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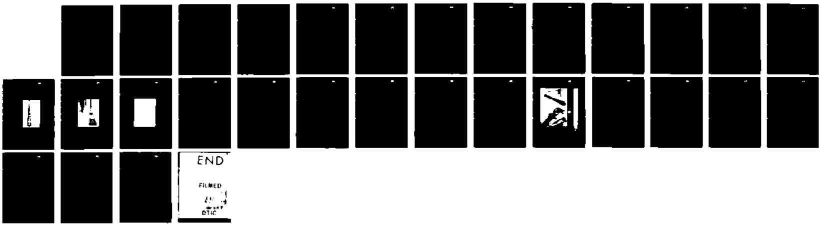

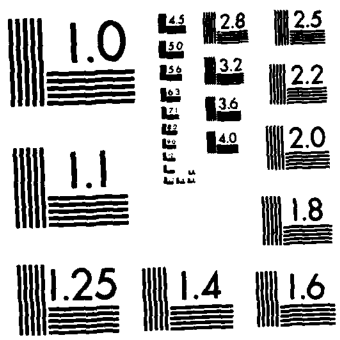

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SINGLE CRYSTAL GROWTH OF KLiNb FOR SAW APPLICATIONS

Final Report
For Period 06/30/81 through 06/29/82
February 1983

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

We have successfully demonstrated the growth of good quality, crack-free medium size KLN single crystals using the Czochralski method, with dielectric and piezoelectric properties comparable or superior to the best known bronze composition SBN. However, we have been unable to grow large (>1 cm diameter) KLN crystals suitable for SAW characterization without considerable cracking. Therefore, in pursuit of alternative

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) bronze compositions with the potential for large crystal growth, we have initiated work on the growth and characterization of PBN and the stuffed bronze BSKNN. Initial characterization work shows both of these materials to be very promising for future SAW device development, and good quality single crystals of BSKNN with >1 cm square cross-section have already been successfully grown. The physical properties of PBN and BSKNN also make them of interest for other piezoelectric, electro-optic, and nonlinear optic applications in addition to SAW devices.

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1.0 PROGRESS AND TECHNICAL SUMMARY

The purpose of this program has been to develop temperature compensated piezoelectric materials which possess high surface acoustic wave electromechanical coupling constants (K^2) with a sufficiently low temperature coefficient of SAW velocity. Concurrent with these requirements is the ability to grow good quality, large diameter single crystals appropriate to the requirements of SAW devices and characterization. As a result of our extensive research investigations in the tungsten bronze structural family, the bronze compositions $K_3Li_2Nb_5O_{15}$ (KLN), $Pb_{1-x}Ba_xNb_2O_6$ (PBN) and $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ (BSKNN) have been identified as the most promising candidates for this work. The goals in this program have been to (1) establish crystal chemistry control for each bronze composition; (2) establish single crystal growth of these bronze compositions by the Czochralski method; and (3) determine the piezoelectric and piezoelastic constants and the acoustical properties of these compositions.

Work has been done to establish the tungsten bronze KLN for surface acoustic wave applications. Phase equilibria studies on the ternary system K_2O-Li_2O-Nb_2O_5 have identified a suitable composition for the bulk single crystal growth work, and it has been shown that the composition corresponding to $K_{2.89}Li_{1.55}Nb_{5.11}O_{15}$ (as given by Adachi)[1] is suitable for crystal growth work. Czochralski growth has now been established and KLN single crystals of this composition as large as 5-10 mm in diameter and 30-40 mm long have been successfully grown along the a-axis. Many of these crystals are crack-free and of excellent quality. Low frequency dielectric measurements on these crystals show a well-defined peak in K_{33} at 408°C in excess of 550 for a frequency of 1 kHz. At room temperature, K_{33} is approximately 80 and shows no frequency dependence up to 100 kHz. The loss tangent was found to be roughly 0.02 independent of frequency and temperature below 408°C.

Although the growth of high quality KLN single crystals is a major accomplishment in this work, we have been unable to grow larger samples (up to 2 cm diameter) of this composition for SAW characterization because of severe cracking problems. However, initial results on the tungsten bronze

$Pb_{1-x}Ba_xNb_2O_6$ and the stuffed bronze $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ show both of these compositions to be extremely promising for future SAW device development, particularly in the case of BSKNN where we have already successfully grown good quality crystals of better than 1 cm square cross section.

2.0 TUNGSTEN BRONZE CRYSTAL GROWTH AND CHARACTERIZATION

2.1 Introduction

The aim of the present research work has been to establish a suitable class of tungsten bronze materials with good SAW electromechanical coupling constants K^2 and low temperature coefficient SAW velocities suitable for further surface acoustic wave device development.

In seeking new materials which have high dielectric constants, high coupling constants or possibly high electro-optic coefficients, it is important to look for families which originate from high prototype symmetry with the possibility for low temperature ferroelectric:ferroelastic phase transitions. In this regard, the tungsten bronze structural family is potentially important and hence it could be used as principal host material. The bronze compositions can be represented by general formulae $(A_1)_4(A_2)_2(B)_{10}O_{30}$ and $(A_1)_4(A_2)_2C_4(B)_{10}O_{30}$, in which A_1, A_2, C and B are 15, 12, 9 and 6-fold coordinated sites in the structure. Table 1 shows the structural transition and ferroic behavior of this family when different ions are substituted in the various crystallographic positions. This family embraces some 120 or more known compounds and various solid solution systems, and hence there is a good possibility of obtaining suitable compositions of the desired properties. Within this very extensive group, several members have high Curie temperatures, and have high dielectric, piezoelectric, electro-optic and pyroelectric coefficients.[1-12] According to recent work by Neurgaonkar et al.,[2,13] some of the bronze compositions such as $Sr_{1-x}Ba_xNb_2O_6$ possess temperature-compensated orientations and are potentially important for surface acoustic wave (SAW) device applications.

