2NaNb_5O_{15}$, have been investigated and are found to have MPB conditions with exceptionally high dielectric and other properties. In this report, we present further data on these bronze systems based on work during the past six months.

4.1 $Ba_2NaNb_5O_{15}$-$Sr_2NaNb_5O_{15}$ System

Tungsten bronze barium sodium niobate (BNN) has been shown to be an outstanding material for electro-optic and nonlinear optic applications, particular'y for second harmonic generation of near-IR laser radiation. The material was first discovered in 1967 by researchers at Bell Labs,[3] and was found to have a number of useful nonlinear optic and piezoelectric properties. Stoichiometric $Ba_2NaNb_5O_{15}$ is orthorhombic at room temperature with lattice constants a = 17.592A, b = 17.626A and c = 3.995A, as determined from high angle x-ray measurements.[4] Above 260°C, an orthorhombic to tetragonal transformation occurs in which microtwinning is usually observed in single crystals, but with no significant dielectric anomalies. The Curie point is at approximately 570°C.

Based on our earlier theoretical work on the tungsten bronze family[5] and experimental work on $Pb_{1-x}Ba_xNb_2O_6$, an enhancement of the piezoelectric, pyroelectric and electro-optic properties can be anticipated for tungsten bronze compositions which exhibit a morphotropic boundary condition between the tetragonal and orthorhombic phases. To this end, we began an investigation of the pseudo binary system $(1-x)Ba_2NaNb_5O_{15}$-$(x)Sr_2NaNb_5O_{15}$ during the

previous reporting period. In the present report, we present further refinements of this work.

The materials used for each particular composition were prepared by the normal procedure of mixing, calcining at 950°C, and then ball-milling for 12-18 h. The cold-pressed disks were then sintered for 2 h at 1280-1380°C, depending on composition. It was found during earlier work that many of the compositions were not well sintered and, hence, a considerable effort was made to determine the optimum sintering conditions. In particular, it was found that much higher sintering temperatures are required for BNN-rich compositions, with an optimum sintering temperature of 1380°C for pure $Ba_2NaNb_5O_{15}$. The resulting dielectric properties are considerably greater at the Curie point T_c, and the characteristics as a function of temperature are substantially sharpened near T_c. The variation in the Curie point as a function of composition is shown in Fig. 6, with the characteristic sharp drop in T_c occurring at the morphotropic (0.40)BNN-(0.60)SNN composition.

Figure 7 shows the dielectric properties as a function of composition. The major enhancement over the previously reported data is an increase in the dielectric properties at T_c for BNN-rich compositions as a result of improved ceramic sintering. The dielectric constant at the Curie point is essentially flat on either side of the morphotropic boundary, with an abrupt factor of two jump in the dielectric constant at the MPB. The dielectric properties at room temperature are generally monotonic with composition, rising from a value of $\varepsilon = 100$ for BNN to nearly 2000 for SNN. However, an anomalously high value of $\varepsilon = 1200$ occurred for $x = 0.67$; it is not presently clear if this is a true local maximum near the morphotropic phase boundary or if the SNN-rich compositions are still inadequately sintered. The steep rise in the room temperature dielectric constant for $x > 0.8$ is due to the onset of a second transition peak which occurs below room temperature. The influence of this second transition can be seen in the dielectric properties for $Sr_2NaNb_5O_{15}$ (SNN) shown in Fig. 8; preliminary low temperature measurements show this to be a very broad dielectric peak with a maximum near -50°C.
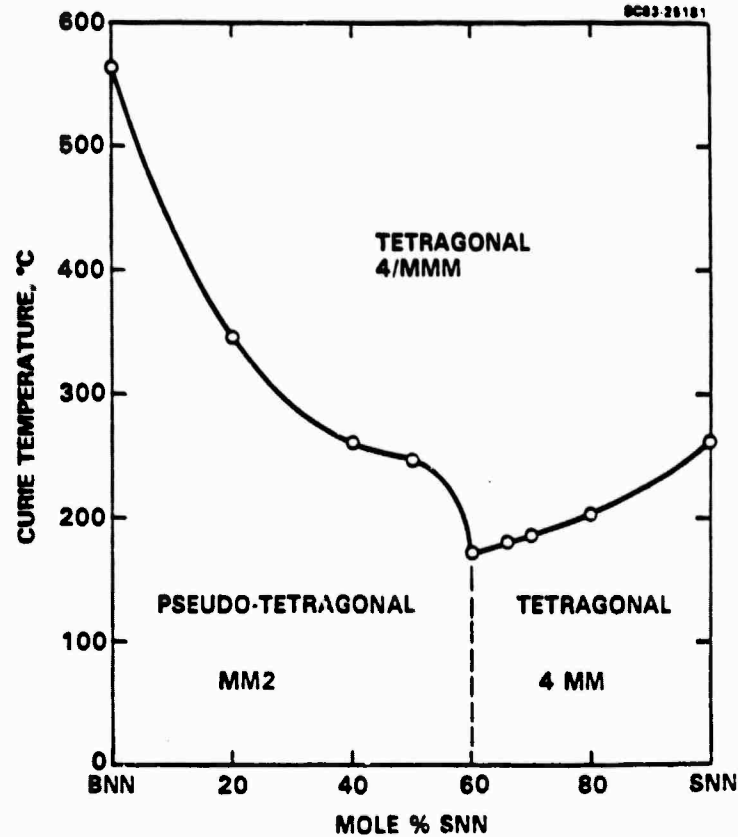
Fig. 6 Morphotropic phase boundary conditions for the system BNN-SNN.

