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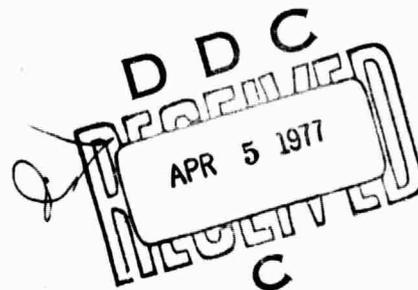TEMPERATURE COMPENSATED
PIEZOELECTRIC MATERIALS

Materials Research Laboratory
The Pennsylvania State University

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AIR FORCE SYSTEMS COMMAND
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Project Engineer: Paul H. Carr (617) 861-2527

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G. R. Barsch and K. E. Spear are the co-principal investigators for this contract. Paul H. Carr (ETEM), is the RADC/ETEM Project Engineer.

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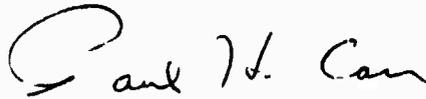
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In order to search for new temperature compensated materials for surface acoustic wave (SAW) devices with low ultrasonic attenuation and high electro-mechanical coupling, the following experimental and theoretical investigations were carried out:

(i) Extensive crystal growth investigations were carried out for →

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$Pb_2KNb_5O_{15}$, Li_2SiO_3, $Ba_2Si_2TiO_8$, $Ba_2Ge_2TiO_8$, and Bi_2MoO_6, using Czochralski or flux-pulling methods. Progress in reducing the cracking problem was made by improved temperature control during growth and subsequent cooling, and by reducing variations in the diameter of the boule during growth. Except for $LiSiO_3$, millimeter size or larger specimen of fair to good quality have been obtained.

(ii) The ferroelectric transition temperature and the lattice parameters have been studied for the system $xK_2O + yPbO + zNb_2O_5$ in the vicinity of the stoichiometric composition corresponding to $Pb_2KNb_5O_{15}$, and the possible implications for the composition dependence of the elastic, thermoelastic and piezoelectric constants and for attaining large electromechanical coupling factors with temperature compensated cuts are discussed.

(iii) The two piezoelectric constants of $AlPO_4$ are presently being measured by the x-ray method.

Acknowledgments

The authors would like to thank their collaborators for their participation in this work: Dr. L. Drafall for most of the crystal growth work, Mr. W. B. Regnault for the crystal growth and the elastic constant measurements on lead potassium niobate, and Dr. Z. P. Chang for the X-ray determination of the piezoelectric constants.

TEMPERATURE COMPENSATED PIEZOELECTRIC MATERIALS

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1. Technical Summary

1.1 Technical Problem

The objective of the research of this contract is to find temperature compensated materials for use in surface acoustic wave (SAW) signal processing devices, i.e. materials with large electromechanical coupling, low ultrasonic attenuation and a vanishingly small temperature coefficient of the delay time. The electromechanical coupling factor should be substantially larger than for α-quartz, which is presently used in temperature compensated SAW devices.

1.2 Methodological Approach

The research consists of: (A) both exploratory and systematic crystal growth studies on a variety of materials which are expected to be temperature compensated for bulk waves and which have been selected earlier under AFCRL Contract F19628-73-C-108 on the basis of certain heuristic criteria (Barsch and Newnham, 1975), and (B) measurements of the single crystal elastic and thermo-elastic properties of the above grown crystals to determine whether they possess temperature compensated crystallographic directions for bulk waves, and measurements of their piezoelectric and dielectric constants and their corresponding temperature coefficients to check the suitability of these materials for surface wave device applications.

1.3 Technical Results

1.3.1 Crystal Growth

The crystal growth effort focussed on lead potassium niobate ($Pb_2KNb_5O_{15}$), lithium metasilicate (Li_2SiO_3), fresnoite and derivatives ($Ba_2Si_2TiO_8$), and bismuth molybdate (Bi_2MoO_6). Czochralski pulling or flux-pulling techniques were used in all experiments. The research on lead potassium niobate was reactivated following interesting property measurement results. The earlier problem of cracking in the crystal boules is now being attacked by increasing temperature stability during

both growth and cooling cycles, and by attempting to maintain a constant boule
diameter to reduce thermal shock. With lithium metasilicate, the problems of
supercooling of the melt and cracking of the boules still persisted after using
modified growth configurations. Since the short term success in growing good
crystals appeared unlikely, further work on this system has been stopped for the
present time. X-ray data on $Ba_2Ge_2TiO_8$ indicate its symmetry is monoclinic rather
than orthorhombic, and x-ray and hot-stage microscopic studies show that the as
grown boules contain microtwins which would require strain-annealing in attempts
to obtain suitable specimens for the ultrasonic measurements of elastic constants.
Therefore, crystal growth efforts on these materials has also been terminated in
order to focus attention on other materials which appear to promise a more rapid
payoff. Crystal growth experiments were initiated on bismuth molybdate (Bi_2MoO_6)
during this reporting period. Its peritectic melting behavior required using a
flux-pulling method with MoO_3-rich solutions. Although cracking has been a problem
as with the other oxide crystals, special efforts to maintain stable thermal con-
ditions during growth and cooling resulted in obtaining crack free sections of
2 to 3 mm across and about 3 mm long.