The composition $Sr_{0.61}Ba_{0.39}Nb_2O_6$ in particular shows an excellent SAW coupling coefficient K^2 of 180×10^{-4} and a low temperature coefficient of SAW velocity at room temperature.[2] However, recent modelling studies under DARPA Contract[13] have shown that these qualities can be substantially improved by selecting other bronze compositions with higher Curie temperatures than SBN. In particular, the compositions $K_3Li_2NB_5O_{15}$ (KLN), $Pb_{1-x}Ba_xNb_2P_6$ (PBN),

Table 1

The Structural Sequences and Ferroelectric Behavior of the Various Tungsten Bronze Phases

Compound	No. of Transitions	Transition Sequences
$K_3Nb_5O_{13}F_2$	None	4/mmm Paraelectric/Paraelastic
$Sr_2KNb_5O_{15}$ $K_3Li_2Nb_5O_{15}$ $Ba_6Ti_2Nb_8O_{30}$	One	4 mm Ferroelectric Ferroelastic → 4/mmm Paraelectric/Paraelastic
$Sr_2K_{0.5}Li_{0.5}Nb_5O_{15}$	One	mm2 Ferroelectric Ferroelastic → 4/mmm Paraelectric Paraelastic
$Pb_2KNb_5O_{15}$	One	mm2 Ferroelectric Ferroelastic → 4/mmm Paraelectric Paraelastic
$Sr_2KTa_5O_{15}$	Two	mm2 Ferroelectric Ferroelastic → mmm Paraelectric Ferroelastic → 4/mmm Paraelectric Paraelastic
$Pb_{2.7}K_{0.56}Nb_{0.91}$- $Ta_{4.15}O_{15}$	Two	mm2 Ferroelectric Ferroelastic → mmm Paraelectric Ferroelastic → 4/mmm Paraelectric Paraelastic
$Ba_2NaNb_5O_{15}$	Three	4mm Ferroelectric Paraelastic → mm2 Ferroelectric Ferroelastic → 4mm Ferroelectric Ferroelastic → 4/mmm Paraelectric Paraelastic
$Ba_{2.14}Li_{0.71}$- $Nb_{2.5}Ta_{2.5}O_{15}$	Three	4mm Antiferroelectric Ferroelastic → mm2 Ferroelectric Ferroelastic → 4mm Paraelectric Paraelastic → 4/mmm Paraelectric Paraelastic

and $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ (BSKNN), are similar to SBN but have much higher Curie temperatures and better piezoelectric properties. The present work on the growth and characterization of these materials is given in the following sections.

2.2 Bulk Single Crystal Growth of $K_3Li_2Nb_5O_{15}$

2.2.1 The System K_2O-Li_2O-Nb_2O_5

The KLN solid solution exists on the ternary phase diagram K_2O-Li_2O-Nb_2O_5 and, as shown in Fig. 1, this solid solution extends over a wide compositional range. This phase relation in this system has been studied by several workers[3,4] and, based on these investigations, it is clear that KLN single crystals with varying K:Li:Nb ratios can be grown. ("KLN" is the generally referred to name for the tungsten bronze solid solution within the compositional range shown in Fig. 1.) The Curie temperature shifts from 540° to 326°C as the Nb_2O_5 concentration changes from 0.50 to 0.55. Recently, Adachi et al.[1] studied the single crystal growth of the composition $K_{2.89}Li_{1.55}Nb_{5.11}O_{15}$ and reported the successful growth of this composition (8-10 mm in diameter) and that the crystals showed excellent piezo-elastic properties. Since this result seemed to be promising for this work, the composition $K_{2.89}Li_{1.55}Nb_{5.11}O_{15}$ was chosen, and single crystals have been grown by the Czochralski technique from both iridium and platinum crucibles with successful results. For iridium crucibles, argon pressure had to be used to prevent loss of iridium, and as-grown crystals were found to be purple or coal black in color. However, the color changed to deep yellow when the crystals were subsequently annealed in oxygen above 800°C. Very low oxygen pressure was directly used when the platinum crucible was used as a container for the growth work; crystals thus obtained were pale yellow in color. Since the lattice mismatch between $Sr_2KNb_5O_{15}$ (a = 12.47A and c = 3.947A) and KLN bronze compositions is minimal, $Sr_2KNb_5O_{15}$ single crystals were used in the initial growth experiments as seed material. After achieving reasonable size KLN crystals, the KLN crystal itself was used as seed material in the subsequent experiments. This proved to be very successful, and crack-free KLN single crystals as large as 5-10 mm in diameter and 30-40 mm long have been successfully grown along the (100) direction. Figures 2-4 show the typical