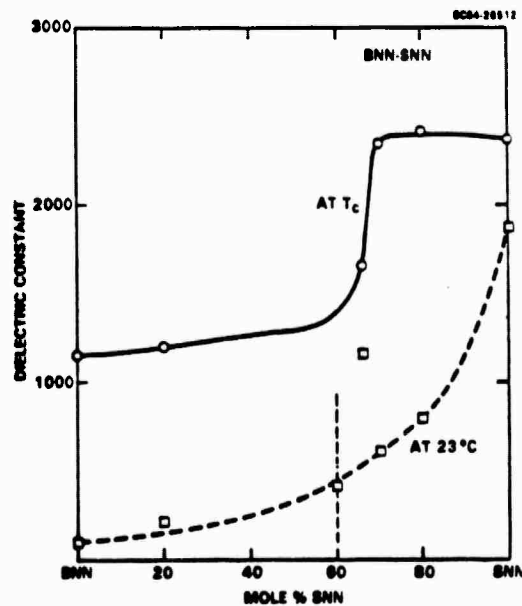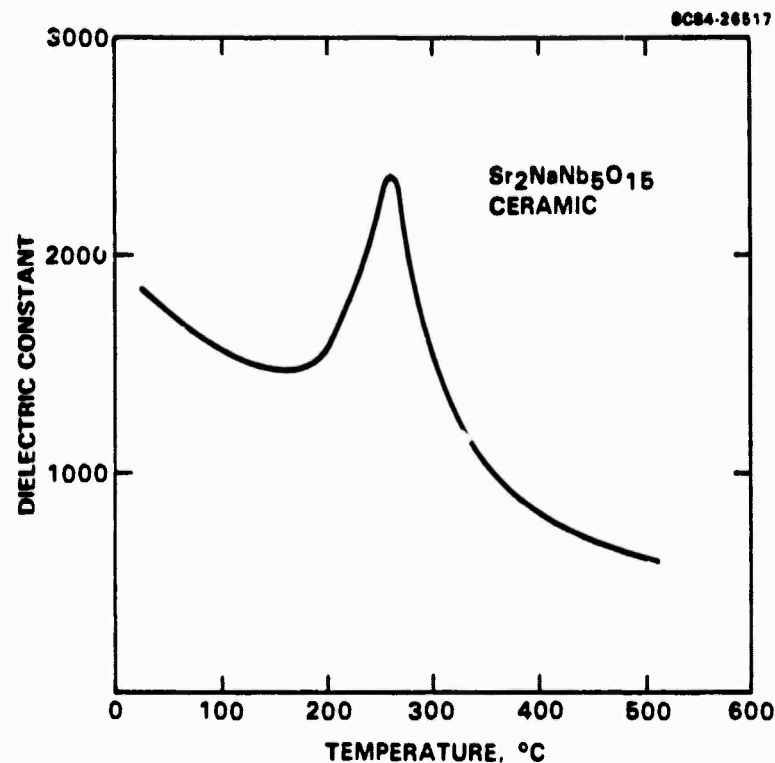Fig. 7 Dielectric constant (at 10 kHz) vs composition for the system BNN-SNN.

Fig. 8   Dielectric constant of ceramic $Sr_2NaNb_5O_{15}$ (SNN) as a function of temperature.

We have performed hot-pressed ceramic densification on two composi-
tions in the region of the morphotropic phase boundary for this system, spe-
cifically 0.40 BNN-0.60 SNN and 0.30 BNN-0.70 SNN. In both cases, the mate-
rial was hot-pressed at 4000 psi for 2 h at 1280°C, and then cooled slowly to
room temperature. Because of the nitrogen ambient atmosphere required by the
graphtie dies for this press, the reduced samples were oxidized for 12 h at
1070°C subsequent to densification. The resulting ceramcs were crack-free and
a uniform off-white in color. The dielectric properties for these densified
ceramic compositions are summarized in Table 8 for measurements taken parallel
and perpendicular to the uniaxial pressing direction. It is interesting to
note that the measured dielectric values are comparable to those measured for
normally sintered ceramic material. The most significant anisotropy appears

for the 0.30 BNN-0.70 SNN composition, indicating partial grain orientation. This result is not unexpected, since in the morphotropic 0.40 BNN-0.60 SNN composition possesses both orthorhombic (pseudo-tetragonal) and tetragonal phases and, hence, is less inclined to demonstrate a preferential grain orientation.

Table 8

Dielectric Properties of Hot-Pressed BNN-SNN

Composition	Cut	Dielectric Constant* @ 23°C	@ T_c	T_c (°C)
0.30 BNN-0.70 SNN	Para.	835	2250	216
	Perp.	925	3140	
0.40 BNN-0.60 SNN	Para.	800	2560	221
	Perp.	800	3230	

* at 10 kHz

4.2   Pb2KNb5O15-Ba2NaNb5O15 System

Another tungsten bronze of interest is $Pb_2KNb_5O_{15}$ (PKN). This compo-
sition has been successfully grown in hot-pressed dense ceramic form by Nagata
et al[6] in Japan with a high electrochemical coupling constant, $k_t = 0.40$, and
good polarization. As such, it represents an attractive candidate for SAW,
piezoelectric and pyroelectric device applications. However, its relatively
high Curie point (470°C) makes it very difficult to completely pole. It is
also prone to cracking above 1200°C growth temperatures[6] and, hence, the
attainment of optically transparent hot-pressed material remains unlikely.

Because of the orthorhombic structure of PKN, the possibility pre-
sented itself of obtaining a morphotropic phase composition in combination
with pseudo tetragonal BNN. To this end, we began an investigation of the
pseudo binary bronze system $(1-x)Pb_2KNb_5O_{15}-(x)Ba_2NaNb_5O_{15}$ using cold-pressed
and sintered ceramic samples. A morphotropic phase boundary condition was,
indeed, found for the composition 0.75 PKN-0.25 BNN with a sharp minimum in T_c
of 270°C. However, cracking was a major problem in these ceramics, even after
lowering the sintering temperature for PKN-rich samples; hence, much of the
dielectric data were not viewed with confidence.

