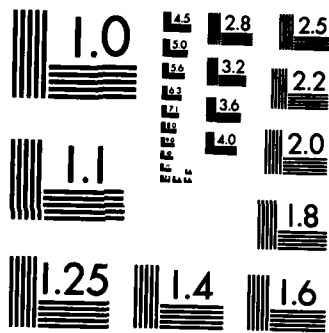END

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Final Technical Report
December 1982

GROWTH AND PREPARATION OF LEAD-POTASSIUM-NIOBATE (PKN) SINGLE CRYSTALS SPECIMENS

Texas A&M University

R. K. Pandey

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Lead-potassium-niobate, $Pb_2KNb_5O_{15}$ (PKN) is a member of the family of tungsten-bronze materials of the type $A_6B_{10}O_{30}$. It is both ferroelastic and ferroelectric and it can be considered as a pseudo-binary compound represented by $2PbNb_2O_6 \cdot KNbO_3$. Its piezoelectric and electromechanical properties make it the leading substrate material for the fabrication of temperature compensated surface-acoustic-wave (SAW) devices. However, it is very difficult to synthesize PKN as a large, crack-free and

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chemically homogeneous single crystal.

This report deals primarily with the problems encountered in crystal growth of PKN and suggests means to circumvent them. Furthermore, it describes two new methods - top-seeded and solution growth - to synthesize crack-free, stoichiometrically uniform large single crystals of the compound. Also the results of PKN characterization by means of x-ray diffraction and dielectric, optical and electrical conductivity measurements are presented and discussed here.

During the course of this research a new single crystal in the $PbO-Nb_2O_5$ system has been discovered. Parts of sections IV and V deal with it in this report.

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I. Introduction

Ferroelectric tungsten-bronze (TB) oxides in general exhibit ferro-
elasticity and are attractive for electro-optic and pyroelectric devices
(1). These oxides can be represented by the formula $A_5B_{10}O_{30}$ or $A_6B_{10}O_{30}$
where A = Ba, Pb, Sr, Ca, Na, K etc. and B = Nb or Ta. Lead-potassium-
niobate (PKN), $Pb_2KNb_5O_{15}$, is one of the members of the family of TB-
ferroelectrics. Single crystals of PKN have been shown to
possess attractive physical properties (2) which make it a very desirable
material for the fabrication of surface acoustic wave (SAW) devices.
Presently α-quartz and lithium niobate are the most commonly used materials
for SAW devices. However, the relatively poor electromechanical coupling
of α-quartz makes it unsuitable for large bandwidth devices. The SAW
devices employing $LiNbO_3$ have poor temperature coefficients which is a
serious drawback for the efficient use of the devices for many applica-
tions where environmental stability is important such as in space and high
altitude flights. Over and above these serious shortcomings the devices
based on α-quartz and $LiNbO_3$ are limited due to their intrinsic physical
properties in the upper frequency limit of operation (3).

In recent years a substantial amount of investigations have been
carried out on new piezoelectric and ferroelectric materials to fulfill
the following objectives:

- to identify materials having high electromechanical coupling
  with a zero temperature coefficient of SAW velocity,

or - synthesize a material which shows a significantly higher SAW
  velocity than α-quartz or $LiNbO_3$.

PKN has been found (2) to satisfy the first objective. The largest electromechanical coupling factors ever observed in a TB oxide are those of $Pb_2KNb_5O_{15}$ (PKN) single crystals - they are: $K_{15} = 0.69$ and $K_{24} = 0.73$. Furthermore, it shows anomalous elastic constant temperature coefficients which make it possible to fabricate zero TCD cuts for SAW devices. These cuts of PKN crystals possess values of k_s^2 as large as 1.88×10^{-2} which are a factor of two less than the values measured for $LiNbO_3$ and their time-bandwidth products are approximately 0.6×10^{-4} sm^{-1} which is compariable to those reported for $LiNbO_3$. These properties make PKN an extremely desirable SAW material. Moreover, it has been reported (5) that PKN is an excellent second harmonic generator. The output measured on samples of particle size of about five microns is about 420% higher than for quartz. Unfortunately, a device quality crystal of PKN is very difficult to grow. The principal difficulties are encountered in obtaining a high quality crack-free large crystal of uniform stoichiometry.

II. Objectives

Most of the work reported on PKN dealing with physical, structural and device properties (2 - 9) have been done using small crystals. For want of large good quality samples with uniform stoichiometry there remains some uncertainties with respect to the exact values of certain important physical properties. For example, the value of the Curie point reported varies from 374° to 460°C (10). Similar is the case for lattice constants, spontaneous polarization, dielectric constants etc. The need of large samples of PKN is obvious for the fabrication of different types of devices. Furthermore, for SAW devices it is desir-

able to have single domain poled large samples which can be obtained only
by poling and annealing a large single crystal simultaneously under the
influence of pressure and an electric field from higher temperature
(temperatures > the Curie point) to about room temperature. PKN crystals
are grown usually at about 1325°C at which PbO has a high vapor pressure
which enables some PbO to leave the crystal growth charge. This contri-
butes to the non-stoichiometry of the crystals and is also believed to
cause severe cracks in them. The lack of large, good quality, crack-free
and uniformly stoichoimetric PKN crystals has been responsible for the
failure of employing this material in making practical devices. Never-
theless, the material possesses very attractive device properties and the
TB family, in general, appear to be promising for synthesizing high-
coupling temperature compensated SAW substrate materials. The purpose
and objectives, therefore, of this research was to:

- develop a crystal growth technique which can produce high quality,
  uniformly stoichiometric and crack-free crystals,
- prepare single domain poled PKN crystals free of twinning and
  ferroelasticity,

and · provide Hanscom AFB with six or more 1 cm^3 such crystals.

III. Theoretical Considerations for PKN Synthesis

Among the $A_5Nb_{10}O_{30}$ - type binary niobates only lead metaniobate,
$PbNb_2O_6$ (PN), has the tungsten-bronze structure. This structure is
characterized by the network of octahedra sharing the corners, i.e.,
this structure can be considered as an intermediate structure between
the perovskite and pyrochlore-type structures. There are two types of

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TB - structures:

- Filled TB - it consists of 10 octahedra and 6 cages which are built up of four 15-coordinated sites and two 12-coordinates sites surrounded by the 10 octahedra. If B ions occupy the octahedra sites and A ions the remaining six sites, the compound is typically represented by the formula $A_6B_{10}O_{30}$. Here either A or B sites can be occupied by more than two kinds of ions;

- Unfilled TB - If the binary system consists of A - oxide and B - oxide the resulting TB - structure can be represented by the formula $A_5B_{10}O_{30}$. Here the six A sites are occupied by 5 ions only leaving one site vacant.

Some cations play an important role in stabilizing the TB - structure in $A_6B_{10}O_{30}$ - or $A_5B_{10}O_{30}$ - type compound. It has been found (7) that the introduction of an alkali ion on the A sites of $A_5B_{10}O_{30}$ type compound yields the more stable $A_6B_{10}O_{30}$ type TB - structure.

It is interesting to note that there are a large number of niobates of $A_5B_{10}O_{30}$ - type. However, only lead meta-niobate, $PbNb_2O_6$, has the TB - structure. On the other hand, all of the $A_6B_{10}O_{30}$ - type niobates synthesize in the TB - structure, where the A_6 ions consist of the combination of Ba^{2+}, Pb^{2+} or Sr^{2+} and Na^{1+} or K^{1+}.

The so-called PKN, $Pb_2KNb_5O_{15}$, is of $A_6B_{10}O_{30}$ - type filled TB - structure. K^{1+} ion stabilizes the $A_5B_{10}O_{15}$ - type unfilled TB - structure of $PbNb_2O_6$ and influences its ferroelectric properties considerably. $Pb_2KNb_5O_{15}$ can be considered as a pseudo-binary compound of the type $2PbNb_2O_5 \cdot KNbO_3$. Lead meta-niobate as well as potassium niobate are

well known ferroelectric materials. Some important physical properties
for these materials are given in Table I.