1.3.2 Measurement of Elastic, Thermoelastic, Piezoelectric and Dielectric Properties

The ferroelectric transition temperature and the lattice parameters were
investigated experimentally as a function of composition in the pseudoternary
system x K_2O + y PbO + z Nb_2O_5 (x + y + z = 1) in the vicinity of the stoichio-
metric composition of lead potassium niobate, $Pb_2KNb_5O_{15}$. Significant variations
were found which suggest that the elastic, thermoelastic, piezoelectric and
dielectric properties could also show a strong composition dependence. This would
explain the discrepancies in the data for the elastic and thermoelastic constants
reported by us (Barsch and Spear, 1976) and those of Nakano and Yamada (1975).
It would further offer the possibility of finding temperature compensated directions

and large electromechanical coupling factors over a whole composition range, thereby increasing the degree of freedom in taylor making SAW-substrate materials for given applications.

For berlinite, $AlPO_4$, we are in the process of measuring the piezoelectric constants by the x-ray method in order to verify earlier approximate data obtained ultrasonically, and in order to substantiate our earlier prediction of the superiority of berlinite over α-quartz.

1.4 DoD Implications

For the materials investigated one may expect the existence of temperature compensated cuts for bulk and surface waves, with substantially larger electro-mechanical coupling than for α-quartz. One of the materials investigated, berlinite, was found to have temperature compensated cuts with electromechanical coupling factors up to 250 percent larger than quartz, and the other materials could be even more superior. Thus by replacing quartz as a substrate material in surface acoustic wave (SAW) devices with one of these materials insertion losses can be reduced and the operating frequency and/or bandwidth can be increased. In this manner the efficiency, reliability and capability of military communications and Radar systems utilizing SAW signal processing devices, such as multichannel communications, secure anti-jam communications for satellites, miniature aivonics and electro-magnetic counter measures, can be improved.

1.5 Implications Further Research

It has been demonstrated that the search for new temperature compensated materials with properties superior to those of α-quartz through the approach used under the present contract can be successful. One may therefore hope that a continued systematic search for new temperature compensated materials under the present contract may, even with the low funding level, eventually lead to the discovery of additional even more suitable materials. To this end continued

crystal growth efforts are required to obtain suitable single crystals for the physical property measurements, which are necessary to assess the use of a given material for SAW device applications.

1.6 Special Comments

No special comments are offered at this time.

2. Crystal Growth Results

2.1 Lead Potassium Niobate, $Pb_2KNb_5O_{15}$

Property measurements obtained during this reporting period on lead potassium niobate specimens cut out of cracked boules indicate this material may be very interesting. Therefore, our decision to terminate further crystal growth efforts was reversed. The cracking problems with this material had not been eliminated earlier by changing various Czochralski crystal growth parameters such as composition, temperature gradients, and cooling rates, so the new efforts have been aimed at (1) utilizing more stable temperature conditions both during growth and during the cooling cycle, (2) maintaining the boule diameter as constant as is possible without constant-diameter-control equipment, and (3) using oriented seed crystals. These new efforts are in their initial stages.

A new rf feed-back unit for temperature control has been installed on our A. D. Little crystal puller and has reduced fluctuations in temperatures measured by a thermocouple touching the bottom of the crucible. Diameter control has been enhanced, but only a few runs on this material have been made. A new temperature programmer was just installed and will greatly increase our temperature stability during the cooling cycle. The programmer is attached to the afterheater located directly above the crucible.

Nucleation on a platinum rod results in preferred growth along the crystallographic c_o-axis, the direction in which cracking has been a problem. Seed crystals with different orientations were used in further attempts to eliminate

or at least reduce the cracking problems. However, the growth direction did not appear to change the tendency to crack. These crystal boules pulled from the melt without problem at 2 to 4 mm/hr, and tended to exhibit facets. At high temperatures the boules appeared transparent and crack-free; cooling below the transition temperature of about 500°C apparently causes the cracking. An afterheater was cooled at 10°/hr from temperatures of about 600°C to room temperature. The cracking was reduced to some extent, but still remains a problem. The diameter of the boule has only a small effect on the cracking.