The addition of excess PbO, on the order of 1-3%, has been found to
dramatically improve the quality of ceramics prepared from this system with
the total disappearance of microcracks. Measured weight losses show the
ceramics to be approximately 1-2% Pb^{2+}-deficient after sintering for 4 h.
Measurements of the Curie transition temperature as a function of composition
for $(1-x)$PKN-(x)BNN are shown in Fig. 9, and are only slightly different from
earlier data. However, measured values for the dielectric constant at T_c and
at room temperature now show much steeper characteristics at the morphotropic
boundary, as can be seen in Fig. 10. The general dielectric behavior of the
near-morphotropic 80/20 composition and the two bronze end members, PKN and
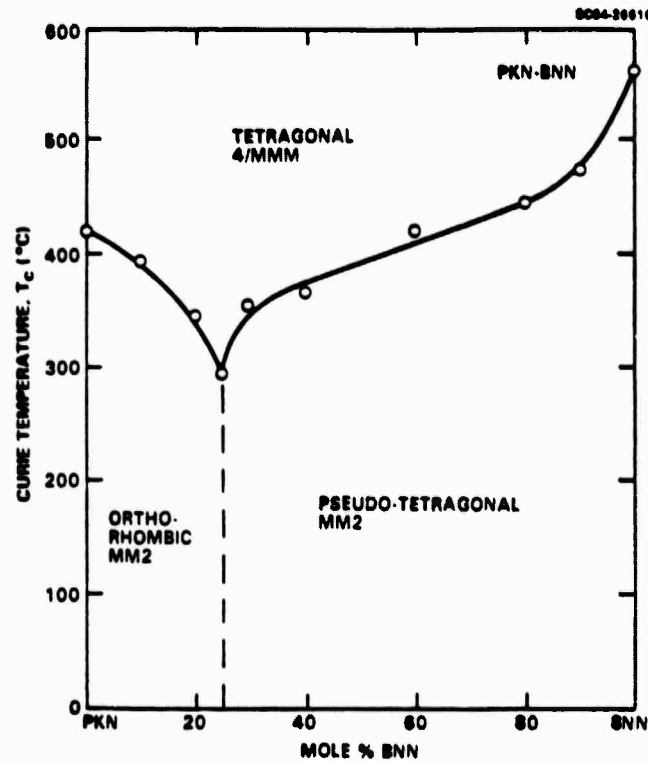BNN, are shown as a function of temperature in Fig. 11.

Fig. 9 Morphotropic phase boundary conditions for the system PKN-RNN.

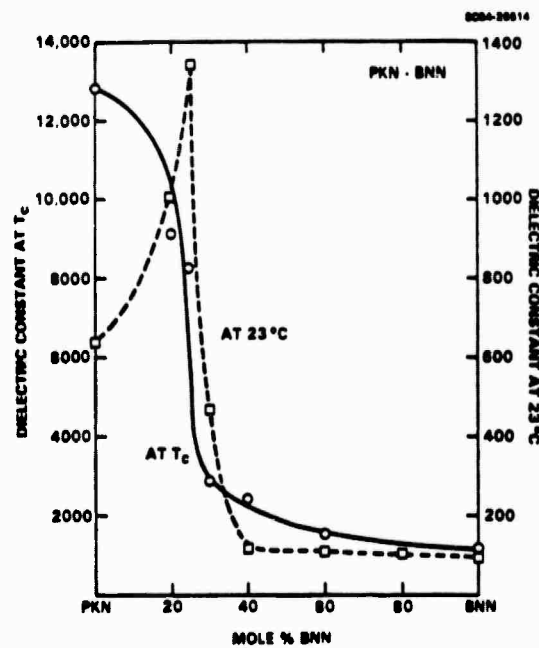Fig. 10 Dielectric constant (at 10 kHz) vs composition for the system PKN-RNN.
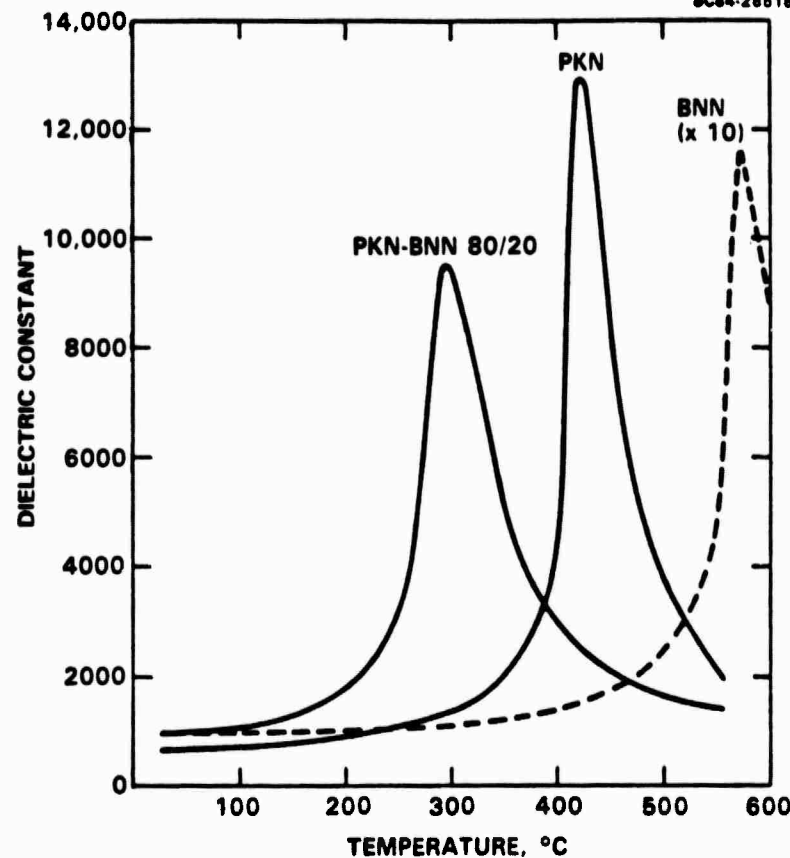
Fig. 11   Dielectric constant of ceramic PKN, 0.8 PKN-0.2 BNN and BNN as a
function of temperature. Data for BNN is expanded by a factor of 10
for clarity.

The dramatic changes in the dielectric properties at morphotropy are
reflected in the behavior of the lattice parameters as a function of composi-
tion, as shown in Fig. 12. These data were obtained by careful least-squares
evaluation of powder x-ray diffraction data, with excellent fits being ob-
tained for all compositions. Of particular interest in Fig. 12 is the smooth
monotonic decrease in the a lattice parameter, whereas b and c remain constant
up to x = 0.25, at which point an abrupt discontinuity occurs. This dramatic
behavior suggests that near-morphotropic compositions in the PKN-BNN system
should display particularly enhanced piezoelectric and electro-optic
properties.