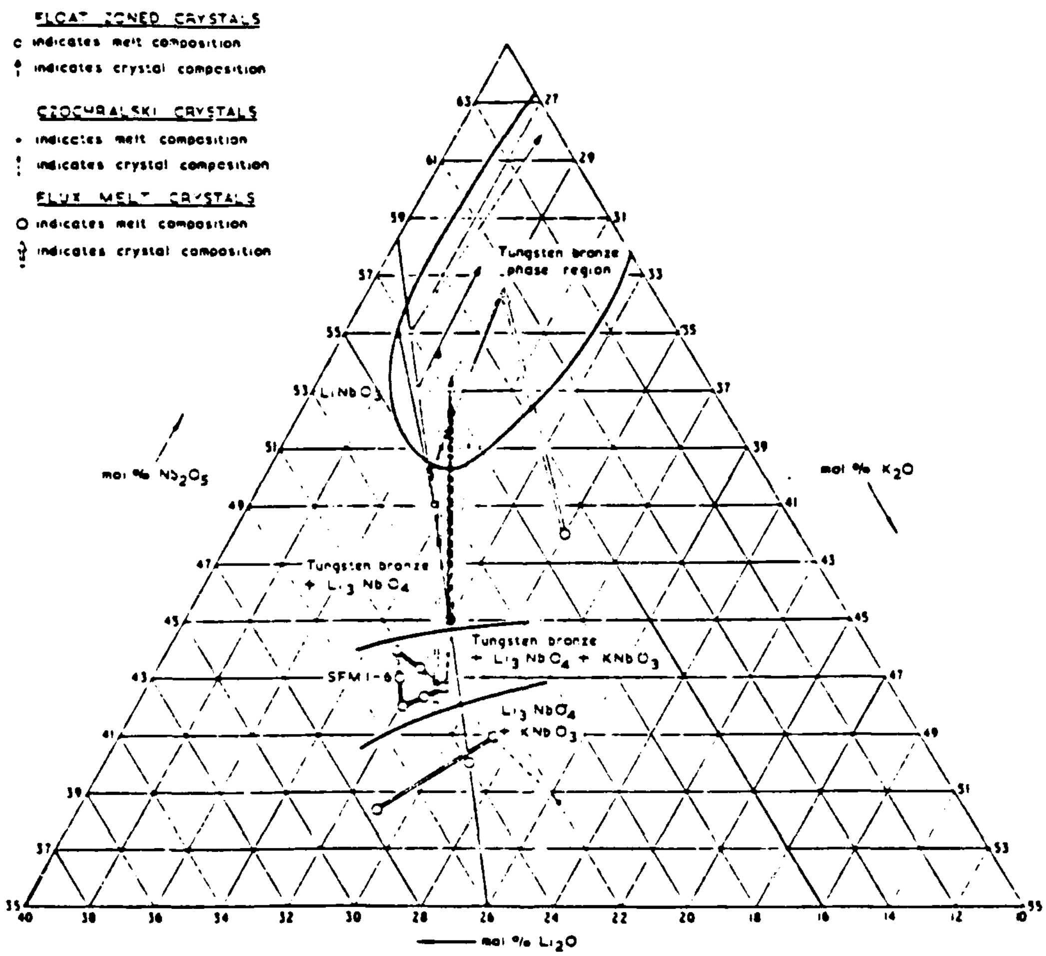

Fig. 1 Partial phase diagram of Li_2O-K_2O-Nb_2O_5 system in region of tungsten bronze field. (a) Float zone crystals, (b) Czochralski crystals, and (c) flux melt crystals.

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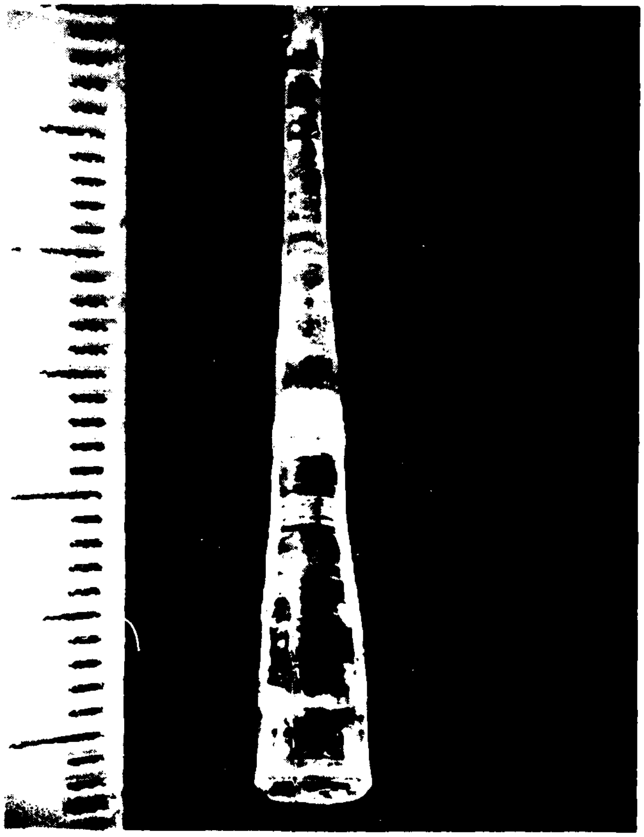

Fig. 2 Potassium lithium niobate $K_3Li_2Nb_5O_2$ single crystal grown along the (100) direction, 6-7 mm in diameter.

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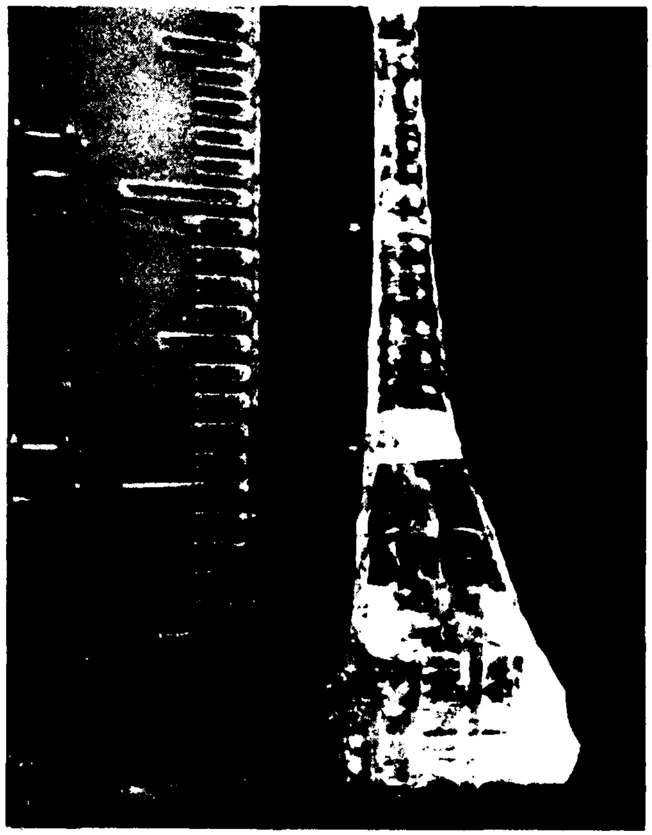

Fig. 3 Potassium lithium niobate $K_3Li_2Nb_5O_{15}$ single crystal grown along the (100) direction, 10-11 mm diameter.