Efforts will continue with more emphasis on growing longer boules with constant diameters. A combination of these precautions will hopefully reduce cracking to a minimum.

2.2 Lithium Metasilicate, Li_2SiO_3

Czochralski crystal growth experiments on lithium metasilicate continued during the first part of this reporting period. The goal was to eliminate or at least reduce the problems of supercooling of the melt and cracking of the pulled boules. A temperature controlled platinum resistance furnace was used to provide increased temperature stability, and thermal gradients were kept to a minimum to avoid cracking. However, the latter precautions enhanced the supercooling problem which is a characteristic of silicates. A water-cooled pulling rod used with a short platinum extension for nucleating the crystal was then installed in an attempt to avoid the supercooling problem. The nucleation on the platinum rod was extremely difficult, and it appears that a seed crystal is required to avoid this problem. Further work on this system has been delayed for the present time.

2.3 Fresnoite and Derivatives, $Ba_2Si_2TiO_8$ and $Ba_2Ge_2TiO_8$

Crystal growth efforts on these compounds were terminated in order to focus attention on other materials which appear to promise a more rapid payoff. X-ray data obtained on $Ba_2Ge_2TiO_8$ indicate its crystal symmetry is monoclinic rather than

orthorhombic. Thus, thirteen independent single crystal elastic constants would be required to determine the complete set of elastic constants and their temperature coefficients. In addition, the x-ray and hot-stage microscopic studies indicate that the as-grown boules contain microtwins which would require strain-annealing in attempts to obtain suitable specimens for the ultrasonic measurements.

2.4 Bismuth Molybdate, Bi_2MoO_6

Survey crystal growth experiments on bismuth molybdate, Bi_2MoO_6, were begun during this reporting period. Czochralski crystal pulling methods were used since this technique usually will yield the largest crystals in the shortest period of time. However, the reported unsuccessful attempts of Miyazawa et al. (1974) to grow crystals of this phase indicated special care would be required.

Bismuth molybdate melts peritectically to give a liquid rich in molybdenum oxide and a solid rich in bismuth oxide (Chen and Smith, 1975). A liquid composition of about (45 mole % Bi_2O_3 • 55 mole % MoO_3) and a flux-pulling method allow for the pulling of Bi_2MoO_6 boules below the phase transition of this phase. Compositions of the liquid richer in MoO_3 reduce the pulling temperature, but flux inclusions were found to be more of a problem. Vaporization of the liquid was significant, but x-ray analysis of vaporization deposits showed the patterns of Bi_2MoO_6. Both high (γ) and low (γ') temperature polymorphs were observed, dependent on the temperature of the surface on which condensation occurred.

As with the other crystals studied in this program, cracking was a problem. Flux inclusions were also evident when growth conditions were not stable. These problems were attacked by using slow growth rates of 2 mm/hr, rotation rates of 20-30 rpm, temperature fluctuations on the outside of the crucible of less than ± 1°, attempts to carefully control the diameter of the boule, reducti n of convection currents in the melt, and cooling of the grown boules at 8°/hr. The temperature gradients in the crucible were reduced to reduce convection currents

in the melt. This was done by modifying the heat shields and by removing the insulation from the bottom of the crucible. Thus the temperature of the top and bottom of the melt were brought closer together. Sections of crack-free boules 2 to 3 mm across and about 3 mm long have been obtained so far.

3. Elastic and Thermoelastic Properties of Lead Potassium Niobate

In our previous Semi-Annual Technical Report (Barsch and Spear, 1976) we presented experimental data for the on-diagonal elastic constants c_{11}, c_{22}, c_{33}, c_{44} and c_{55} of $Pb_2KNb_5O_{15}$, for their temperature coefficients, and for the temperature coefficients of the transit times of longitudinal waves along the three orthorhombic axes. These results differed significantly from those of Yamada (1975).

In order to determine whether there are significant differences in other properties, and in order to determine whether the differences in the elastic properties could arise from differences in stoichiometry we have measured the ferroelectric transition temperature T_c and determined the composition for three samples grown in this laboratory. The transition temperature was measured on millimeter size single crystals by using a polarization microscope and a hot stage, and the composition was determined by means of electron microprobe analysis. The results are compiled in Table 1. Also included are the data of Giess et al. (1969) for the pseudobinary solid solution series $(\xi/2)K_2O \cdot Nb_2O_5 + (1 - \xi)PbO \cdot Nb_2O_5$, and the value for T_c given by Nakano and Yamada (1975) for the nominally stoichiometric composition $KPb_2Nb_5O_{15}$. In Figure 1 the compositions of all samples and their associated transition temperatures are displayed graphically in a triangular coordinate plot.