Both the PKN-BNN and BNN-SNN systems have been shown to be promising for electro-optic, pyroelectric and millimeter wave device application studies. A few compositions exhibit enhanced dielectric properties at room temperature and at T_c. Some of these will be selected for future single crystal Czochralski growth, and the ferroelectric and electro-optic properties will be established in greater detail.
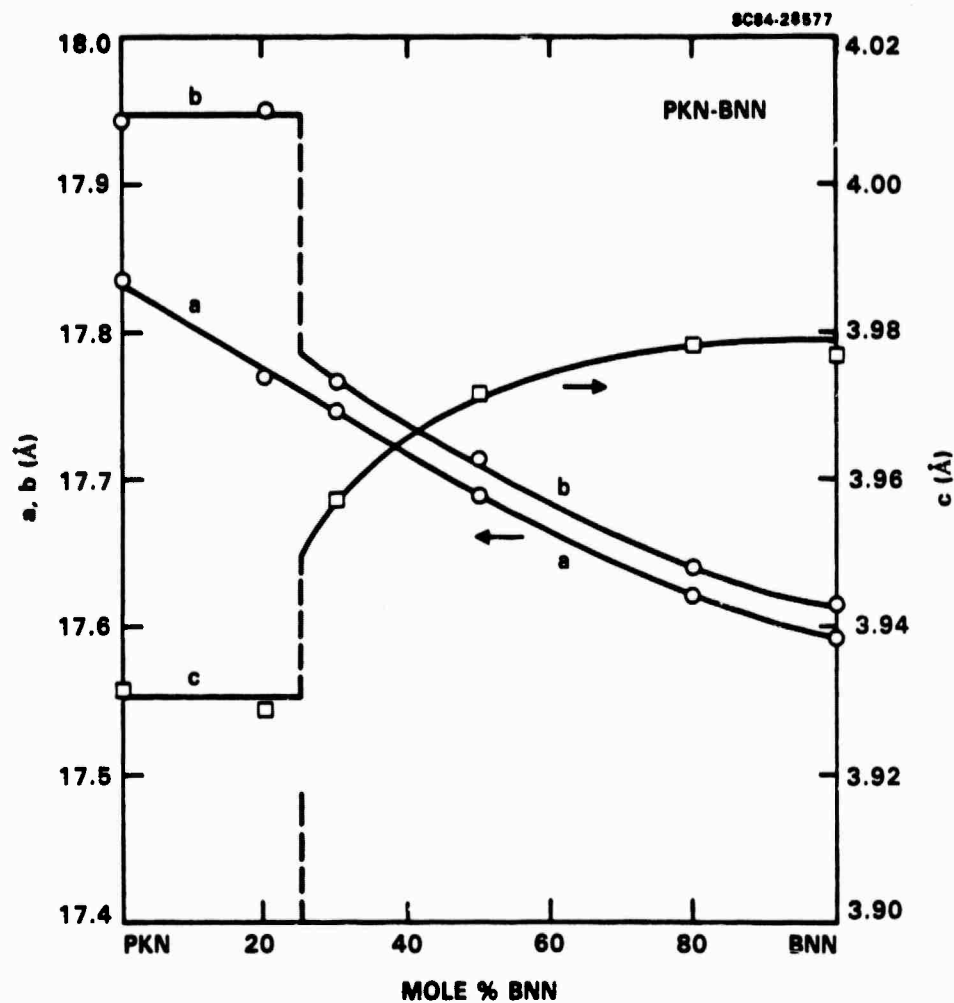

Fig. 12 Structural lattice parameters as a function of composition for PKN-BNN. Note the abrupt discontinuity for the b and c parameters at the morphotropic 0.75 PKN-0.25 BNN composition.

5.0 OPTICAL EVALUATION OF PBN

5.1 Introduction

The task taken up in the current contract period has been to complement the crystal growth work carried through last period and develop $Pb_{1-x}Ba_xNb_2O_6$ (PBN) compositions close to morphotropy, but on the orthorhombic side of the phase boundary.

In the family of orthorhombic ferroelectric bronzes in the Shuvalov species 4/mmm (2)D2F mm2, the nonzero polarizations in the ferroelectric phase are $P_1^2 = P_2^2 \neq 0$, $P_3 = 0$, and the equations for the spontaneous perturbation of the optical impermeability induced by the phase change at T_c become

$$\Delta B_{11} = (g_{11} + g_{21})P_1^2$$

$$\Delta B_{22} = (g_{11} + g_{21})P_1^2$$

$$\Delta B_{33} = 2g_{13}P_1^2 \tag{5.1}$$

$$\Delta B_{12} = g_{66}P_1^2 \quad .$$

For the single domain state, the optical indicatrix becomes biaxial with three inequivalent principle indices. In Eq. (5.1), the nonzero ΔB_{12} is due to the use of the original prototypic tetragonal axes. Rotating the axial system 45° in the ab (12) plane eliminates ΔB_{12} and destroys the equivalence between $\Delta B_{11}'$ and $\Delta B_{22}'$ in the new correct orthorhombic axial system.

Similarly to the tetragonal case, the morphic linear electro-optic r coefficients are given by

$$r_{11} = r_{22} = 2g_{11}P_1\epsilon_{11}$$

$$r_{12} = r_{21} = 2g_{21}P_1\epsilon_{11}$$

$$r_{13} = r_{23} = 2g_{13}P_1\epsilon_{33} \qquad\qquad (5.2)$$

$$r_{34} = r_{35} = 2g_{44}P_1\epsilon_{33}$$

$$r_{16} = r_{26} = 2g_{44}P_1\epsilon_{11}$$

In the ferroelectric phase, the dielectric stiffness χ_{33}^T is given by

$$\chi_{33}^T = 2\alpha_3 + 4\alpha_{13}P_1^2 \qquad . \qquad\qquad (5.3)$$

Because the longitudinal Curie temperature θ_3 is now close to θ_1 in compositions on the orthorhombic side but close to morphotropy, α_3 will be negative and increasing with decreasing temperature. The transition at T_c is, however, first order and thus P_1 is less than parabolic against T, so that χ_{33} will be small and decreasing with T. Thus, ϵ_{33} will be large and increasing with decreasing temperature, leading to large values of r_{13}, r_{34} and r_{35}.

5.2   Exploratory Measurements

A number of PBN crystals have been pulled with compositions increasingly rich in Ba. For a morphotropic composition, ceramic studies suggest that $T_c \simeq 260°C$.