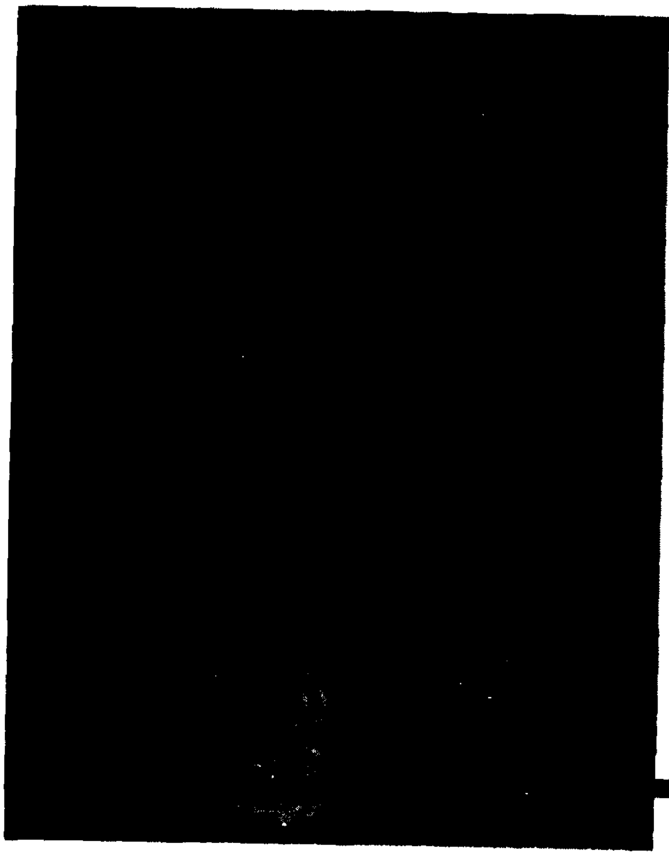

Fig. 4 $K_3Li_2Nb_5O_{15}$ single crystal grown along the (100) direction, 3 mm in diameter.

crystals grown along the (100) direction. In the course of this study, it was clearly observed that the rate of crystallization along the c-axis was much faster than those along any other directions; the crystals, however, cracked when grown along the c-axis. This cracking problem was nearly eliminated when the crystals were grown along the a-axis and such crystals are of excellent quality. Optimum growth conditions were found to be as follows:

Pulling Rate:	2-3 mm/hr
Rotation Rate:	20-30 rpm
Growth Direction:	Along the a-axis
Growth Temperature:	1000°C

Table 2 summarizes the physical constants obtained for KLN single crystals grown along different crystallographic orientations. The single crystal growth of KLN compositions has also been studied and reported by various other workers[3-12] and the results of this investigation are in close agreement with their findings. Although the KLN crystals obtained in the present work have been sufficiently large to initiate characterization studies, we have done considerable additional work on the Czochralski growth technique in an attempt to obtain larger diameter, crack-free crystals. Based on our on-going research work on tungsten bronze family single crystals, it has been found that the growth of large-sized crystals depends strongly on the ability to control the diameter of the crystal and the thermal gradient in the crystal near the solid-liquid interface. However, in the case of KLN, we have not been able to grow crystals of >1 cm diameter without considerable cracking.

2.2.2 Physical Properties of KLN Crystals

Low-frequency dielectric measurements for KLN single crystals are very relevant to selecting appropriate compositions for future surface acoustic wave and other important device applications. The dielectric properties were determined by measuring the temperature dependence of capacitance over the temperature range -50°C to 500°C. Crystals used for these measurements were approximately 1 mm in thickness with aluminum electrodes deposited

Table 2

Growth Conditions for Tungsten Bronze $K_3Li_2Nb_5O_{15}$ Single Crystals

Composition	Diameter of Crystal	Growth Direction	Crystal Quality	Curie Temp (°C)	Dielectric Constant, K_{33}	Lattice a_A	Constant c_A
$K_3Li_2Nb_5O_{15}$	5-8 mm	(100)	Excellent	408	105	12.585	4.015
$K_3Li_2Nb_3O_{15}$	10-11 mm	(100)	Few Cracks	408	105	12.585	4.015
$K_3Li_2Nb_5O_{15}$	2-4 mm	(001)	Excellent	408	550	12.585	4.015
$K_3Li_2Nb_5O_{15}$	5-6 mm	(001)	Cracked	---	---	12.585	4.015
$K_3Li_2Nb_5O_{15}$	5-7 mm	(110)	Excellent	408	---	12.585	4.015

on both sides. The dielectric measurements were performed using three different frequencies, i.e., 1, 10 and 100 kHz, and results of these measurements are in close agreement with the results reported by Adachi et al,[1] except for the dielectric constant K_{33}. As summarized in Table 2, K_{33} peaks above 5.5×10^2 at the Curie temperature of 408°C; in general, the value of K_{33} will vary to a great extent with the amount of K and Li in the crystal. Above the Curie temperature, a Curie law functional relationship, $K_{33} = C/(T-T_c)$, is found to hold for the crystals measured, with C in the range $4\text{-}5 \times 10^2$ °C. A summary of the key piezoelectric and electromechanical coupling coefficients for this material is given in Table 3.

Optically, the KLN single crystals are of excellent quality, clear and transparent. Crystals showed room temperature tungsten bronze tetragonal structure and, according to structural refinements for this family, this composition belongs to the poing group 4 mm. Lattice parameter measurements for the ceramic and single crystal samples of the present composition from X-ray powder diffraction data give values a = 12.585Å and c = 4.015Å, which are in close agreement with values reported by Adachi et al. for this composition.[1]

2.3 Other Tungsten Bronze Materials

2.3.1 $Pb_{1-x}Ba_xNb_2O_6$ Single Crystal Growth and Characterization

In pursuit of alternative compositions to KLN with the potential for large size, good quality single crystal growth, we have initiated the growth of the tungsten bronze composition $Pb_{1-x}Ba_xNb_2O_6$ (PBN). Single crystal growth of this composition at Penn State University was again by the Czochralski method, with the initial aim of obtaining crystals of sufficient size (5-8 μm diameter) and quality to characterize the dielectric and piezoelectric properties. The various compositions grown to date are indicated by the open circles in the phase diagrams of Fig. 5. In order to obtain suitable samples, it was necessary to enhance the PbO content of the melt, and in each case the final composition was determined by chemical analysis from the tip and the base of the boule.