Since the transition temperatures measured for the three single crystal specimen grown in this laboratory (WFR-X, LD-2 and LD-7) refer to three arbitrary compositions (x,y,z) of the pseudoternary system $x\ K_2O + y\ PbO + z\ Nb_2O_5$ in the vicinity of the stoichiometric composition of $KPb_2Nb_5O_{15}$ $(x,y,z) = (0.1, 0.4, 0.5)$,

Table 1. Ferroelectric Transition Temperature T_c (°C) for various Compositions in the Pseudoternary System $x\ K_2O + y\ PbO + z\ Nb_2O_5$ $(x + y + 2 = 1)$

Specimen	T_c	x	y	z
WFR-X	500	0.111	0.396	0.493
LD-2	485	0.101	0.401	0.4 .
LD-7	300	0.109	0.384	0.506
Nakano and Yamada (1975)	460	0.100[a]	0.400[a]	0.500[a]
Giess et al. (1969)	560	0	0.500	0.500
Giess et al. (1969)	465	0.0263	0.4735	0.500
Giess et al. (1969)	428	0.0556	0.444	0.500
Giess et al. (1969)	360	0.0883	0.411	0.500
Giess et al. (1969)	374	0.1000	0.400	0.500
Giess et al. (1969)	331	0.125	0.375	0.500

[a]Nominal Composition
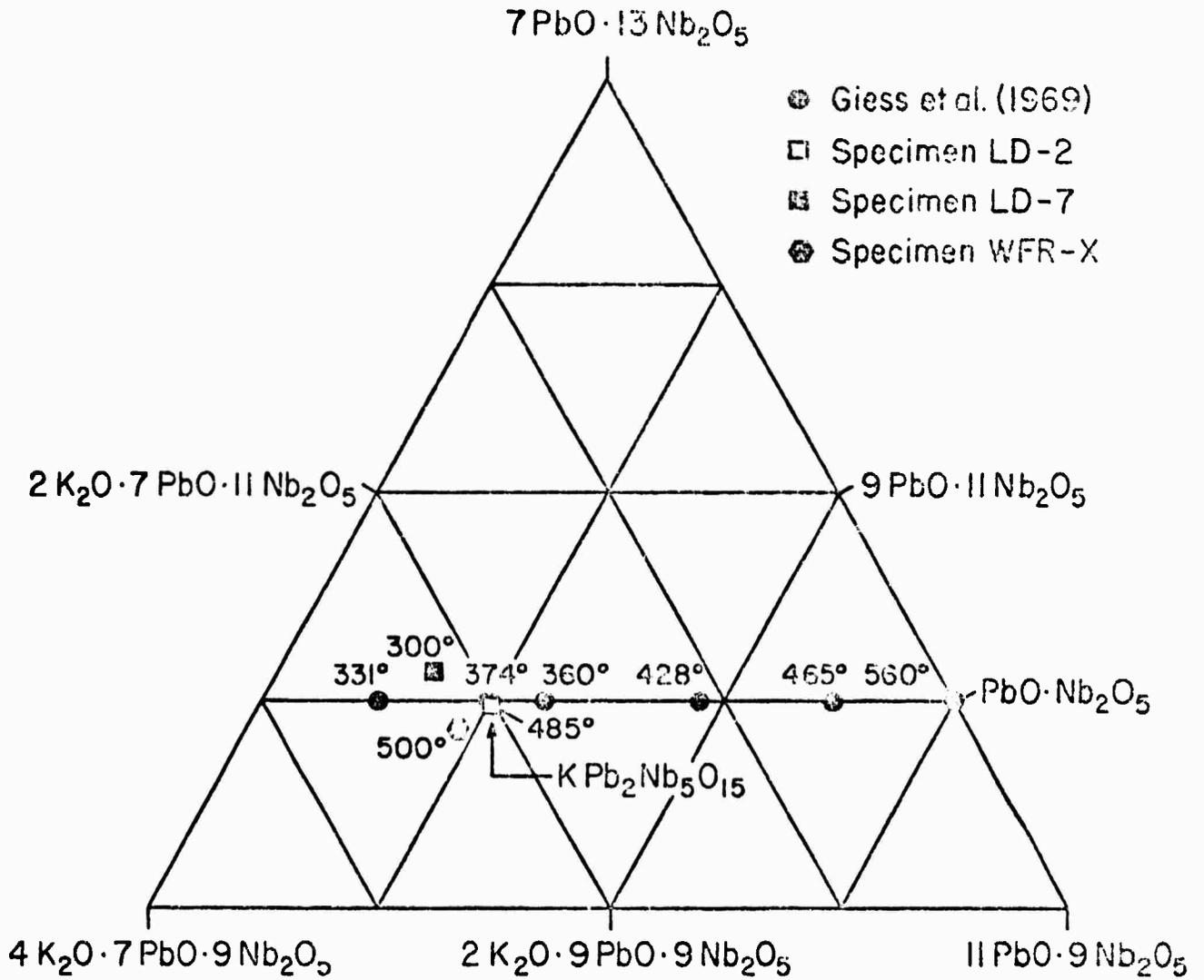
Figure 1. Variation of the Ferroelectric Transition Temperature T_c (°C) in the Pseudoternary System x K_2O + y PbO + z Nb_2O_5.