In Fig. 13, dielectric data are shown for a poled single crystal region of a composition just in the orthorhombic stability region. It is evident that the transition temperature $T_c = 268°C$ is very close to the morphotropic value. The high value of K_c (the relative permittivity ϵ_{33}), is clearly evident, and the slow increase with decreasing temperature is also evident. The rather small difference between K_a and K_b (ϵ_{11} and ϵ_{22}) is unexpected and, if confirmed in future measurements, suggest an unusually small value for α_{12}.
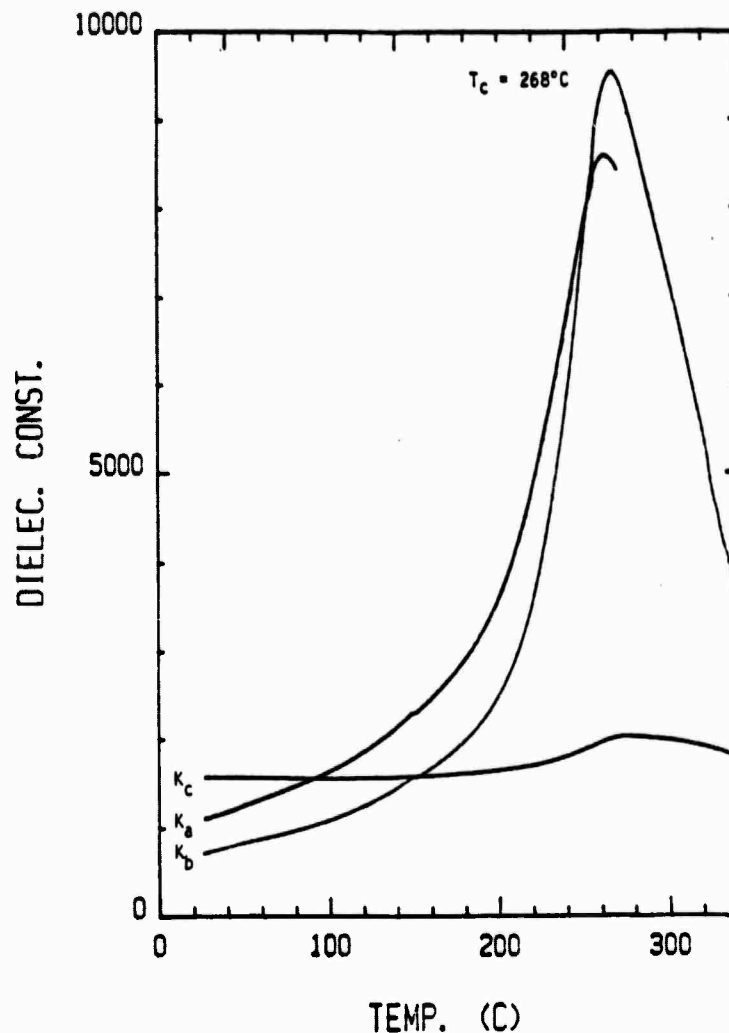
Fig. 13 K vs T measurements along the a, b, c axes of orthorhombic PBN (composition near the morphotropic boundary).

It was gratifying to find that even for compositions very close to the morphotropic boundary, we could find areas quite clear of ferroelastic 90° twins (Fig. 14) and, thus, that we will be able to make measurements of the full family of single domain dielectric, piezoelectric, elastic and electro-optic parameters. A clear confirmation of the quality of the crystal and of

the pure orthorhombic symmetry is given by the conoscopic figure taken in monochromatic NaD light, as shown in Fig. 15. Evidence of the weak biaxial character is as would be expected for a composition close to the MPB.

Current work is concerned with accumulating data upon the single domain properties of these orthorhombic compositions. We are making more detailed measurements of the r_{42} and r_{51} coefficients in tetragonal crystals with compositions just on the other side of the MPB, and also preliminary measurements to explore the possibility of forcing the phase change from orthorhombic to tetragonal by using high electric field applied along the crystallographic c-axis.
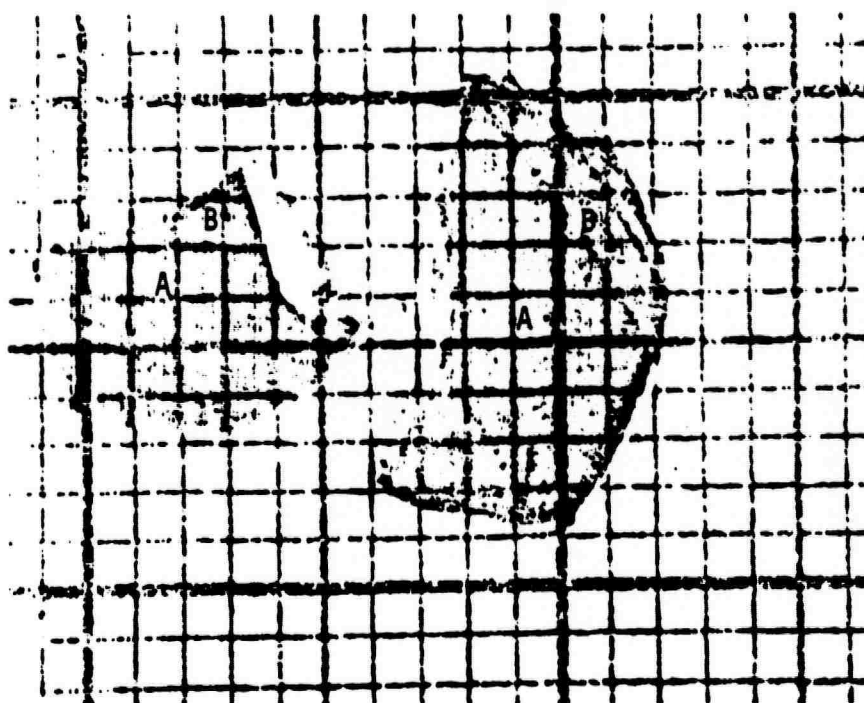

Fig. 14 PBN single crystals of composition near the morphotropic boundary. The large areas (A) are free of 90° domains, (B) show good optical quality of the crystals grown in the composition around $Pb_{0.6}Ba_{0.4}Nb_2O_6$.

Fig. 15 Optical conoscopic figure of orthorhombic PBN, c-plate.

6.0 EVALUATION OF THE PHOTOREFRACTIVE EFFECT IN DOPED AND UNDOPED SBN:60

6.1 Introduction

The effectiveness of undoped SBN:60, SBN-Fe^{3+} (1% by wt.) and SBN-Ce^{3+} (0.1% by wt.) as photorefractive media is studied here using the method of two-beam coupling. In particular, the absorption coefficient, the two-beam coupling coefficient, and the writing sensitivity of each crystal is determined, and then used to compare the materials with one another.