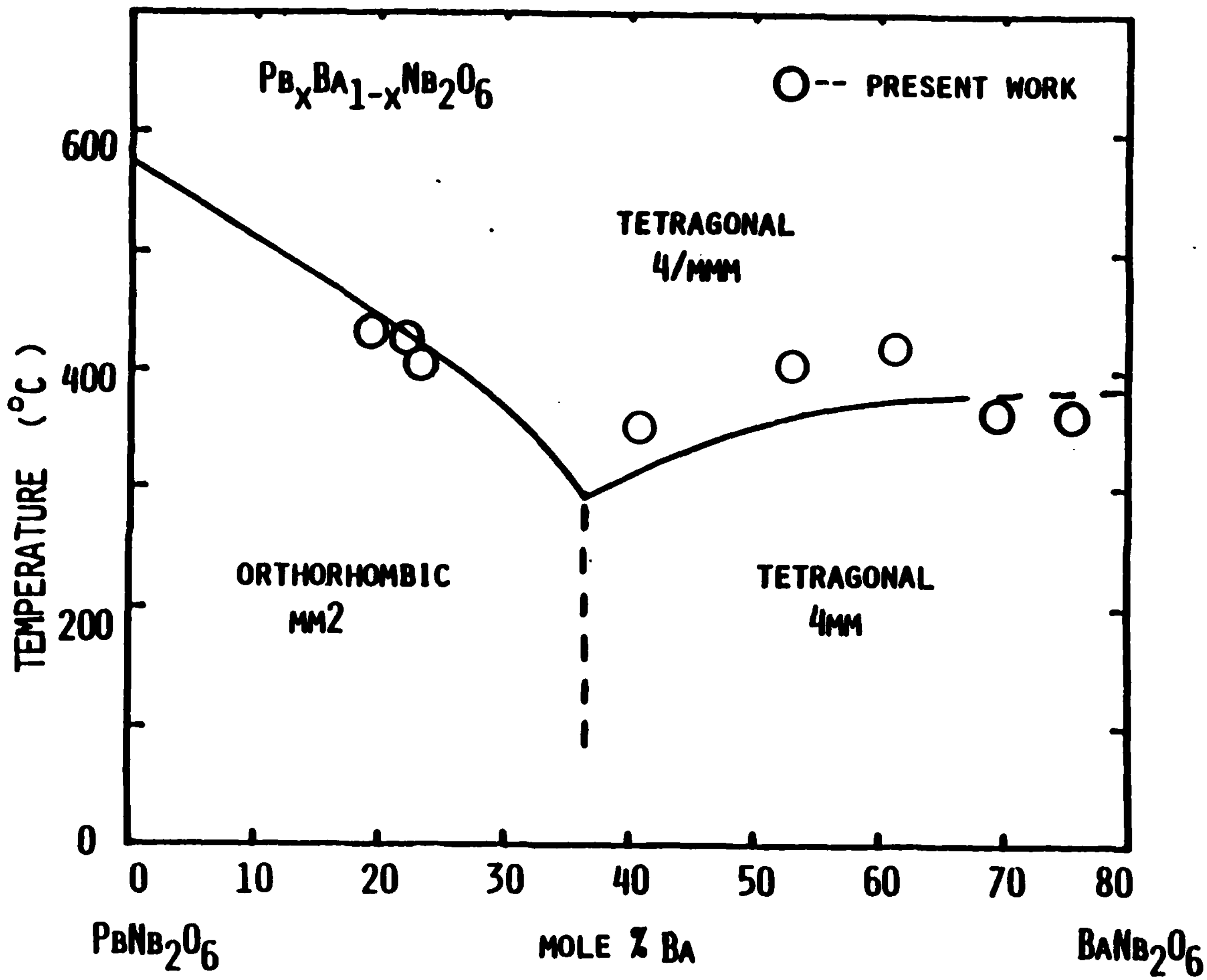

Fig. 5 Phase diagram for ferroelectricity in the solid solution system $Pb_xBa_{1-x}Nb_2O_6$.

Table 3

Piezoelectric Properties of the Tungsten Bronze Compositions

Property	PKN	SBN	KLN	SKN	PBN	BSKNN
Curie Temp (°C)	460	72	408	156	345	203
Dielectric Constant, K_{33}, at Room Temp.		800	80	1200	200	285
Coupling Coefficient						
k_{15}	0.69	0.13	0.35	0.12	----	0.28
k_{31}	----	0.14	0.18	0.15	0.22	----
k_{33}	----	0.47	0.54	0.44	0.55	0.47
k_{24}	0.73	----	----	----	----	----
Piezoelectric Stress Coefficient (c/m^2)						
e_{33}	6.90	4.30	5.50	8.0	----	----
e_{15}	14	2.0	4.6	4.3	----	----
e_{24}	15	----	----	----	----	----
Piezoelectric Strain Coefficient (1×10^{-12} C/N)						
d_{31}	-1.3	-30.0	-14.0	-11.0	-57	----
d_{33}	6.2	130	57	80	110	----
d_{15}	470	31	68	35	250	----
d_{24}	470	----	----	----	----	----
Temperature Coefficient, of SAW Velocity	Y-cut, +25 ppm	Z-cut, 0 ppm at -20°C	----	----	----	----
	Z-cut, -30 ppm	X-cut, 0 ppm at 15°C	----	----	----	----
References	5,6	2,13	1,3-12	14	13	

Compositions:

PKN = $Pb_2KNb_5O_{15}$

SBN = $Sr_{0.6}Ba_{0.4}Nb_2O_6$

KLN = $K_3Li_2Nb_5O_{15}$

SKN = $Sr_2KNb_5O_{15}$

PBN = $Pb_{0.6}Ba_{0.4}Nb_2O_6$

BSKNN = $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$

Concurrent theoretical modelling work on this material[13] has predicted very high values of ε_{11} and d_{15} for tetragonal PBN near the morphotropic phase boundary between the tetragonal and orthorhombic ferroelectric forms. This has been verified by dielectric and piezoelectric measurements on PBN crystals in this composition region, with the best results being for the tetragonal $Pb_{0.60}Ba_{0.40}Nb_2O_6$ composition, as given in Table 3. The coupling coefficients and piezoelectric strain coefficients for this composition are seen to be comparable to or better than those for KLN.