but the data of Giess et al. (1969) refer to the pseudobinary system $(\xi/2)K_2O \cdot Nb_2O_5 + (1 - \xi)PbO \cdot Nb_2O_5$, they cannot be directly compared. However, since the pseudobinary system is obtained from the pseudoternary system by setting

$$x = \frac{\xi}{2(2-\xi)} \quad , \qquad y = \frac{1-\xi}{2-\xi} \quad , \qquad z = \frac{1}{2} \tag{1}$$

it is possible to obtain a relationship for T_c in terms of the single composition variable ξ if the data obtained from the three crystals grown in this laboratory are fitted to an analytical relation in x, y, z. Choosing for this purpose as the simplest possible form a linear dependence of T_c on x, y, z one obtains

$$T_c[°C] = 2,568.5 \ x + 8,645.4 \ y - 6,508.5 \ z \tag{2}$$

Here x,y,z denote the respective mole fractions, and $x + y + z = 1$. By substituting (1) into (2) one obtains for the composition dependence of the transition temperature along the pseudobinary system $(\xi/2)K_2O \cdot Nb_2O_5 + (1 - \xi)PbO \cdot Nb_2O_5$ a relation, which can in the vicinity of $\xi = \frac{1}{3}$ be approximated by the Taylor expansion

$$T_c[°C] = 460.8 - 2,187.7\left(\xi - \frac{1}{3}\right) - 2,650.0\left(\xi - \frac{1}{3}\right)^2 \tag{3}$$

On the other hand, the data of Giess et al. (1969) for the pseudobinary system $(\xi/2)K_2O \cdot Nb_2O_5 + (1 - \xi)PbO \cdot Nb_2O_5$ obey approximately the linear relationship

$$T_c[°C] = 550 - 588 \ \xi \tag{4}$$

Comparison of the relations (3) and (4) shows that the present data as described by (3) exhibit a much stronger composition dependence than the data of Giess et al. (1969). In addition, the transition temperature $T_c = 461°C$ calculated from equ. (2) or (3) for the stoichiometric composition $KPb_2Nb_5O_{15}$ $\left(\xi = \frac{1}{3}\right)$ is considerably larger than the value of 374°C measured by Giess et al. (1976) or the value of 354°C calculated from equ. (4). Possible causes for these discrepancies are

(a) experimental errors in the compositions of the present specimen, which are compounded by the small number of data points (without redundancy checks) and by the fact that the compositions are very close to the stoichiometric composition $KPb_2Nb_2O_{15}$,

(b) genuine differences in the properties of our single crystal specimen and the polycrystal samples studied by Giess et al. (1969), for which the properties could be affected, for example, by grain boundary effects and internal strains,

(c) the straight line approximation of the data of Giess et al. (1969) according to (4), and the random deviations of the data points from equ. (4), amounting to about ± 25°C,

(d) the fit of the data for our three sample (WFR-X, LD-2 and LD-7) to the linear relationship (2) may not be justified, especially if the stoichiometric composition corresponding to $KPb_2Nb_2O_{15}$ would represent a eutecticum,

(e) compositional deviations of the cation/oxygen ratio from their stoichiometric values K_2O, PbO and Nb_2O_5, which are not detected by the electron microprobe analysis.

At present, there is no clear indication that $KPb_2Nb_2O_{15}$ corresponds to a eutecticum; however, the lattice parameter versus composition data of Giess et al. (1969) reproduced below as Fig. 2 show small anomalies at this composition.

To substantiate the above conjectures (a) to (d) further investigations would be required which are not, however, compatible with the main thrust of the present contract and with the limited budget allocation.