TABLE I

Compound	Crystal System	Lattice Constant ($\overset{\circ}{A}$)	Curie Temp- ature (°C)	Reference
1. $PbNb_2O_5$	Orthorhombic	a = 17.51, b = 17.81 c = 7.73	560	11
2. $KNbO_3$	Orthorhombic	a = 4.038, b = 3.969	435	12

$KNbO_3$ is a stable ferroelectric material whereas $PbNb_2O_6$ is not.
The later is metastable at room temperature (11) and at the Curie point
its structure changes from orthorhombic to tetragonal. Its paraelec-
tric structure resembles to that of some tetragonal alkali tungsten-
bronzes. For piezoelectric studies and its eventual use as SAW device
substrate large samples of $PbNb_2O_6$ are necessary. However, large crys-
tals of this material is almost impossible to obtain because of its
metastability at room temperature. Large crystals could be synthesized
by quenching it from a stable state above 1250°C if this procedure would
not introduce multiple cracks (9).

Incorporating $KNbO_3$ in $PbNb_2O_6$ not only stabilizes its TB - struc-
ture, it also eliminates its metastability. Presence of K^{1+} ions in
$PbNb_2O_6$ reduces its Curie point as well - from 560°C it is reduced to
about 460°C when the concentration of K^{1+} equals 1 in the formula-
unit (7).

Single crystals of PKN, $Pb_2KNb_5O_{15}$, have been grown by Czochralski
technique (5, 6, 9) using a stoichiometric charge consisting of PbO,

K_2CO_3 and Nb_2O_5 at about 1325°C. According to references (6 and 9) large crystals at PKN can be synthesized but the crystals develop severe cracks during the process of cooling from 1300°C to room temperature. Some slow cooling techniques to prevent cracks were tried unsuccessfully (5). As mentioned earlier in this report, PbO is very volatile above 1200°C and therefore it becomes difficult to obtain uniformly stoichiometric PKN crystals. In the three references (5, 6, & 9) it is reported that different values of Curie point have been measured using sample from different sections of the same crystal. This positively confir, the belief that the conventional Czochralski technique can not yielc uniformly stoichiometric PKN crystals. The growths were most likely performed using radio frequency heating sources. In general, it is very difficult to maintain a slow rate of cooling to prevent cracking of oxide crystals in a Czochralski system which employs radio frequency heating. Therefore it is evident that the following measures should be taken to obtain device quality PKN crystals in which stoichiometry is uniform and no cracks develop.

- Czochralski growth from stoichiometric $Pb_2KNb_5O_{15}$ melt using resistive heater with programmer and controller units capable of annealing the crystals and cooling it at a very slow rate.
- Develop a charge composition other than the stoichiometry reported in literature, specially in references (5, 6, 9) which can yield TB-type PKN crystal without cracks.
- Use an encapsulent in such proportions in the charge that it does not enter the PKN crystal but acts as encapsulent on the crystal surface to protect it from thermal shock and thus prevent cracks.

· Find a suitable flux in which PKN crystals can grow and then
modify it for Czochralski or perhaps top-seeded (Kryopoulous)
growth techniques to obtain a large oriented crystal.

IV. Crystal Growth Experiments

A. Instrumental Set Up and Practical Problems

For PKN growth the instrumental set up consisted of i) a SiC resis-
tive heater capable of operation at about 1550°C and having an isother-
mal zone of about 3" in diameter by 4" high; ii) an Eurotherm unit for
the furnace consisting of power supply, controller and programmer. Rate
of heating or cooling varied according to the needs of an individual
experiment - the typical values used were $5°Ch^{-1}$, $10°Ch^{-1}$, $20°Ch^{-1}$,
$50°Ch^{-1}$ etc. and iii) a stable puller with variable rates of pulling
and seed rotation.

B. Practical Problems

In all experiments Ir, Pt, and Pt - 3% Rh crucibles were used
whose capacities varied from 50 cc to 120 cc. Due to a tremendous pres-
sure exerted by PKN during solidification and also at about 460°C
(ferroelectric Curie point) the crucibles containing PKN were badly
deformed in shape after each successive run and eventually developed
cracks and holes which made them useless for further crystal growth.
New crucibles had to be used after about every 5 to 6 experiments. This
naturally causes delay and frustrations. Thick walled crucibles would
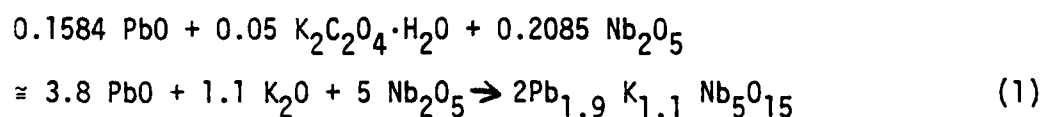be better for the PKN growth.

C. Czochralski Growth

The charge for crystal growth was prepared by using appropriate amounts of high purity PbO, Nb_2O_5 and $K_2C_2O_4 \cdot H_2O$ powders purchased from Alfa Inorganics, Inc. A typical charge of 100 g. consisted of the three chemicals as presented in Table II.

TABLE II

Compound	Weight	Mole	Mole %
1. PbO	35.364	0.1584	38
2. $K_2C_2O_4 \cdot H_2O$	9.2187	0.05	12
3. Nb_2O_5	55.4173	0.2085	50

The above combination of chemicals should react at high temperature obeying the following reaction:

$$0.1584 \ PbO + 0.05 \ K_2C_2O_4 \cdot H_2O + 0.2085 \ Nb_2O_5$$
$$\cong 3.8 \ PbO + 1.1 \ K_2O + 5 \ Nb_2O_5 \rightarrow 2Pb_{1.9} \ K_{1.1} \ Nb_5O_{15} \qquad (1)$$

The above charge yields crystals of $Pb_{1.9} \ K_{1.1} \ Nb_5O_{15}$ instead of $Pb_2 \ K \ Nb_5O_{15}$ which is supposed to be the theoretical composition of PKN. However, according to reference (6) good crystals of the composition $Pb_{1.9} \ K_{1.1} \ Nb_5O_{15}$ are obtained rather than using the charge which should yield crystals of the composition $Pb_2 \ K \ Nb_5O_{15}$ for which the mole ratio of PbO: K_2O: Nb_2O_5 is 4:1:5. We have attempted to grow crystals using both these types of charges and we too have found that the crystals tend to grow more easily when the charge composition corresponds to the formula expressed as $Pb_{1.90-1.95} \ K_{1.2-1.1} \ Nb_5O_{15}$.

The chemicals were thoroughly mixed in a platinum crucible and heated to about 800°C without a cover for about 4 hours. Then after cooling to room temperature the reacted mass, in which color varied from white to bright yellow from site to site, was crushed to fine powder and put into a platinum crucible. It was covered by a tightly fitting cover to prevent loss of chemicals, specially PbO, during subsequent reactions at high temperatures. Now the covered charge was reacted at about 1200°C for about 24 to 30 hours. After cooling it to the ambient temperature and grinding, a fine powdery mass of faint yellow color was obtained. During these steps small loss of weight was observed which could be fully accounted for by the conversion of potassium oxalate into potassium oxide. There was no detectable loss of PbO due to evaporation.

The above mentioned charge melts at about 1320°C which is close to the reported (8) melting point (1325°C) of $Pb_2 K Nb_5 O_{15}$ (PKN). In Czochralski growth experiments it was attempted to nucleate crystal on a platinum wire at about 1300°C. After obtaining a properly shaped PKN seed about 5 mm long x 3 mm diameter, larger crystals were grown by using 20 to 30 rpm for seed rotation and a pulling rate of about 2-3 mm per hour. For 100g melt the largest crystal grown was about 1.5 cm long and 6 to 7 mm in diameter. As observed by other investigators these crystals broke into small pieces (~5 mm x 3 mm) during the process of cooling them to room temperature. In order to prevent cracking the crystals were slowly cooled at various rates in different temperature regions. This measure too was of little help - crystals did develop multiple cracks in each case. Such an observation has been reported also in reference (5). Some of the examples of slow cooling are given in Table

III.