$Pb_{0.60}Ba_{0.40}Nb_2O_6$ belongs to the point group 4 mm, with lattice constants $a_{Å} = 12.49$ and $c_{Å} = 3.99$ as determined from x-ray diffraction measurements. We are continuing our efforts to grow large diameter (>1 cm) crack-free single crystals for this bronze composition for SAW device characterization. However, an attractive alternative for this material is liquid phase epitaxial growth on SBN substrates, which has a good lattice match to this PBN composition. We have already demonstrated the successful use of LPE growth to produce high quality simple or complex tungsten bronze compositions for SAW devices on 1.5-2 cm diameter SBN substrates, and therefore work on the epitaxial growth of PBN would appear to be of great interest in the future.

2.3.2 $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ Single Crystal Growth and Characterization

In addition to the work on KLN and PBN, we have initiated the single crystal growth and characterization of the stuffed bronze $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ (BSKNN). Good quality, medium-sized (1 cm square) crystals of the composition $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ have been successfully grown using the Czochralski method; an example of one such growth is shown in Fig. 6. Crystal growth is found to occur most rapidly along the c-axis with the resulting boule showing four well-defined facets parallel to the growth direction. This is a unique property of this large unit cell structure and it contrasts with the 24 facet growths typically found in smaller unit cell tungsten bronze materials. The present growth conditions for this material are as follows:

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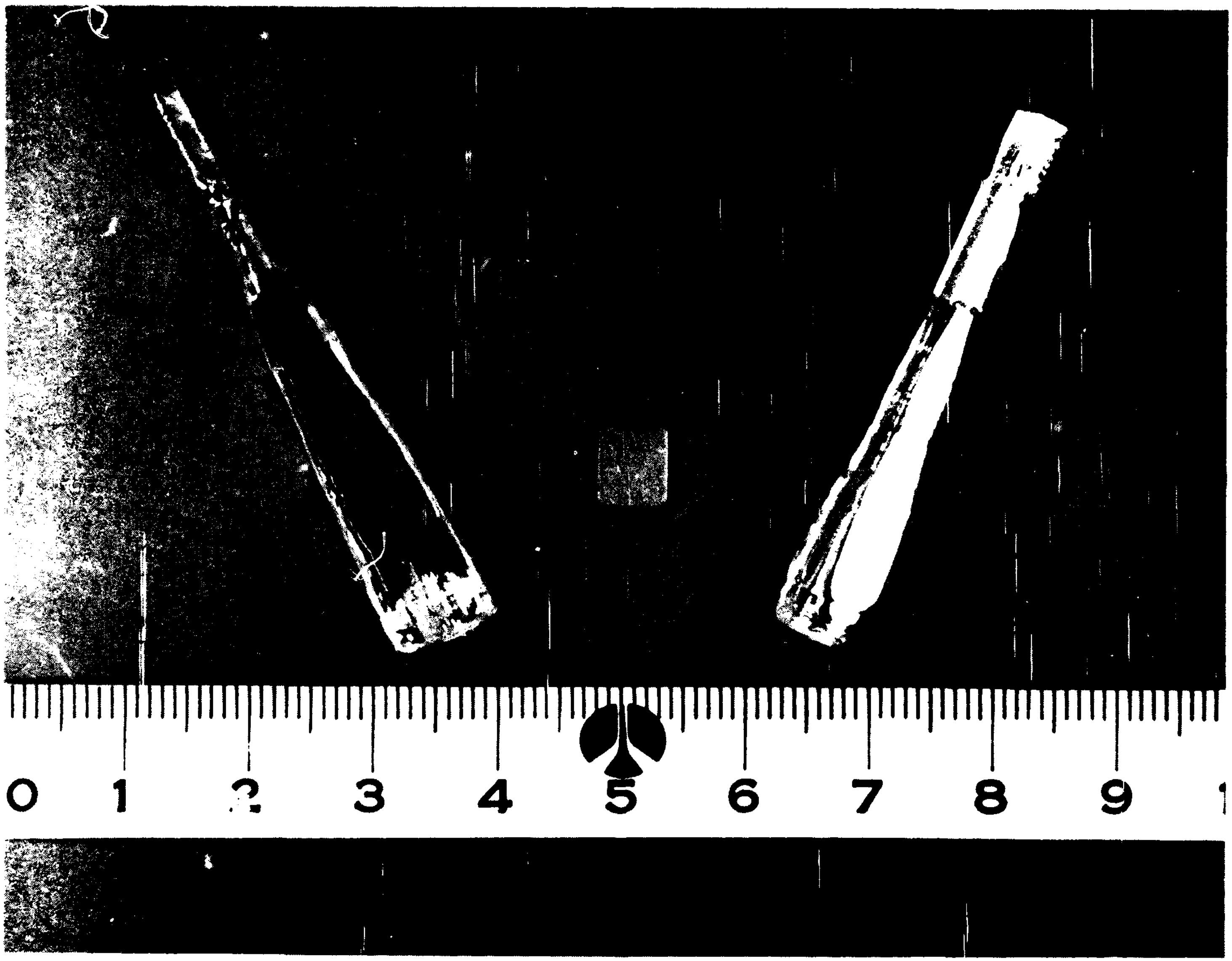

Fig. 6 $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.15}Nb_5O_{15}$ single crystal grown along the (001) direction, 10 mm in diameter.