Consider the two-wave mixing experiment shown in Fig. 16. Beams 1 and 2 are plane waves which intersect in the crystal and thus form an intensity interference pattern. Charge is excited by this periodic intensity distribution into the conduction band, where it migrates under the influence of
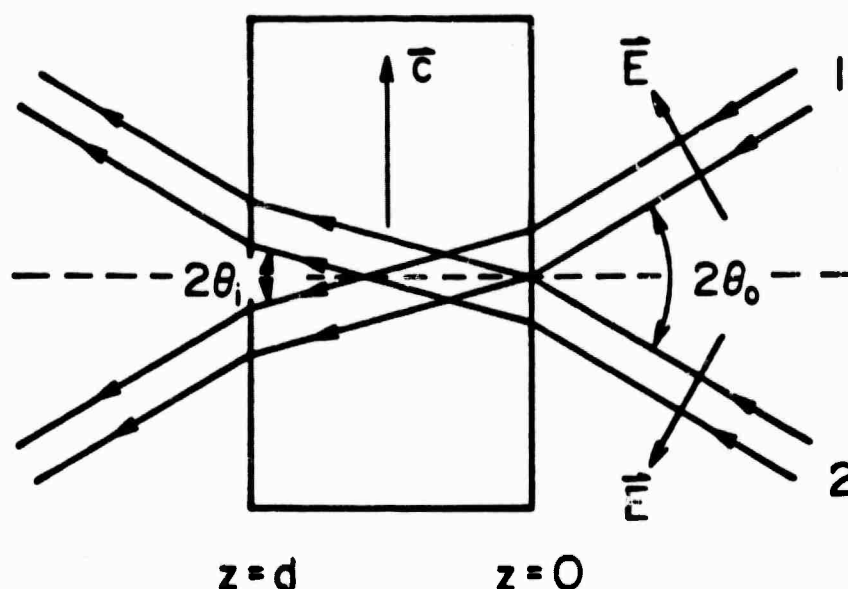

Fig. 16 Experimental setup for two-beam coupling experiments.

diffusion and drift in the internal electric field, and then preferentially recombines with traps in regions of low irradiance. A periodic space-charge is thus created which modulates the refractive index via the electro-optic effect. This index grating, being out of phase with the intensity distribut introduces an asymmetry that allows one beam to be amplified by const ive interference with light scattered by the grating, while the other beam is attenuated by destructive interference with diffracted light.

Mathematically, this two-beam coupling may be described in the steady-state as follows:

$$\frac{dI_1}{d\xi} = -\gamma \frac{I_1 I_2}{I_1 + I_2} - \alpha I_1$$

$$\frac{dI_2}{d\xi} = \gamma \frac{I_1 I_2}{I_1 + I_2} - \alpha I_2 \tag{6.1}$$

where I_1 and I_2 are the intensities of beams 1 and 2 inside the crystal, γ is the two-beam coupling coefficient, α is the absorption coefficient, and $\xi \equiv z/\cos\theta_i$, where $0 < \xi < \ell \equiv d/\cos\theta_1$. The transient behavior is modeled by

$$I_i(\xi;t) = (1-e^{-t/\tau})I_i(\xi;t \to \infty) + e^{-t/\tau}I_i(\xi;t = 0), \quad i - 1,2 \tag{6.2}$$

where τ is the characteristic time constant and $I_i(\xi;t \to \infty) \equiv I_i(\xi)$.

The solutions of the above coupled wave equations are

$$I_1(\ell) = \frac{[I_1(0) + I_2(0)] \, e^{-\alpha\ell}}{1 + \frac{I_2(0)}{I_1(0)} e^{\gamma\ell}}$$

$$I_2(\ell) = \frac{[I_1(0) + I_2(0)] \, e^{-\alpha\ell}}{1 + \frac{I_1(0)}{I_2(0)} e^{-\gamma\ell}} \tag{6.3}$$

Maximum coupling will, therefore, result in crystals with large γ, but small α. However, α and γ are not independent. In fact, since charge must first be excited into a conduction band by the intensity interference pattern in order to start the photorefractive process, some absorption is necessary. This is precisely where the role of the dopant enters. By purposely introducing impurities into the crystal, donor sites are created which become the absorption centers. It must be noted, however, that any absorption which does not contribute to the photorefractive mechanism is undesirable.

6.2   Photorefractive Measurements

Figures 17 and 18 show qualitatively the effect of Ce and Fe impurities on the absorption spectra of undoped SBN:60, whose spectra is given in Fig. 19. Several interesting observations can be made. For one, the band edge shifts from 400 nm in SBN to 430 nm in SBN-Ce and 500 nm in SBN-Fe. Secondly, although the SBN in Fig. 19 was not intentionally doped, there are signs of deep level impurities evidenced by perturbations in the spectra near 550 nm. Finally, the effects of Ce and Fe in SBN are seen to be significantly different. While the spectra of SBN-Ce is rather featureless with a broad deep level centered at 480 nm, the spectra of SBN-Fe displays a structured but otherwise broad absorption extending from 500 nm to 700 nm, with characteristic peaks at 500 nm and 590 nm. Future investigation of these lines will indicate whether or not they contribute to the photorefractive effect.