TABLE III

Cooling of PKN Crystals to Room Temperature

Temperature Range	Cooling Rate
1. ~1300°C to 800°C	$50°Ch^{-1}$
2. 800°C to 500°C	100° or 75° or $50°Ch^{-1}$
3. 500°C to 400°C	10° or $5°Ch^{-1}$

It is not exactly known when and where during the process of cooling the cracks originate and propagate in the bulk. It is believed (5, 6, 9) that PKN develops cracks while undergoing phase transition at about 460°C, i.e. the ferroelectric Curie point. On the other hand, we have not seen any development of cracks around 460°C in thin samples of PKN while measuring the temperature dependence of dielectric constant and electrical conductivity. It then raises the fundamental question in one's mind regarding the major causes contributing to the origination and propagation of cracks in the bulk of the PKN crystal. Before we attempt to answer it we should point out one important fact observed during the various Czochralski growth runs. Contrary to the claim regarding the small loss of PbO due to evaporation (5, 6, 9) during Czochralski growth we invariably observed a substantial amount of vapor escaping the melt. It deposited on the cooler regions of the furnace and its cover. Its color was bright yellow indicating that the major constituent of the vapor was PbO. The loss of PbO varied between 20 to 30% by weight from one experiment to another. This naturally makes one suspicious about the quality and stoichiometry of the PKN

crystals grown by the Czochralski technique.

The samples obtained by us and those grown at Pennsylvania State University (supplied by Dr. John J. Larkin of Hanscom AFB) exhibit large regions of polycrystalline mass surrounding small single crystals. They are yellow and not transparent.

Attempts were also made to grow PKN under excess of Ar pressure in the growth chamber in order to minimize the loss of PbO by evaporation. Our experimental set up did not permit us to use pressure larger than 1.2 atmospheres. Loss of PbO was slightly reduced but it was not significant. Moreover, the absence of air in the growth chamber reduced part of PbO to Pb-vapor which vigorously attacked the crucible, seed holder, furnace lining and the growth chamber.

Due to the difficulties experienced in the growth of PKN as outlined above it was decided to abandon the Czochralski technique for the growth of PKN crystals. Subsequently, we concentrated our efforts to flux and top-seeded growth which shall be described in detail later in this chapter.

D. Drawbacks of Czochralski Technique

At this stage it is important to focus some light on the probable causes for the development of cracks in PKN crystals. These are:

- Presence of grain boundaries due to the polycrystalline mass in the bulk. Once the cracks develop they will tend to propagate throughout the bulk of the crystal along the grain boundaries.

- Loss of PbO due to evaporation changes the stoichiometry of the

bulk from one site to another and thus introduces mis-matching of thermal expansion in the crystal. Due to the difference in expansion coefficients in a certain temperature region multiple cracks may develop.

- PKN tends to grow (9) along the c-axis of the orthorhombic struc-ture. It is interesting to note from reference (9) that the thermal expansion coefficient of PKN along a- and c-axis is positive in sign whereas it is negative along the b-axis. More-over, it is zero at the Curie point for a- and b-axis but $8 \times 10^{-6}/C°$ along the c-axis. It is possible that the cracks may be prevented if the crystal can be grown with a- or b-axis orientation.

E. Flux Growth of PKN Crystals

From the discussion and observations presented above it becomes obvious that device quality PKN can not be grown so long as loss of PbO by evaporation is not stopped completely or minimized. This can be achieved by taking the following measures:

- Develop a charge composition other than 4:1:5 molar ration of PbO: K_2O:Nb_2O_5 which has been invariably used by all investi-gators,

- Grow the crystal at a temperature significantly lower than ~1300°C. It is well known that above 1250°C (13, 14) PbO has high vapor pressure and, therefore, it will be very difficult to control its loss at temperatures above 1250°C.

- Use an appropriate encapsulent like B_2O_3 to suppress the vapor

pressure of PbO as well as to protect the surface of the crystal to prevent cracks.

PbO is very toxic and hazardous affects on health must be considered carefully. From the health point of view as well it is advisable to reduce its loss due to evaporation as much as possible during a crystal growth run.

There is no published phase-diagram for the Pb Nb_2O_6 and K NbO_3 pseudo-binary system or for the $PbO-K_2O-Nb_2O_5$ ternary system. This adds to the difficulties of finding a suitable charge composition such that PKN can be grown at a temperature lower than ~1300°C. Furthermore, it limits the alternatives of the growth techniques. Fortunately, phase diagrams for the systems $PbO-Nb_2O_5$ (15) and $K_2O-Nb_2O_5$ (16) are available and they can be used to some extent for developing a new charge composition and alternative techniques for the growth of PKN crystals.

Various fluxes were tried to synthesize PKN single crystals with the following objectives in mind:

- To find a suitable solvent, preferably non-volatile, in which relatively large and good quality single crystals can be grown,

- To grow PKN crystals well below its melting point,

- To prevent the loss of individual oxides, specially volatile PbO, so that stoichiometry of PKN remains uniform throughout the sample.

- To prevent cracks by cooling the crystals slowly.

Our attempts were limited to $PbO \cdot B_2O_3$, $PbO \cdot P_2O_5$, $PbO \cdot V_2O_5$, K_2CO_3 and $K_2CO_3 \cdot Li_2CO_3$ solvents. We shall now describe the merits of each of these fluxes with respect to the growth of PKN crystals.

PbO·B$_2$O$_3$ Flux

It is a well known solvent for the growth of various types of oxide single crystals. Addition of B$_2$O$_3$ to PbO has the advantages that: i) it reduces the vapor pressure of PbO and therefore makes the melt relatively non-volative; ii) it improves nucleation conditions, iii) it is less damaging to platinum crucible and iv) B$_2$O$_3$ is a widely used encapsulent compound.

This flux has been used to grow single crystals (14, 17) of Pb$_3$ Ni Nb$_2$O$_9$, Pb$_3$ Mg Nb$_2$O$_9$, Pb$_2$ Fe NbO$_6$ and Pb$_2$ Sc NbO$_6$. We used three different ratios between the PbO·B$_2$O$_3$ - flux and PKN charge of the nominal composition, Pb$_2$ K Nb$_5$O$_{15}$. In each case single crystals were obtained. They are now described below.

1. Flux: PbO + 3 weight % B$_2$O$_3$

    Flux to PKN charge = 4:1 by weight,

    (i.e. PbO: Nb$_2$O$_5$ = 11.38:1 by mole,

    and K$_2$O: Nb$_2$O$_5$ = 1:1 by mole)

It is assumed here that only Pb$_2$KNb$_5$O$_5$ forms and B$_2$O$_3$ just acts as an additive and does not enter the Pb-K-Niobate lattice. The later assumption proves to be valid as no trace of boron has been detected in the grown crystals.

This mixture was heated to about 1200°C and held there for about six hours to obtain a homogeneous liquid. Then it was cooled to 850°C at a rate of 5°Ch^{-1}. Below 850°C it was cooled rapidly. This growth process was followed in all trials employing PbO·B$_2$O$_3$ flux.

A large number of platelets, approximately 5 mm x 5 mm x 0.1 mm, were obtained after dissolving the flux in hot dilute HNO$_3$ acid.

Shiny yellow crystals exhibit the characteristic interference canoscopic pattern of a uniaxial crystal. The perpendicular direction to the major face of the platelets corresponds to crystallographic c-axis. They are highly birefringent and patterns resembling ferroelectric domains are visible when viewed in a polarized light in which the polarization direction corresponds to the c-axis of the crystal. Unfortunately, the crystal are very fragile and they cleave easily. The cleavage plane is parallel to the c-axis.

2. Flux: PbO + 6 weight % B_2O_3

Flux to PKN charge = 3:1 by weight

(i.e., $PbO:Nb_2O_5$ = 7.78:1 by mole

and $K_2O:Nb_2O_5$ = 1:1 by mole)

Range of Cooling = 1200°C to 850°C

Rate of Cooling = $5°Ch^{-1}$

Both thin plates, as in the previous experiment, and large bulk single crystals grew. They are bright yellow in color; in thicker crystals brown color also appears. The largest crystals were about 1 cm x 1 cm x 0.5 cm and thin plates are about 1 cm x 1 cm x 0.1 cm. Here too uniaxial interference patterns are seen in polarized light along the crystallographic c-axis. They too exhibit patterns similar to ferroelectric domains. In contrast to the crystals grown in 4:1 by weight flux, these do not cleave easily.