Pulling Rate:	6-8 mm/hr
Rotation Rate:	5 rpm
Growth Direction:	Along the c-axis
Growth Temperature:	1480°C

All of the $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ crystals to date have been grown using a platinum crucible with an oxygen atmosphere. The resulting crystals are optically transparent and essentially colorless in appearance.

Dielectric measurements as a function of temperature and frequency (1 kHz-1 MHz) have been performed on (100) and (001) oriented single crystals of BSKNN using sputtered platinum electrodes; the results of these measurements are shown in Figs. 7 and 8. The Curie temperature T_c for the $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ composition was found to be 203°C for both the (100) and (001) orientations, with a maximum dielectric constant value of greater than 18,000 at T_c for the (001) direction. Although the Curie temperature for this material is greater than that for SBN:60, it is substantially less than that for KLN. However, dielectric measurements on BSKNN sintered ceramics for Sr_x contents of $0.7 < x < 0.9$ show that T_c increases with decreasing Sr content, and that the Curie temperature is also affected by the ionic site preference between the 12- and 15-fold coordinated sites in the lattice. Further research into this area is currently in progress.

Powder x-ray diffraction data for this material show a tetragonal structure with lattice constants $a_Å = 12.51$ and $c_Å = 3.975$ for the $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ composition. Congruent melting was found over the range of Sr_x composition $0.7 < x < 0.9$ examined thus far.

The electromechanical coupling coefficients k_{33} and k_{15} were evaluated for the $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ composition using platinum electrodes. Single crystal samples were initially poled along the (001) axis in an oil bath at 165°C, but indications were that the samples were not completely poled at this temperature. However, poling <u>in air</u> at fields up to 7.5 kV/cm at temperatures beginning slightly above T_c give very encouraging results for k_{15} and k_{33}; these are summarized in Table 3.

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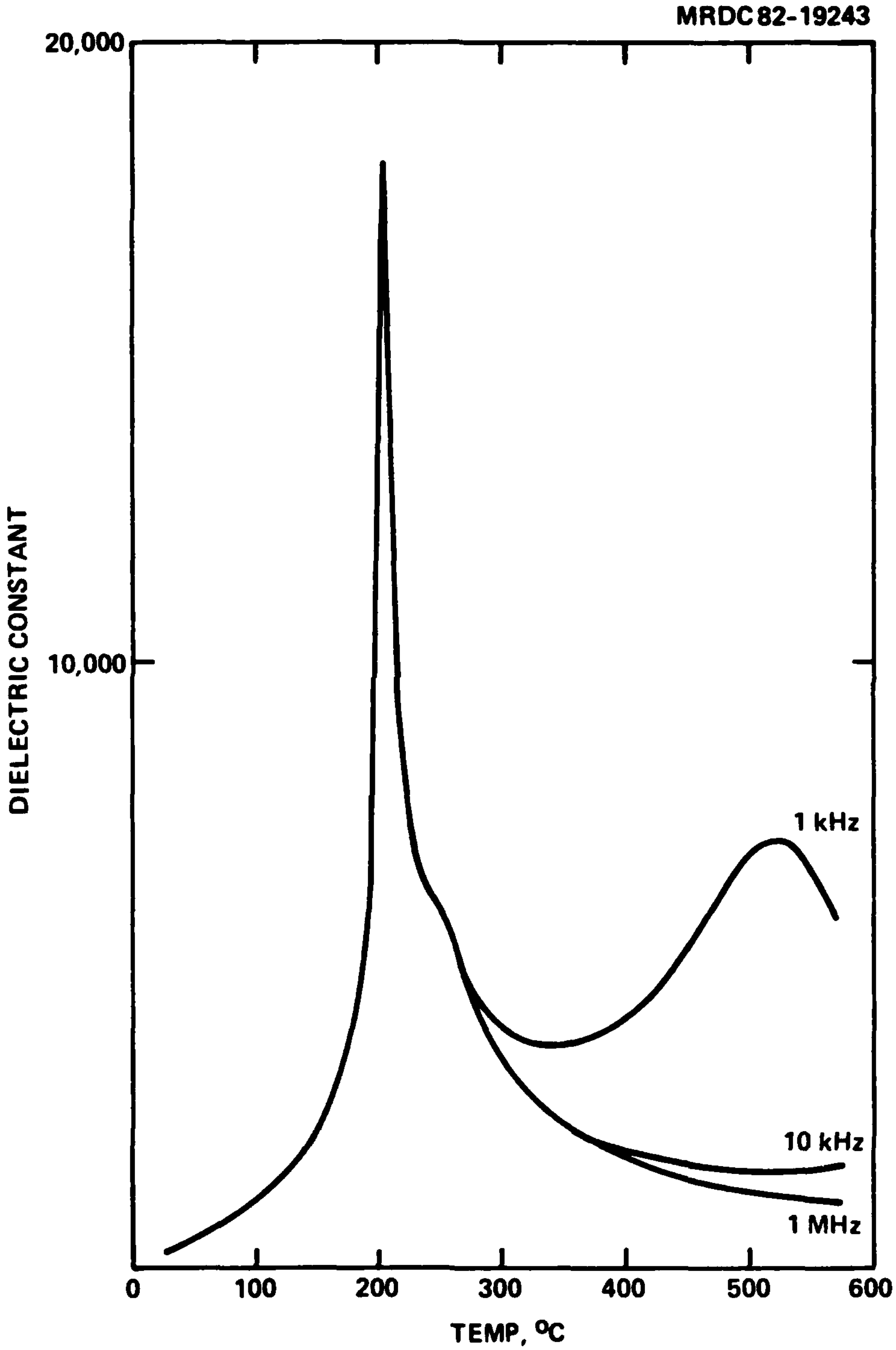

Fig. 7 Dielectric constant vs temperature for $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ single crystal, measured along (001) axis.