The final quantity of interest, the writing sensitivity W, defined by $W \equiv [I_1(0) + I_2(0)]\tau$, is a measure of the incident energy needed to produce the index grating. Since, in basic photorefractive theory, W is a constant, the writing sensitivity also serves, therefore, as an indicator of the speed of response of the crystal for arbitrary values of irradiance.
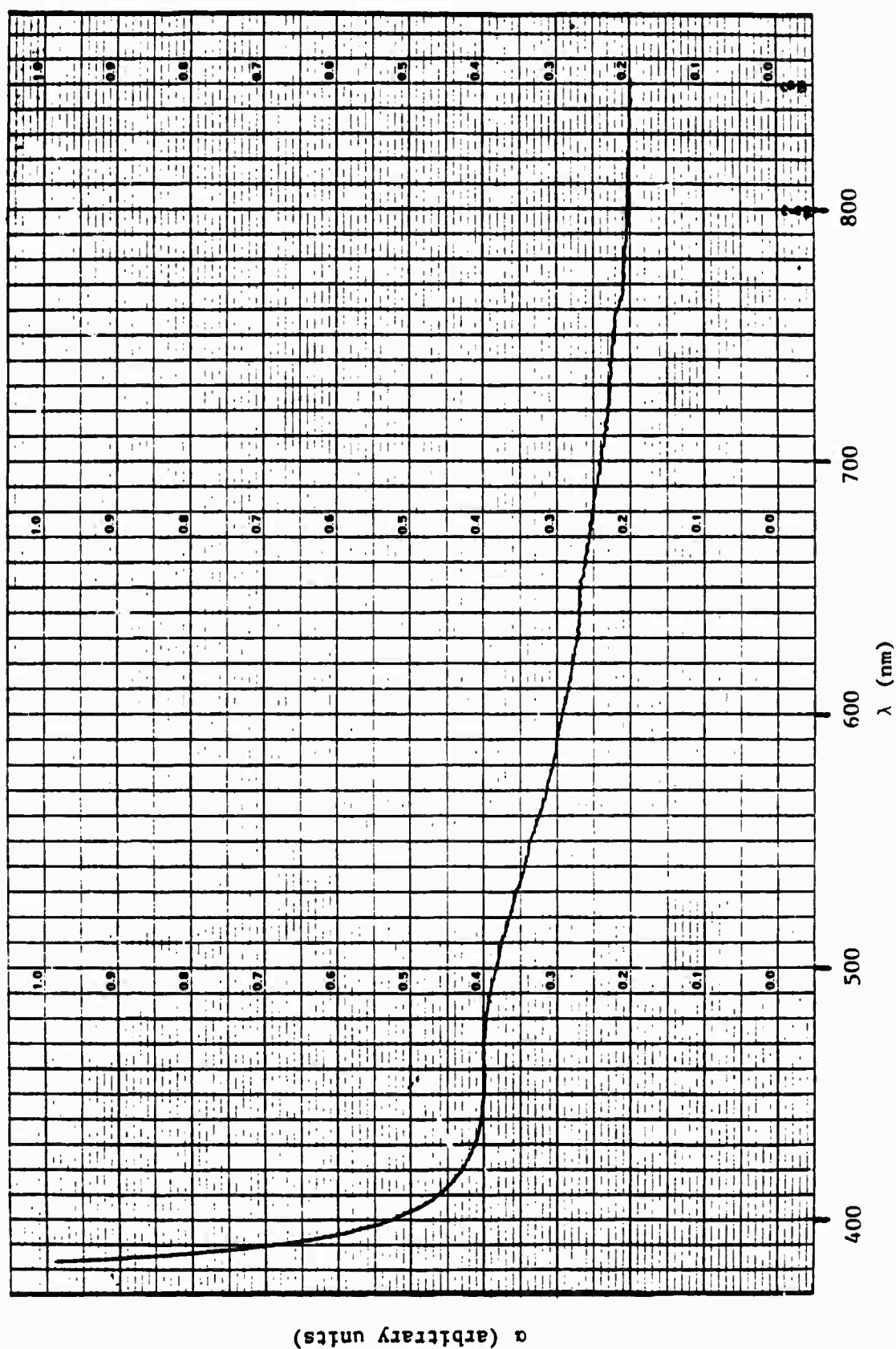
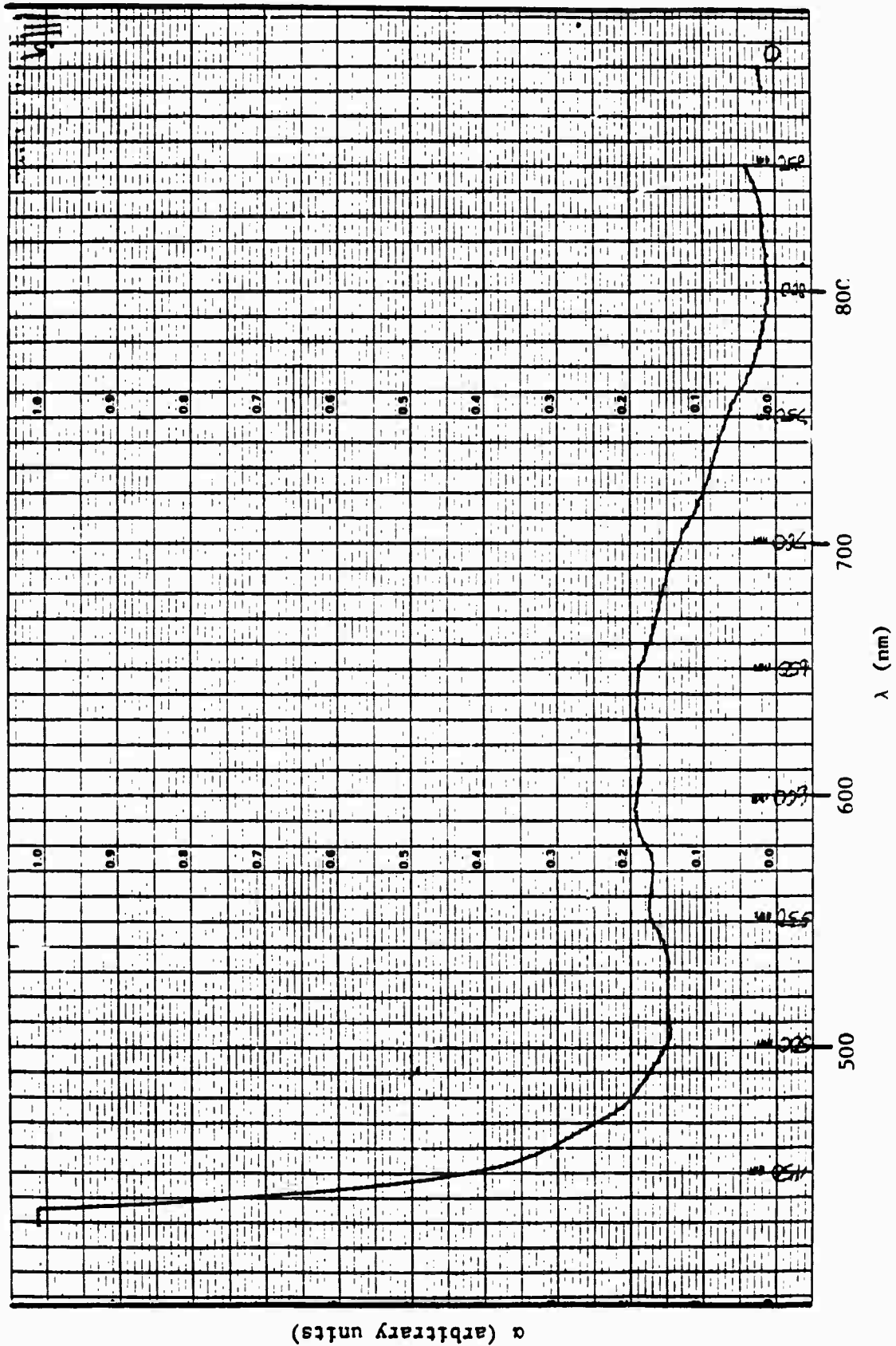Fig. 17 Absorption spectra of SBN:60-Ce (0.1%)

λ (nm)

α (arbitrary units)

Fig. 18 Absorption spectra of SRN:60-Fe (1.0%).