3. Flux: PbO + 6 weight % B_2O_3

Flux: PKN charge = 2:1 by weight

(i.e., $PbO:Nb_2O_5$ = 5:19:1 by mole

and $K_2O:Nb_2O_5$ = 1.1 by mole)

Rate of Cooling = $5°Ch^{-1}$.

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In this experiment also both thin plates and large bulk crystals were obtained. The largest crystal was about 2 cm x 0.5 cm x 0.4 cm and weighed about 5 g. It too exhibits the characteristic uniaxial interference pattern when viewed along the crystallographic c-axis by means of a polarization microscope. As in the previous cases, here too we observe patterns resembling domains of a typical ferroelectric material. These crystals are bright yellow in color and they do not cleave easily.

Some other properties of the crystals grown from $PbO \cdot B_2O_3$ flux will be discussed in Chapter V. It should be mentioned here that addition of B_2O_3 by 6 weight % of PbO significantly reduces the loss of PbO by evaporation. In all these three flux growth experiments the weight loss due to evaporation was less than 4%. For crystal growth, the sequential loading was done, i.e. first the PKN charge, then PbO on top of it and finally B_2O_3 on the top most level. It has been, furthermore, observed that by adding 5% B_2O_3 rather 3% on top of PbO flux, one increases the size of the crystals. The largest crystals grew when the ratio of $PbO \cdot B_2O_3$ - flux to PKN charge was 3:1 by weight.

Attempts to synthesize PKN crystals using other fluxes such as $PbO \cdot P_2O_5$, $PbO \cdot V_2O_5$, K_2CO_3 and $K_2CO_3 \cdot Li_2CO_3$ were not successful. In some cases very minute crystals grew whereas in others no crystals grew at all. Also, the flux consisting of PbO and 6 weight % B_2O_3 yielded minute crystals when flux to PKN weight ratio was 9:1. In Table IV we summarize the experiments using fluxes other than $PbO \cdot B_2O_3$.

Even though no crystals were grown in these trials it may be advisable to investigate the fluxes, K_2CO_3 and $K_2CO_3 \cdot Li_2CO_3$ for the

growth of PKN crystals. For lack of time no further efforts were made to synthesize PKN crystals using these fluxes. Both these solvents are water soluble and the crystals can be recovered from the flux in a few hours by dissolving it in hot water.

TABLE IV

PKN Growth Using Some Well Known Fluxes Other Than $PbO \cdot B_2O_3$

Flux	Flux: PKN Weight Ratio	Temperature Range, °C	Cooling Rate °Ch^{-1}	Result
1. $PbO \cdot P_2O_5$	1:1	1230 - 830	30	No growth; no solubility
2. $PbO \cdot V_2O_5$	1:1	1200 - 850	30	No growth but complete solubility; no weight loss
3. K_2CO_3	10:1	1200 - 850	20	- do -
4. $K_2CO_3 \cdot Li_2CO_3$	33:3:1	1200 - 850	10	- do -
2:33:1 by mole				

They tend to suppress the evaporation loss of PbO which is also of important consideration provided PKN can be grown. It has been reported (18) that also Na_2CO_3 is good flux for PKN. Though we have not ourselves tried Na_2CO_3 it may be worthwhile to investigate the Na_2CO_3 - PKN system for the growth of PKN crystals.

Plate 1 shows some of the crystals grown by using $PbO \cdot B_2O_3$ flux: I - Flux to PKN ratio = 2:1 by weight; II - Flux to PKN ratio = 4:1 by weight; and III - Flux to PKN ratio = 3:1 by weight.
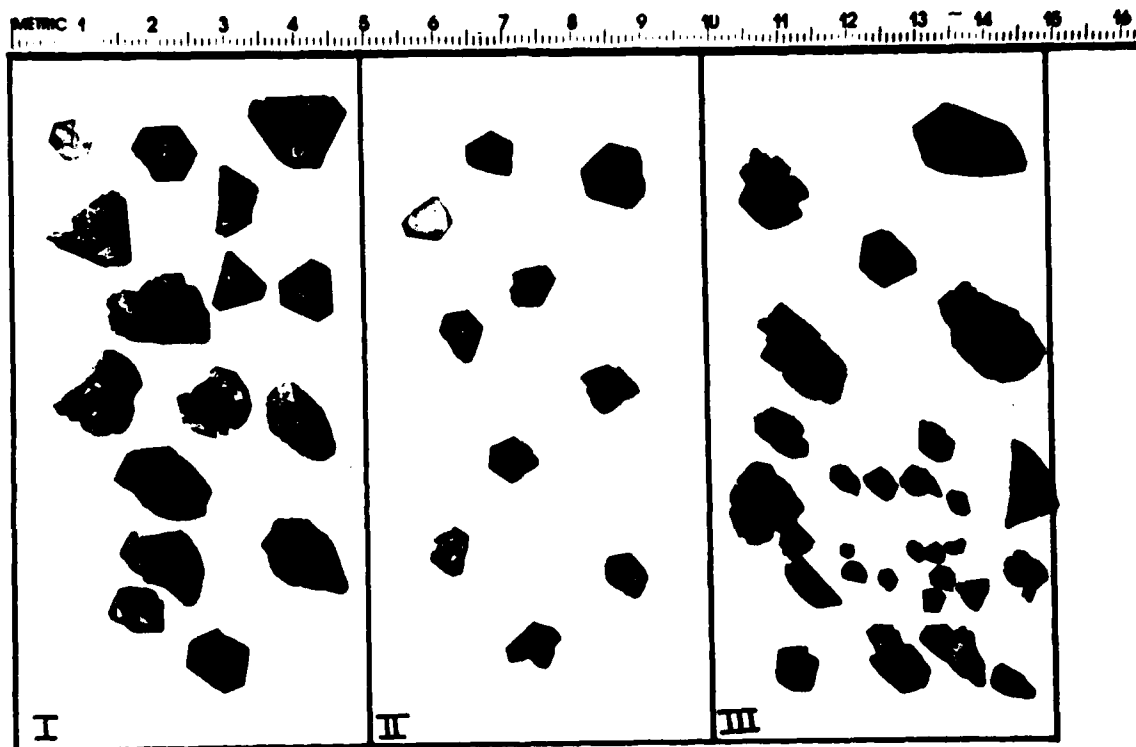
Plate 1: Crystals Grown Using PbO·B$_2$O$_3$ Flux

    I: Flux: PKN = 2:1 by weight;

   II: Flux: PKN = 4:1 by weight;

  III: Flux: PKN = 3:1 by weight.

F. Top-Seeded Growth of PKN Crystals

For want of a PbO - K_2O - Nb_2O_5 phase diagram we had to depend heavily on PbO - Nb_2O_5 (15) and K_2O - Nb_2O_5 (16) phase diagrams. From these diagrams one observes that:

- PbO·Nb_2O_5, i.e. lead metaniobate, $PbNb_2O_6$, can be synthesized when amount of Nb_2O_5 varies from 33% to 50% by mole in the charge consisting of PbO and Nb_2O_5. The range of stable growth corresponds to 1343° to about 1233°C.

- K_2O·Nb_2O_5, i.e. potassium niobate, $KNbO_3$, is the only stable compound between 1039° and about 845°C when the ratio of Nb_2O_5 and K_2CO_3 potassium carbonate varies from 50% to about 67% by mole.

Like PKN, postassium niobate is a very difficult crystal to grow. However, the top-seeded technique has been successfully used to synthesize it (19) when the charge consists of K_2CO_3:Nb_2O_5 = 1.20:1 by mole. A large crystal weighing roughly about 12 to 15 g was grown (19) in only eight hours. Cooling at the rate of $3°Ch^{-1}$ had almost eliminated cracks in the crystal which had frustrated other investigators for a long time.