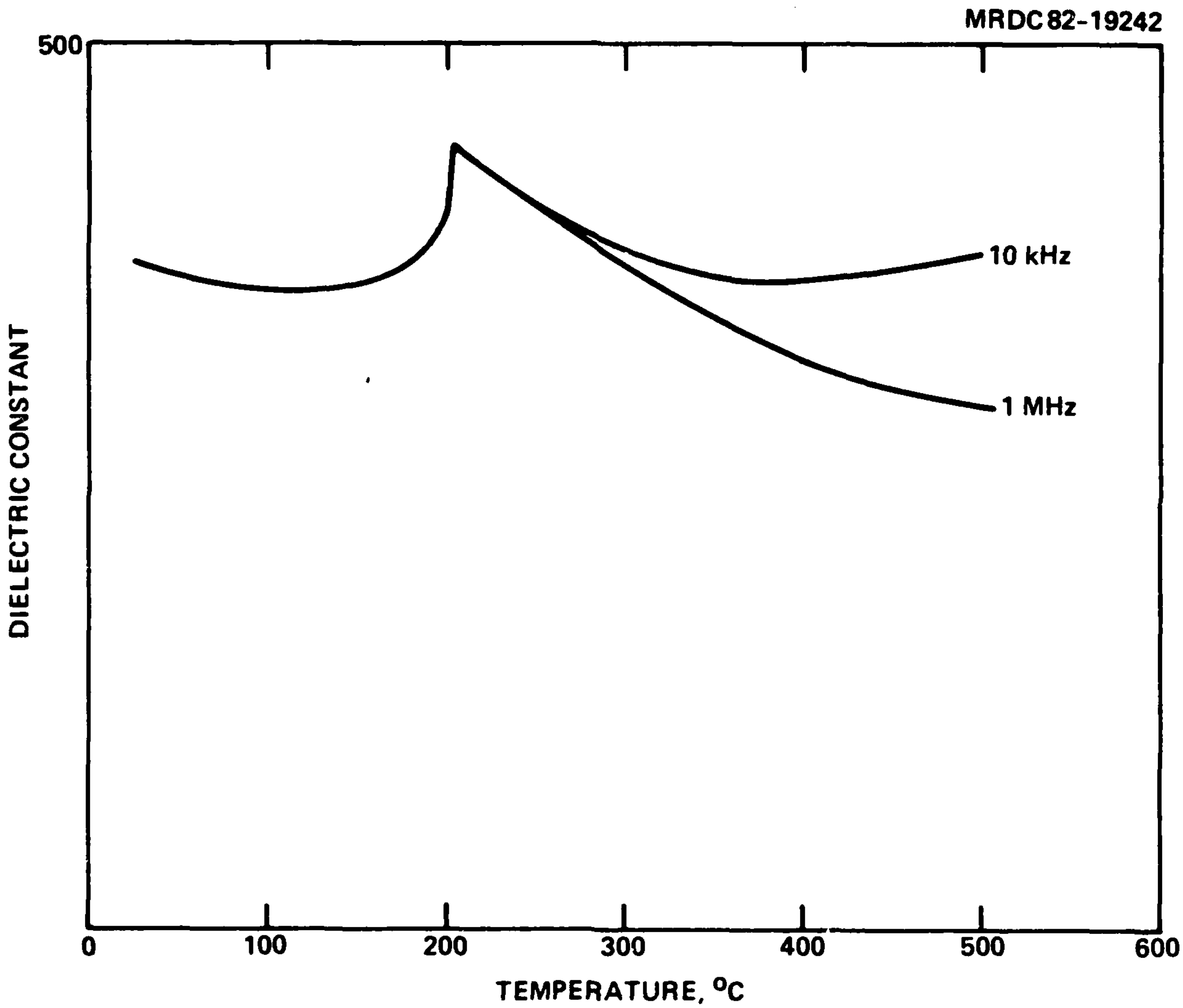

Fig. 8 Dielectric constant vs temperature for $Ba_{1.2}Sr_{0.8}K_{0.75}Na_{0.25}Nb_5O_{15}$ single crystal, measured along (100) axis.

We are continuing our research into the crystal chemistry and growth of the stuffed bronze BSKNN, and anticipate further improvements in crystal quality and size, and the electromechanical, dielectric, optical, and piezoelectric properties of this very promising material. The excellent piezoelectric and optical properties of BSKNN should find considerable interest in a number of device application areas in addition to SAW devices, including electro-optic, pyroelectric, acoustic-optic and millimeter wave applications.

3.0 SUMMARY

During the course of this work, we have successfully demonstrated the growth of good quality, crack-free medium size KLN single crystals using the Czochralski method. Although the dielectric and piezoelectric properties of this material show it to be comparable or superior to the best known bronze composition SBN, we have been unable to grow large (>1 cm diameter) KLN crystals suitable for SAW characterization without considerable cracking. Therefore, in pursuit of alternative bronze compositions with the potential for large crystal growth, we have initiated work on the growth and characterization of PBN and the stuffed bronze BSKNN. Initial characterization work shows both of these materials to be very promising for future SAW device development, and good quality single crystals of BSKNN with >1 cm square cross section have already been successfully grown. The physical properties of PBN and BSKNN also make them of interest for other piezoelectric, electro-optic, and nonlinear optic applications in addition to SAW devices. Furthermore, the excellent lattice match of these materials to a number of other tungsten bronze compositions make PBN and BSKNN potentially useful as substrate material for the liquid phase epitaxial growth of thin film bronze compositions which cannot otherwise be easily grown in single crystal form. We are continuing our efforts in the growth and characterization of large dimeter, crack-free single crystals of PBN and BSKNN, and anticipate that both of these bronze compositions will find interest in a number of these device application areas in the future.

4.0 PUBLICATIONS

1. R. R. Neurgaonkar, W. K. Cory, and J. R. Oliver, "Single Crystal Growth and Piezoelectric Properties of Tungsten Bronze $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ Crystals," to be submitted to Mat. Res. Bull.

2. R. R. Neurgaonkar, J. R. Oliver and W. K. Cory, "Single Crystal Growth and Piezoelectric Properties of $K_3Li_2Nb_5O_{15}$ Crystals," to be submitted to Mat. Res. Bull.

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