Fig. 19 Absorption spectra of SBN:60

λ (nm)

α (arbitrary units)

Table 9 summarizes the experimental results for the three materials. Unfortunately, the SBN:60-Fe crystal was excessively doped, which created striations that interfered with measurements of γ and α. Therefore, only the writing sensitivity was obtained, and was found to be about 25% larger than that of undoped SBN. However, this result should not be used to conclude that doping SBN with Fe results in a slower photorefractive materials, since the quality of the particular SBN-Fe crystal was lower than that of the other two crystals. A crystal with lower Fe content will probably render much better results.

The data in Table 9 indicate that the introduction of Ce into SBN:60 results in a crystal with a larger two-beam coupling coefficient and a better writing sensitivity. However, the absorption coefficient is affected negatively. This increase in absorption may, indeed, be unavoidable, since it probably contributes to the better values of γ and W. Also, future experimentation with the reduction ratio of SBN-Ce, i.e., the fraction of Ce^{3+} to Ce^{4+} in the crystal, may further increase the effectiveness of SBN-Ce as a photorefractive material.

Table 9

Optical Properties of Doped and Undoped
SBN:60 Crystals*

	SBN	SBN:Ce	SBN:Fe
$\alpha(cm^{-1})$	0.04	1.8	--
$\gamma(cm^{-1})$	3.0	11.0	--
$W(mJ/cm^2)$	122.0	101.0	152.0

* Experimental results for $2\theta_0 = 15°$, $\lambda = 5145A$, $I_1(0) + I_2(0) = 100$ mW/cm^2, $I_2(0)/I_1(0) = 2$

7.0 FUTURE PLANNED WORK

- Further refine and evaluate the growth of high purity single crystal SBN:60.

- Establish optimum concentrations of Fe and Ce dopants in SBN:60 necessary for improved photorefractive sensitivity and speed.

- Examine the dielectric and optical properties of SBN crystals doped with other cations.

- Establish SBN:75 LPE growth from the $SrO-BaO-Nb_2O_5-V_2O_5$ flux system.

- Continue development of the $BaV_2O_6-PBN:60$ and $Pb_{1-x}Ba_xV_2O_6-PBN:60$ flux system for LPE growth.

- Attempt single crystal growth of near-morphotropic BNN-SNN and PKN-BNN bronze compositions for dielectric, structural and optical evaluation.

- Continue measurement of the E-O coefficients of near-morphotropic single crystal PBN.

8.0 PUBLICATIONS AND PRESENTATIONS

8.1 Publications

1. R.R. Neurgaonkar, W.K. Cory and J.R. Oliver, "Growth and Applications of Ferroelectric Tungsten Bronze Family Crystals," Ferroelectrics 51, 3 (1983).

2. R.R. Neurgaonkar, J.R. Oliver and L.E. Cross, "Ferroelectric Properties of Tetragonal Tungsten Bronze Single Crystals," Ferroelectrics 56, 31 (1984).

3. T.R. Shrout, L.E. Cross and D.A. Hukin, "Ferroelectric Properties of Tungsten Bronze Lead Barium Niobate (PBN) Single Crystals," to be published in Ferroelectrics.

8.2 Presentations

1. R.R. Neurgaonkar, W.K. Cory and J.R. Oliver, "Growth and Applications of Tungsten Bronze Family Crystals," presented at the 1983 IEEE Int. Symp. on Applications of Ferroelectrics, June 1-3, 1983, Gaithersburg, MD.

2. R.R. Neurgaonkar, J.R. Oliver and L.E. Cross, "Growth and Application of Ferroelectric Tungsten Bronze Family Crystals," presented at the 5th European Meeting on Ferroelectrics, Sept. 26-30, 1983, Benalmadena, Spain.

3. T.R. Shrout, H.C. Chen and L.E. Cross, "Dielectric and Piezoelectric Properties of Tungsten Bronze Lead Barium Niobate ($Pb_{1-x}Ba_xV_2O_6$) Single Crystals," presented at the 5th European Meeting on Ferroelectrics, Sept. 26-30, 1983, Benalmadena, Spain.

4. J.R. Oliver and R.R. Neurgaonkar, "Ferroelectric Solid Solutions Based on the Tungsten Bronze Structure," presented at the 86th Annual Meeting of the Am. Ceram. Soc., April 30-18, 1984, Pittsburgh, PA (invited paper).

5. J.R. Oliver and R.R. Neurgaonkar, "Morphotropic Tungsten Bronze Solid Solutions," accepted for presentation at the 37th Pacific Coast Regional Meeting of the Am. Ceram. Soc., October 28-31, 1984, San Francisco, CA.

6. R.R. Neurgaonkar, W.K. Cory and J.R. Oliver, "Ferroelectric Tetragonal Tungsten Bronze Crystals for Optoelectronic Applications," accepted for presentation at the 37th Pacific Coast Regional Meeting of the Am. Ceram. Soc., October 28-31, 1984, San Francisco, CA.

9.0 REFERENCES

1. U.V. Voronov, I.R. Dorosh, Y.S. Kusiminov and N.V. Tkachenko, Sov. J. Quantum Electronics 10, 1346 (1980).

2. K. Megumi, H. Kozuka, M. Kobayashi and Y. Furuhata, Appl. Phys. Lett. 30, 631 (1977).

3. J.E. Geusic, A.J. Levenstein, J.J. Rubin, S. Singh and L.G. Van Uitert, Appl. Phys. Lett. 11, 269 (1967).

4. R.L. Barus, J. Appl. Cryst. 1, 290 (1968).

5. R.R. Neurgaonkar and L.E. Cross, Final Report (DARPA), Contract No. F49620-78-C-0093 (1982).

6. K. Nagata, T. Yamazaki and K. Okazaki, Proc. 2nd Int. Meeting on Ferroelectric Materials and Their Applications, 251 (1979).