Assuming that $PbNb_2O_6$ and $KNbO_3$ mix in molar proportion of 2:1 to form $Pb_2KNb_5O_{15}$ we decided to try the technique of top-seeded flux growth. For this the charge composition was so selected that:

1. PbO:Nb_2O_5 = 1.22:1 by mole

   i.e. PbO = 55 mole % and Nb_2O_5 = 45 mole %

2. K_2CO_3:Nb_2O_5 = 1.22:1 by mole

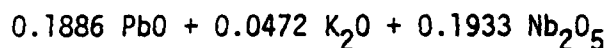   i.e. K_2CO_3 = 55 molr % and Nb_2O_5 = 45 mole %
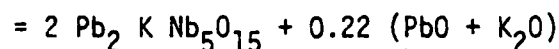
A typical 100 g charge has the following composition:

TABLE V

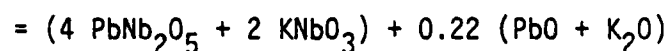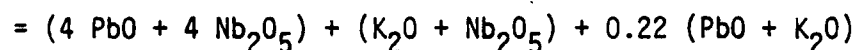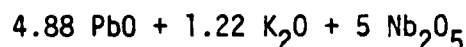PKN Charge for Top-Seeded Growth

Compound	Weight (g)	Mole	Mole %
1. PbO	42.10	0.1886	43.95
2. K_2CO_3	6.52	0.0472	11.00
3. Nb_2O_5	51.38	0.1933	45.05

The above chemicals were mixed and prepared for crystal growth as described in section IVC of this chapter. The weight loss amounted to the theoretical loss expected due to the evolution of CO_2. In order for PKN to form the following chemical reaction takes place:

$$0.1886 \ PbO + 0.0472 \ K_2O + 0.1933 \ Nb_2O_5$$

Multiplying by 25.867 we get,

$$4.88 \ PbO + 1.22 \ K_2O + 5 \ Nb_2O_5$$

$$= (4 \ PbO + 4 \ Nb_2O_5) + (K_2O + Nb_2O_5) + 0.22 \ (PbO + K_2O)$$

$$= (4 \ PbNb_2O_5 + 2 \ KNbO_3) + 0.22 \ (PbO + K_2O)$$

$$= 2 \ Pb_2 \ K \ Nb_5O_{15} + 0.22 \ (PbO + K_2O)$$

$$\qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

$$\qquad\quad PKN \qquad\quad Liquid \ or \ solid \qquad\qquad (2)$$

Furthermore, on heating K_2CO_3 yields K_2O according to the reaction:

$$K_2CO_3 = K_2O + CO_2\uparrow \qquad\qquad\qquad (3)$$

That is, 0.0472 mole of K_2CO_3 will transform into 4.44 g of K_2O and 2.07 g of CO_2. Therefore, after the completion of reaction at 1200°C

100 g of charge of Table III should weigh about 97.93 g. This was found to be correct and there was no loss of PbO even after the charge was maintained at 1200°C for 30 hours. After the completion of solid state reaction the charge assumed a uniform light yellow color.

The charge was seeded with a PKN crystal by means of a platinum wire and covered using a tightly fitting lid. It was heated to about 1310°C and held there for about 4 hours to allow the liquid to attain equilibrium and phase homogeniety. It was cooled from 1310°C to 1270°C at the rate of $10°Ch^{-1}$ and subsequently at the rate of $4°Ch^{-1}$ from 1270°C to 1200°C. By cutting off the power to the furnace it was cooled rapidly to room temperature. The entire process of crystal growth lasted for about 26 hours. On weighing the crucible it was found that the weight loss was less than 1%. Very high quality, almost transparent crystals had grown; its color was light yellow. It was impossible to recover the crystals by dissolving the remaining solid in hot HNO_3-acid. Even after days the mass remained undissolved in acid. Not much success was achieved by using HCl and H_2SO_4 acids. The crystals were completely lost on trying to recover them by heating it at 1250°C. Only a few very small crystals were recovered. Nevertheless, ferro-electric domains similar to ones for PKN reported in reference (6) were clearly observed.

In the next trial we found that the charge melts at 1260°C and so-lidifies at 1230°C. Now the crucible containing the charge was heated to about 1275°C and held there for about 2 hours. It was cooled at the rate of $5°Ch^{-1}$ to 1255°C at which point a PKN seed was introduced by means of a platinum wire. While continuing the cooling to 1235°C at

the rate of 2 to $3°Ch^{-1}$ the seed was rotated at about 5 rpm. At about 1235°C an attempt was made to pull the crystal out of the melt. Unfortunately, the crystal had attached itself to the wall of the crucible and it could not be withdrawn from the melt. So it was left in the melt and cooled to room temperature at about $25°Ch^{-1}$.

Large crystals had grown - they were as clear and transparent as in the previous attempt. There were two crystals of the following approximate dimension: 2.5 cm x 6 mm x 4 mm. Viewing them with the help of a magnifying glass it was found that there were no cracks at all. Recovery of the crystals, which are shown in Plate 2, remained an unsuccessful endeavor. Finally, the crucible was inverted on an alumina plate and its wall heated with a high temperature torch. This released the crystals from the crucible but they broke into several small pieces. The largest pieces were only about 4 mm x 3 mm x 3 mm.

In spite of our failure to recover the large crystals undamaged it is encouraging to note that the top-seeded method seems to be very appropriate for the growth of a high quality large PKN crystal. The growth temperature can be further reduced by making a charge in which $PbO:Nb_2O_5$ and $K_2CO_3:Nb_2O_5$ is greater than 1.5:1 but smaller than 1.22:1 by mole. Furthermore, about 6% by weight of PbO boron-oxide can be added to stop the loss of PbO by evaporation. In our top-seeded experiments loss of PbO even in the absence of B_2O_3 was very small. By further studies of the top-seeded method,we feel confident that a large high quality oriented PKN crystal can be grown.

In Chapter V characterization of the top-seeded grown PKN crystal will be presented and the results will be compared with the ones ob-
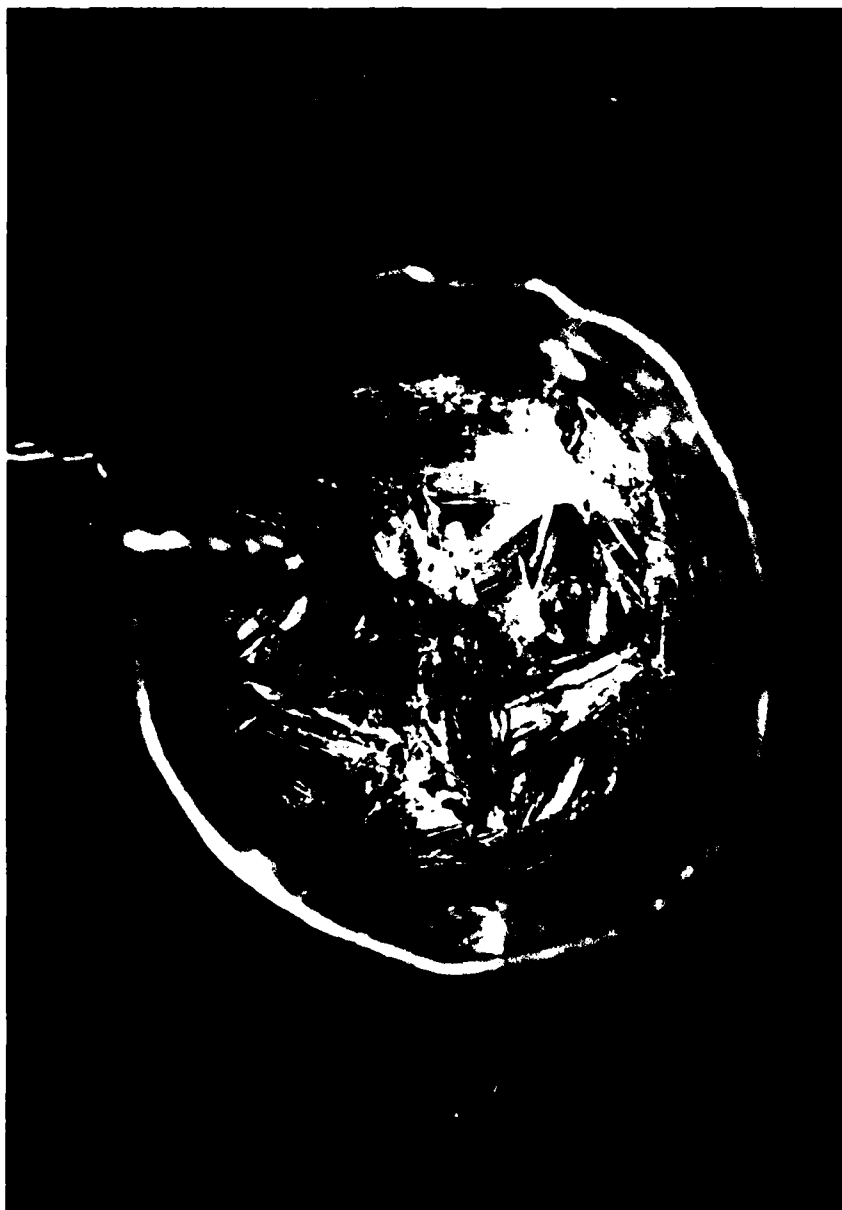
Plate 2: Top-Seeded Grown PKN Crystals.