Somewhat surprisingly, the transition temperature of 460°C reported by Nakano and Yamada (1975) lies in the neighborhood of the values found for our samples WFR-X (500°C) and LD-2 (485°C), but the elastic constants and the temperature coefficients of the resonance frequencies for the sample of Nakano and Yamada (1975)
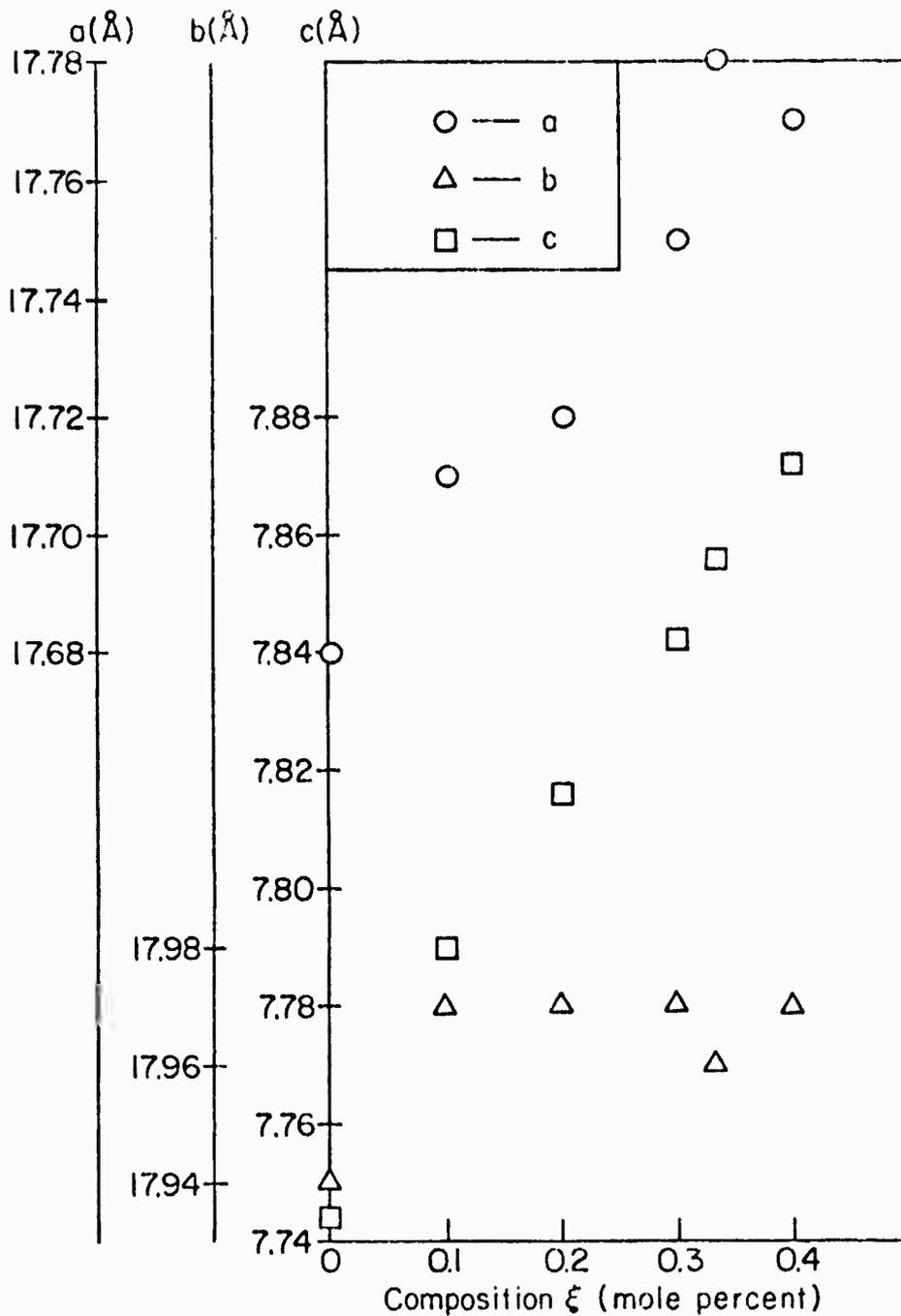
Figure 2. Composition Dependence of Lattice Parameters
a, b, c for Pseudobinary System $(\xi/2)K_2O \cdot Nb_2O_5$
+ $(1-\xi)PbO \cdot Nb_2O_5$ (from Giess et al., 1969).

and for our sample WFR-2 differ significantly (Barsch and Spear, 1976). (Samples LD-2 and LD-7 are too small for elastic constant measurements.) However, since Nakano and Yamada (1975) do not report the precise composition as determined by analytical methods, the proximity of their value for T_c (460°C) to the two values of our two samples (500°C for WFR-X and 485°C for LD2) need not at all be taken as an indication of the near-stoichiometry of Nakano and Yamada's sample. In fact, according to equ. (2) a wide range of compositions is compatible with a constant value of the transition temperature. For example, the condition for T_c = 460°C. is given by $z = 0.6695 y + 0.2322$ with $0 \leq y \leq 0.46$. This has as widely different solutions as $(x,y,z) = (0.768, 0, 0.232)$ and $(x,y,z) = (0, 0.46, 0.54)$. Of course, these extreme compositions are no longer isostructural with $KPb_2Nb_5O_{15}$. However, this argument is presented here to emphasize that the proximity of the transition temperature to the "correct" value is no indication for the stoichiometry of the sample. Thus it is not unlikely that the differences between the elastic and thermoelastic data of sample WFR-X (Barsch and Spear, 1976) and those of Nakano and Yamada (1975) may be attributed to differences in composition. As mentioned before (Barsch and Spear, 1976) another possible cause for the differences could be the presence of residual strains in the specimen of Nakano and Yamada (1975) resulting from the detwinning by strain-annealing in an electric field, which was not required in our essentially single domain specimen.