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tained on Penn State grown crystals provided to us by Dr. Larkin of Hanscom AFB.

V. Characterization of PKN Crystals

We have characterized our crystals by means of x-ray diffraction, polarization microscope and by studying the temperature dependence of dielectric constant and electrical conductivity. First we shall present here the results obtained on $PbO \cdot B_2O_3$ - flux grown crystals and then the characterization results of top-seeded PKN crystals.

A. $PbO \cdot B_2O_3$ - Flux Grown Crystals

i. X-ray Diffraction

These crystals were analyzed both at Texas A&M University and at Hanscom AFB. X-ray studies revealed that there was no trace of K^{1+} in the crystals - either it is completely absent or it is present in such a small amount that it is not detected. Therefore, it is reasonable to assume that the crystals are some type of lead-niobate and not $Pb_2 KNb_5O_{15}$.

This niobate is classified as rhombohedral, space group r3 with hexagonal unit cell having the following lattice constant: $a = 7.437\overset{\circ}{A} = b$ and $c = 48.002\overset{\circ}{A}$. Translating the hexagonal unit cell to a rhombohedral unit cell one gets $a_R = 16.57\overset{\circ}{A}$ and $\alpha_R = 26°$.

It should be pointed out here that the hexagonal c-axis $= 48.002\overset{\circ}{A}$ has an extremely large lattice constant and that very rarely has such a large value for a lattice constant been reported in literature. Furthermore, no known lead-niobate compound has a lattice constant equal

to those of these crystals. This indicates that perhaps a new compound has been discovered in this system which warrants further studies to identify and characterize it.

The molar ratios in the charge between PbO and Nb_2O_5 (outlined in IVe) are as follows:

TABLE VI

Ratio of PbO to Nb_2O_5 in $PbO \cdot B_2O_3$-Flux Grown Crystals

Charge PbO:PKN by weight	PbO:Nb_2O_5 Mole Ratio	% Mole PbO	Nb_2O_5
1. 4:1	11.376:1	92	8
2. 3:1	6.23 :1	86	14
3. 2:1	4.15 :1	80.6	19.4

The growth temperature was between 1200°C to 850°C. Based on the phase-diagram of PbO - Nb_2O_5 (15) one should expect the following two compounds to synthesize:

1. $Pb_2 Nb_2O_8$ which is face-centered tetragonal with a = 10.658Å and c = 10.824Å; no ferroelectricity has been observed in this material (15).

2. $Pb_5 Nb_4O_{15}$ which is rhombohedral with a_R = 10.709Å and α_R = 88° 14'; it is not ferroelectric (15).

Our x-ray diffraction data show that our crystals are neither of the above two compounds.

Similarly it is also not lead-metaniobate, $Pb Nb_2O_6$ because lead-mataniobate is orthorhombic with a = 17.63Å, b = 17.93Å and c = 7.736Å (11). It has an orthorhombic - tetragonal transition at 570°C, which

is considered to be its ferroelectric Curie point (20). It is, moreover, a well known metastable ferroelectric material.

Our flux grown crystals of lead-niobate appears to be a new material and it is interesting for further studies both from the viewpoint of crystal structure and dielectric properties. We are investigating its structural properties currently and shall try to get its formula unit soon. Preliminary measurements indicate that its density is approximately 5.07 g. cm^{-3}.

ii. Dielectric and Optical Properties

Some optical properties of these crystals have already been discussed previously in this report. It should be emphasized that optically the compound is uniaxial, i.e. it is either rhombohedral or hexagonal or tetragonal. X-ray diffraction investigations support this.

The temperature dependence of dielectric constant shows an anomaly at about 420°C in the heating cycle. No such anomaly is found in the cooling cycle when the crystal is cooled from about 550°C to room temperature. But the dielectric anomaly in the heating cycle in a virgin crystal strongly suggests that it is ferroelectric or, perhaps, the ferroelectric phase is metastable. Its thermal behavior of electrical conductivity (see Figure 3, Curve III) also does not exhibit any ferroelectric anomaly around 420°C. However, its exponential behavior at elevated temperatures suggest its semiconducting behavior.

B. Top-Seeded PKN Crystals

i. X-ray diffraction

Our crystal is determined to be c-centered orthorhombic with a = 17.723Å, b = 17.987Å and c = 3.895Å. This is consistent with the literature values of a = 17.78Å, b = 17.96Å and c = 3.928Å (10) and a = 17.78Å, b = 18.05Å and c = 3.917Å (6). PKN belongs to the space group C_{2v}^{14} - Cm 2m (6). Furthermore, it has been found (18) to be exactly identical to the PKN samples grown at Penn State University - each and every spectral line and intensity are the same in our PKN samples and in the samples of Penn State University. It should be emphasized that Penn State samples were grown by Czochralski technique whereas we synthesized our crystals using top-seeded (Kryopoulos) method. Based on the x-ray results and other properties, to be described next, there is absolutely no doubt that PKN crystals can be grown by the Kryopoulos technique.

ii. Dielectric and Optical Properties

When viewed by means of polarized light the crystals exhibit domains characteristic of PKN as reported in reference (6). Both 90° and 180° domains are present. No characteristic canoscopic pattern typical of an optically biaxial crystal were seen. This could be due to the fact that we had not oriented our samples such that the polarized light was passing through the crystal parallel to the c-axis of orthorhombic structure.

Temperature dependence of dielectric constant and electrical conductivity were measured also using PKN samples grown here and at Penn State. First, Fig. 1 shows the percentage change in the dielectric constant, ε_r, as a function of temperature of Penn State samples in two
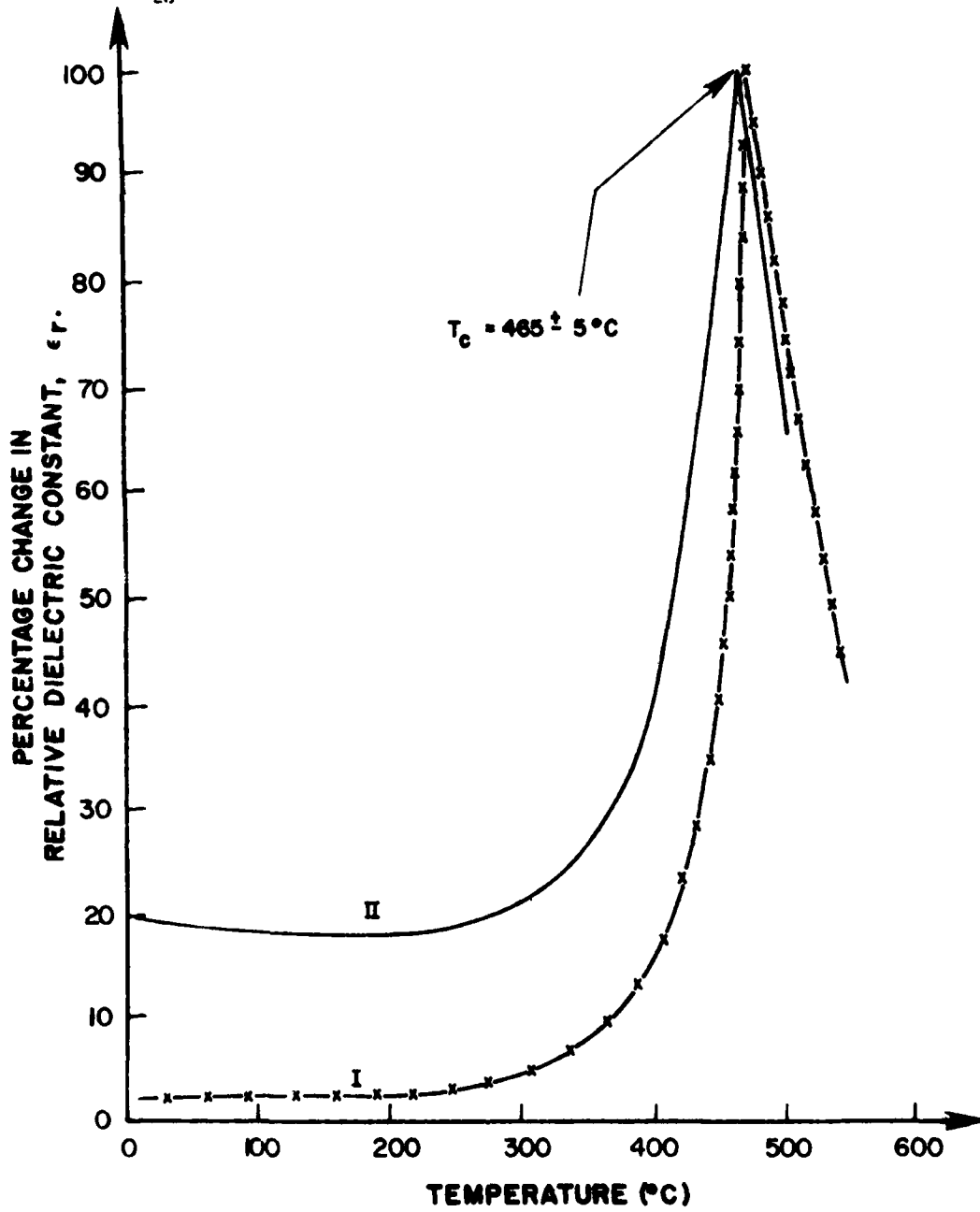
Fig. 1 - Relative Dielectric Constant as a Function of Temperature. Samples - Single Crystal PKN (Penn State Growth); I: ⊥ to c-axis; II: II to c-axis.
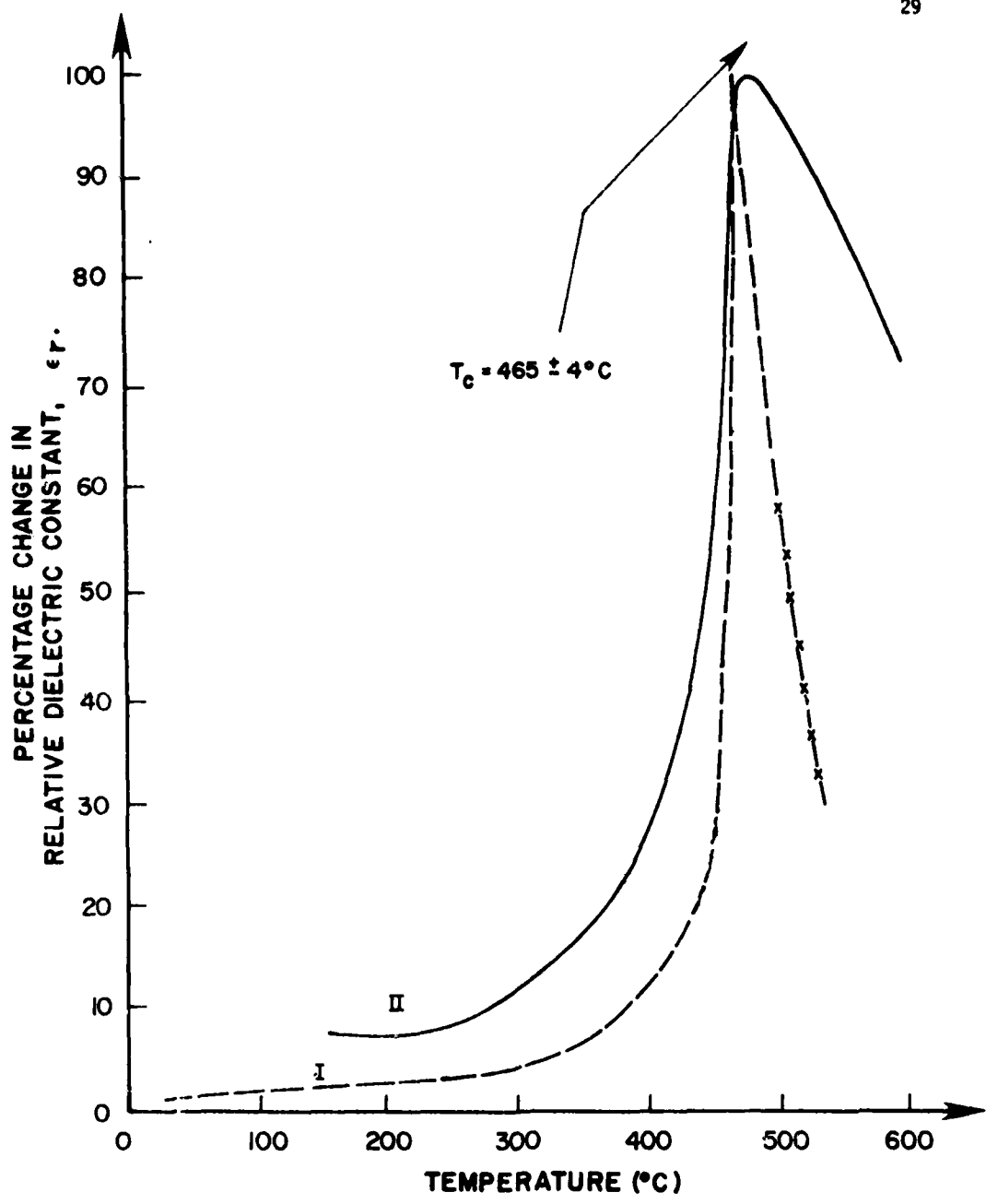
Fig. 2 - Dielectric Constant vs. Temperature. Samples - Single Crystals PKN (TX A&M Grown), I & II: Two different arbitrary orientations.

different orientations - normal to the c-axis; and parallel to the c-axis.
A large anomaly occurs at about 465 $\pm$ 5°C - this value is consistent
with the value of the Curie point for PKN (6). Fig. 2 presents the ther-
mal behavior of ε_r for our PKN samples. Both curves I and II represent
arbitrary crystallographic orientations of the samples. Here too we
observe that the maximum value of ε_r is attained at about 469 $\pm$ 4°C, i.e.
the Curie point of our top-seeded grown samples is in good agreement with
the value obtained for the Penn State's PKN as well with the value
given in reference (6).

In Fig. 3 the temperature dependence of electrical conductivity,
σ, is shown for the two types of PKN samples and the lead-niobate samples
using $PbO \cdot B_2O_3$ flux. The results are represented by the following
curves:

- Curve I - our sample, PKN

- Curve II - Penn State's PKN sample

- Curve III - flux grown lead-niobate sample

As expected, σ increases with increasing temperature. In Curve I
it reaches its maximum at 476°C and then drops to a lower value at
496°C. After that it increases again. Its anomalous behavior at 476°
and 496° is very interesting. The conductivity shows a distinct dis-
continuity at these temperatures. It is presumed that 476°C is the
ferroelectric transition point and 496°C is perhaps the ferroelastic
Curie point. No value for ferroelastic transition in PKN has been
reported in literature. But it is well known that PKN is both ferro-
elastic and ferroelectric simultaneously. In the case of Penn State's
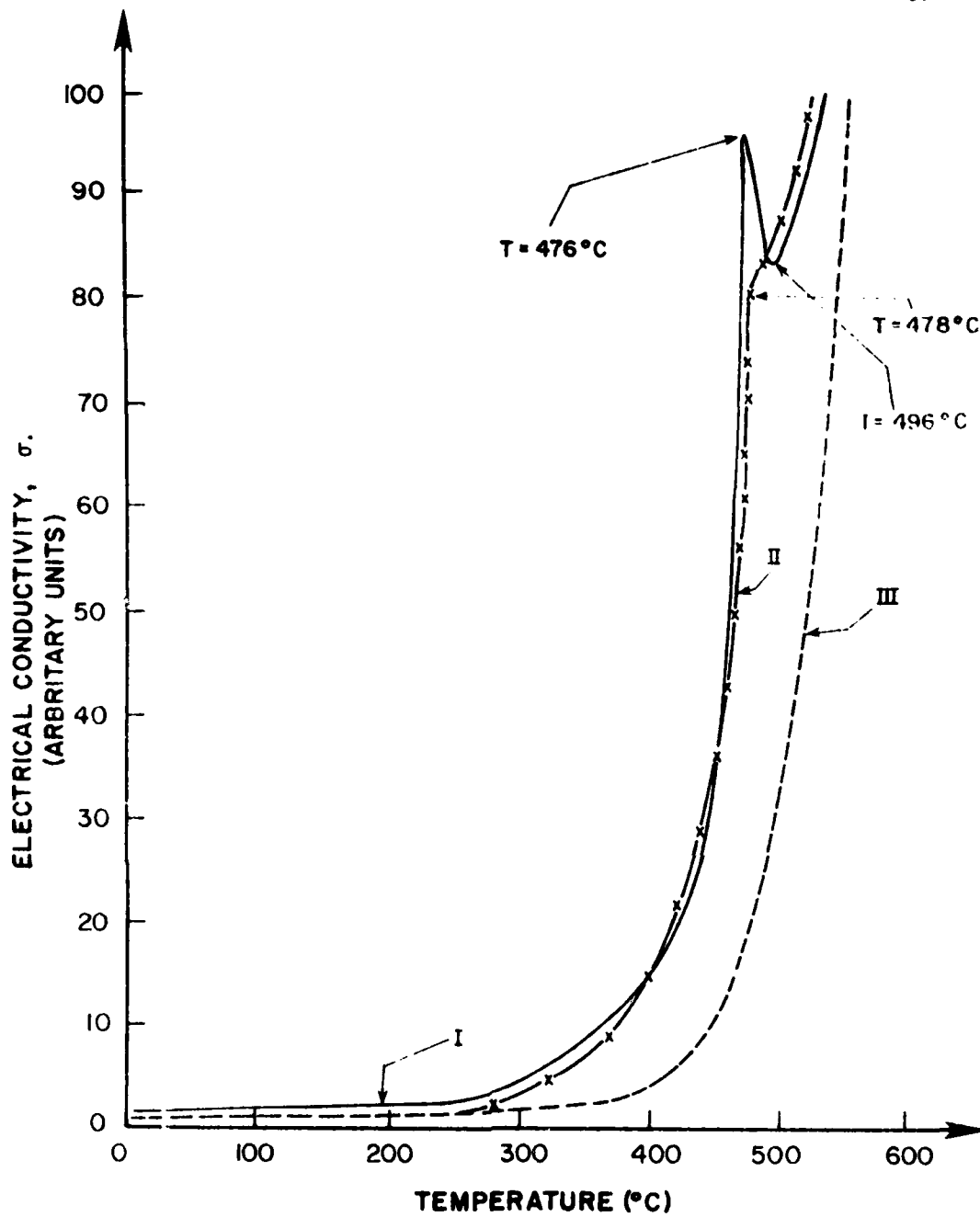sample, the temperature dependence of σ is similar until the ferro-

Fig. 3 - Temperature Dependence of Electrical Conductivity. Samples - Single Crystals FKN; Unoriented I: TX A&M; Top Seeded Growth, II: Penn State; Czochralski Growth, III: TX A&M; Flux Growth.

Curie point at 478°C is attained. There the σ vs. temperature curve simply changes its slope; and this change is quite distinct. No other anomaly is found, as in the case of our crystal, at temperature up to 510°C.

The thermal behavior of electrical conductivity between 476°C and 515°C is vastly different between the two types of PKN crystals. In our crystal a second transition point is clearly exhibited which lies 20°C above the ferroelectric Curie point. Only above the second transition point does our crystal show almost the same value of $d\sigma/dt$ as the Penn State's PKN crystal. The absence of the second transition point in Penn State's sample can be attributed to the fact that the samples were not uniformly single crystals - they appeared to have polycrystalline inclusions. One can clearly see by means of a microscope regions in which grain boundaries are present. Birefringence too is not uniform in these crystals whereas they are uniform throughout in our PKN samples.

In the case of flux grown samples no anomaly is detected either at 420°C which we have found in thermal behavior or dielectric constant, or up to about 550°C (Fig. 3, Curve III). It is possible that one would miss the transition if the crystal has metastable ferroelectricity. For conductivity measurements we had used non-virgin samples.

VI. Conclusions

Lead-potassium-niobate, $Pb_2 K Nb_5 O_{15}$ (PKN) is a very important member of the family of tungsten-bronze type materials both for scientific investigations and its potential applications in the areas of electro-optics, acousto-optics and propagation of surface acoustic waves. It is considered to be the best SAW-device substrate material capable of

operating at elevated temperature. For all these applications device quality single crystal is essential. They must be free of twins and cracks and must have the same stoichiometry of the constituent elements throughout the bulk. Unfortunately, PKN crystals develop cracks easily during the process of cooling from about 1300°C to room temperature. Furthermore, one of its components, i.e. PbO, has very high vapor pressure above 1250°C which causes it to escape from the melt during the course of crystal growth. Because of this the PKN crystal, specially for large samples, end up having non-stoichiometric distribution of Pb, K, Nb and O. This naturally changes the values of the important physical parameters to some extent which poses a problem for the fabrication and design of reliable sensitive devices.

At present it is universally agreed that the major problem lies in the growth of device quality and large PKN crystals.

Our efforts were concentrated during the duration of the contract toward developing a technique for the growth of good quality, crack-free large crystals of PKN. We have demonstrated that this can be achieved by using Kryopoulos technique (top-seeded). With additional efforts in research in the future, I am firmly of the opinion that this problem can be solved. Besides this technique it is also advisable to develop the appropriate flux method using $K_2 CO_3$, $Na_2 CO_3$ and $K_2CO_3 \cdot Li_2CO_3$ as solvents to synthesize PKN.

During the search for a suitable flux for the growth of PKN we have most likely discovered a new lead-niobate compound which appears to have attractive semi-conducting property for high temperature applications. Its exact composition is not yet known but our investigations

indicate that it is a new compound and it exhibits metastable ferro-electricity and semi-conducting properties. More work is obviously required to ascertain its physical properties and potential applications, if any.

During this contract period we have also built an apparatus which can be used to produce single domain poled PKN crystals provided large samples are available. Using this instrument it will be possible to apply pressure and high electric field simultaneously at high tempera-tures to a ferroelastic-ferroelectric material like PKN to obtain single domain and twin-free large crystals.

The results of our characterization experiments is summarized in Table VI.

Suggested Future Emphasis:

1. Prospect appears to be very good for synthesizing a good quality, crack-free large single crystal of PKN using top-seeded technique outlined in section IV-F.

2. It is also possible to grow PKN crystals by using potassium carbo-nate, sodium carbonate and potassium carbonate-lithium carbonate fluxes. This area too warrants attention.

TABLE VII

Characterization of PKN and Flux Grown Pb-Niobate Crystals

	1. PKN (Top-Seeded Growth)	2. PKN (Czochralski Growth, Penn State)	3. Pb-Niobate (Flux Growth)
1. Structure:	orthorhombic	orthorhombic	rhombohedral
2. Lattice Constant (Å)	a = 17.723, b = 17.987 c = 3.895	a = 17.78, b = 17.97 c = 3.91	a = b = 7.437 c = 48.002Å or (a_R = 16.57 α_R = 26°)
3. Curie Point (°C): Ferroelectric			
i. Dielectric	469 $\pm$ 4	465 $\pm$ 5	~420 (meta-stable)
ii. Conductivity Measurement	476	478	---
4. Ferroelastic Transition Point (°C)	496	?	---

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