Assuming that the linear composition dependence according to equ. (2) is appropriate and correct one may expect the transition temperature to increase moderately with increasing content of K_2O, and strongly with increasing content of PbO. On the other hand, increasing content of Nb_2O_5 causes a strong decrease in the transition temperature. In this context one may also discuss, for example, the reason for the low value of T_c = 300°C for sample LD-7. The data in Table 1 indicate that this sample has an excess of K_2O and Nb_2O_5, and is deficient in PbO as referred to $KPb_2Nb_5O_{15}$. While the excess in K_2O would raise the transition

temperature by about 23°C, the deficiency in PbO and the excess in Nb_2O_5 would lower the transition temperature by about 138°C and 40°C, respectively. Thus the main reduction of T_c arises from the deficiency in PbO. This deficiency, in turn is due to the fact that sample LD-7 was prepared from a boule pulled from the same melt after several other boules had been pulled from it, so that it was deficient in PbO because of evaporation resulting from the high vapour pressure of PbO.

From equ. (2) one may also deduce the composition dependence of the transition temperature for the pseudobinary systems x = const, y = const, z = const and obtains, respectively:

$$T_c = A(x) + 15,154 \, y \qquad (x = const) \qquad (5a)$$

$$T_c = B(y) - 3,940 \, x \qquad (y = const) \qquad (5b)$$

$$T_c = C(z) + 6,077 \, y \qquad (z = const) \qquad (5c)$$

Here $A(x)$, $B(y)$, $C(z)$ depend on the isocompositional variable. It is apparent from (5a) and (5c) that the strongest variation of T_c occurs by varying the ratio of the PbO/Nb_2O_5 compositions, and the smallest variation occurs for varying ratio of the K_2O/Nb_2O_5 composition.

Similar discrepancies as those found for the ferroelectric transition temperature between our data and those of Giess et al. (1969) exist for the lattice parameters. In Table 2 the lattice parameters a, b and c as determined from powder x-ray measurements are listed for our three samples WFR-X, LD-2 and LD-7, and for the data of Giess et al. (1969) for the pseudobinary system $(\xi/2)K_2O \cdot Nb_2O_5 +$ $(1 - \xi)PbO \cdot Nb_2O_5$. The data for our three samples can be fitted to the following expressions linear in the compositions x, y, z (x + y + z = 1):

Table 2. Lattice Parameters a,b,c (Å) for various Compositions in the
Pseudoternary System x K_2O + y PbO + z Nb_2O_5 (x + y + z = 1)

Specimen	x	y	z	a	b	c
WFR-X	0.111	0.396	0.493	17.74	17.98	7.81
LD-2	0.101	0.401	0.498	17.72	17.98	7.82
LD-7	0.109	0.384	0.506	17.68	17.86	7.79
Nakano and Yamada (1975)	0.100[a]	0.400[a]	0.500[a]	17.78	18.05	7.834
Giess et al. (1969)	0	0.500	0.500	17.68	17.94	7.744
Giess et al. (1969)	0.0263	0.4735	0.500	17.71	17.97	7.790
Giess et al. (1969)	0.0556	0.444	0.500	17.72	17.97	7.816
Giess et al. (1969)	0.0883	0.411	0.500	17.75	17.97	7.842
Giess et al. (1969)	0.1000	0.400	0.500	17.78	17.96	7.856
Giess et al. (1969)	0.125	0.375	0.500	17.77	17.97	7.872

[a]Nominal Composition

$$a[\overset{\circ}{A}] = 19.727 \ x + 19.881 \ y + 15.573 \ z \tag{6a}$$

$$b[\overset{\circ}{A}] = 18.428 \ x + 23.043 \ y + 13.812 \ z \tag{6b}$$

$$c[\overset{\circ}{A}] = \ \ 7.003 \ x + \ \ 8.849 \ y + \ \ 7.157 \ z \tag{6c}$$

For the pseudobinary system $(\xi/2)K_2O \cdot Nb_2O_5 + (1 - \xi)PbO \cdot Nb_2O_5$ one obtains

by inserting (1) into (6a) to (6c) in the vicinity of the composition $KPb_2Nb_5O_{15}$

corresponding to $\xi = \frac{1}{3}$ the Taylor expansion

$$a[\overset{\circ}{A}] = 17.712 - 0.055 \left(\xi - \frac{1}{3}\right) - 3.606 \left(\xi - \frac{1}{3}\right)^2 \tag{7a}$$

$$b[\overset{\circ}{A}] = 17.966 - 1.662 \left(\xi - \frac{1}{3}\right) - 4.979 \left(\xi - \frac{1}{3}\right)^2 \tag{7b}$$

$$c[\overset{\circ}{A}] = \ \ 7.819 - 0.665 \left(\xi - \frac{1}{3}\right) - 1.925 \left(\xi - \frac{1}{3}\right)^2 \tag{7c}$$

In Fig. 2 the data of Giess et al. (1969) for the composition dependence of the

three lattice parameters a, b, c are shown. It is apparent, that equs. (7a) to

(7c) differ significantly from these data, both qualitatively and quantitatively.

The reasons for these differences may be similar to those for the transition

temperature listed above under (a) to (e).

In Table 3 the density values calculated from the lattice constant and compo-

sition data are compared with the values measured directly by the liquid immersion

method. The good agreement indicates the consistency of the x-ray, electron

microprobe and gravimetric data, and the small differences may be attributed

primarily to experimental error in the composition data, and perhaps to a minor

extent also to deviations of the ratios of the cation/oxygen compositions from

their stoichiometric values. The density value of the sample of Nakano and

Yamada (1975) agrees more closely with that of our sample LD-7, which is deficient

in PbO, but the transition temperature of the sample of Nakano and Yamada (1975)

agrees more closely with our samples WFR-X and LD-2, which are closer to the

stoichiometric composition $KPb_2Nb_5O_{15}$ (see Table 1). Since the constraints on

the composition (x,y,z) are not identical for the curves T_c = const and ρ = const,

Table 3. Density values (g/cm^3) for various compositions in the

Pseudoternary System $x\,K_2O + y\,PbO + z\,Nb_2O_5$ (x+y+z = 1)

Specimen	x	y	z	ρ_{calc}	ρ_{meas}
WFR-X	0.111	0.396	0.493	6.22	6.23
LD-2	0.101	0.401	0.498	6.19	6.20
LD-7	0.109	0.384	0.506	6.12	6.13
Nakano and Yamada (1975)	0.100[a]	0.400[a]	0.500[a]	6.12[a]	6.14

[a]Nominal Composition

the most likely cause for this discrepancy is a significant compositional devia-
tion of the sample of Nakano and Yamada (1975) from the stoichiometric value
corresponding to $KPb_2Nb_5O_{15}$.

The strong variation of T_c on composition suggests that the elastic and
thermoelastic data may also significantly depend on composition. Ideally, this
composition dependence should therefore be measured. Because of the difficulties
of growing suitable sufficiently large single crystals for varying composition,
and because of the modest budget, this task will not be pursued under the present
contract. Instead, we are planning to proceed with the measurement of the complete
set of elastic and thermoelastic constants for our sample WFR-X.

4. X-Ray Determination of Piezoelectroc Constants of Berlinite

Previously we have measured the single crystal elastic constants of berlinite,
$AlPO_4$, as a function of temperature (Chang and Barsch, 1976). Because of the
piezoelectric stiffening term in the Kristoffel tensor it was also possible to
obtain estimates for the piezoelectric constants and their temperature derivatives
from ultrasonic velocity measurements along different crystallographic directions.
On the basis of these results it was predicted that berlinite should have

temperature compensated cuts for bulk waves with orientations similar to those for the AT and BT cuts in α-quartz, but with electromechanical coupling factors up to 250 percent larger than for α-quartz (Chang and Barsch, 1976).

Because of the considerable technological relevance of this prediction it is mandatory to verify the ultrasonically measured piezoelectric constants through independent and more direct measurements. The method selected for this purpose consists of the precise x-ray measurement of the electromechanical strain induced in a piezoelectric crystal through the application of an externally applied electric field (Bhalla et al., 1971). In a previous paper the general theoretical equations required for the application of this method to the twenty non-centro-symmetric crystal classes have been derived (Barsch, 1976). By using these equations in connection with the previously determined piezoelectric constants of berlinite changes of the Bragg angle of the order of one second may be calculated for the magnitude of the effect to be expected if a potential difference of several thousand volts is applied to a platelet about 1 mm thick, as required for the determination of both piezoelectric constants d_{11} and d_{14}.

At present we are engaged in the precise measurement of this effect with the aid of a SIEMENS Single Crystal Diffractometer, Model U13-006. The smallness of the effect puts high demands on the mechanical and thermal stability of the mount for the monochrometer crystal and the test specimen. We hope to be able to present the results for berlinite in our next Semi-Annual Report.

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