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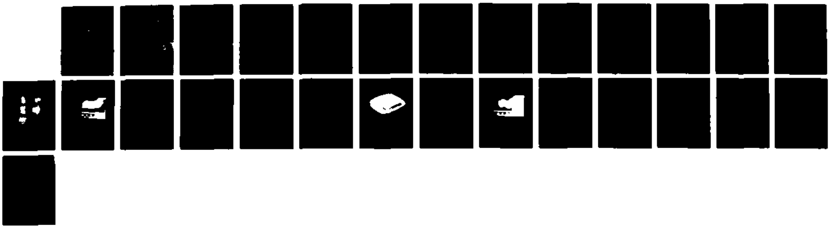

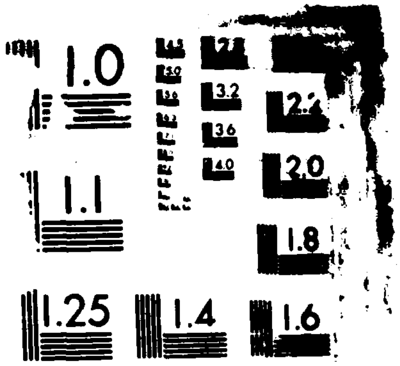

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for

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SYNOPSIS

During the course of this research, in which growth of device quality single crystal of PKN was of primary importance, our experience and first hand knowledge gained in PKN growth enabled us to discover an additional new ferroelectric material in the $PbO{\cdot}Nb_2O_5$ series. It is K-doped $Pb_3Nb_4O_{13}$ having super-lattic pyrochlore structure. This program helped us greatly in learning the various techniques for the growth of ferroelectric crystals, in general, and PKN, KTN, Pb-niobate etc. in particular. This has led to the discovery of four new ferroelectric members of the PKN family and one new member in the Pb-niobate series. Even though the funding was available only until the end of December 1985, the work actually has been continuing until now. The results have been presented at various technical conferences both in the U.S.A. and India and about three journal papers are under preparation. They will be submitted for publication during the next few months. Also, this research has produced two M.S. theses and one Ph.D. level research is in progress.

In this report the following information are presented and discussed:

- Single Crystal Growth of PKN, KTN and Pb-niobate
- Dielectric Characterization of these materials as a function of temperature and composition.

In short, this report deals with the single crystal growth and ferroelectric properties of important ferroelectric and electrooptical materials, $Pb_{1-x}K_{2x}Nb_2O_6$ (PKN) and $KTa_{1-x}Nb_xO_3$ (KTN). The first one crystallizes in saturated tungsten-bronze (TB) structure, whereas the structure of KTN is perovskite. Also, the growth technique and properties of four new members of the PKN family are discussed. These new ferroelectrics are x = 0.23, 0.34, 0.43 and 0.50. In the KTN series high quality crystals having x = 0.66, 0.77 and 0.95 have been grown with no apparent compositional gradient by isothermal mass transport technique. Furthermore, also the growth and properties of a new ferroelectric material, $Pb_3Nb_4O_{13}$, are discussed here.

I. INTRODUCTION

Oxide compounds possessing structures like garnet, perovskite, distorted tungsten-bronze and pyrochlore show a large variety of solid solutions. In these compounds, in general, large anion to cation radius ratio exists. The cations with radii between 0.5 to 1.2$\mathring{A}$ are replacable within the oxygen lattice with the ionic radius of O^{2-} of 1.4$\mathring{A}$ [1]. In the recent past tungsten-bronze and perovskite ferroelectrics have gained added importance because of their suitability as superior substrate materials for pyroelectric detection and a large number of electro-optical applications. Ferroelectrics are those materials which possess switchable spontaneous polarization which disappears at a well defined temperature called the Curie point. Below this temperature the dielectric properties are non-linear with respect to temperature, frequency and electric field. At the Curie point the ferroelectrics undergo a phase transition, i.e., above this point the linear behavior of the dielectric parameters dominates. These materials lend themselves to a variety of electronic applications because of the presence of the spontaneous polarization, high dielectric constant, piezoelectricity, pyroelectricity, ferroelasticity etc. in a wide range of temperature and frequency. In many ferroelectric oxide solid solutions the Curie point and, therefore, the large values of the relative dielectric constant ($\approx$ 10.000) and electric susceptibility can be manipulated with respect to specific applications. The anomalously high electro-optical and birefringence effects can be used for numerous applications. In this paper, the results of crystal growth experiments for Pb-K-niobate (TB-structure) and K-Ta-niobate (perovskite structure) are presented. Pb-K-niobate, usually referred to as PKN, is a fairly new material and it is considered to be the leading material for surface acoustic wave devices (SAW devices). Until recently, it was believed that PKN is to be represented only by the formula, $Pb_2KNb_5O_{15}$ which is equivalent to $Pb_{1-x}K_{2x}Nb_2O_6$ where x = 0.2. We have in the very recent past synthesized four additional ferroelectric members of the PKN family in bulk single crystalline form.

In the family of perovskites, K-Ta-niobate (KTN) is a well known solid solution ferroelectric in which the value of the ferroelectric transition point is extremely sensitive to the ratio between K and Ta. Crystals of KTN having the transition point close to room temperature and with no compositional gradient within the bulk of the material are in great demand for pyroelectric detection and for many electro-optical applications. Also, high quality single crystals of KTN exhibiting transition from ferroelectric to paraelectric state at low temperatures are ideally suited for studies of quantum field effects at low temperatures. We have been successful in growing high quality single crystals of $KTa_{1-x}Nb_xO_3$ with different values of x; and these samples show practically no compositional variations. These are now being studied in a wide range of temperatures for understanding the nature of ferroelectricity at low temperatures and potential applications at elevated temperatures, both in low and high temperature regimes. All KTN crystals synthesize in perovskite structures represented by ABO_3. In the process of finding a suitable self-fluxing ratio for the growth of PKN with $x = 0.2$, we could grow large transparent single crystal of $Pb_3Nb_4O_{13}$ doped with K^{+1}. It crystallizes in pyrochlore structure and this compound has interesting ferroelectric properties. Recent x-ray analysis shows the evidence of superlattice in its structure. This is an important discovery and it can lead to many fundamental results and applications.

II. Crystal Growth and Ferroelectric Studies

II.1 PKN, $Pb_{1-x}K_{2x}Nb_2O_6$

Pb-K-niobate synthesizes in tungsten bronze structure of the type $A_6B_{10}O_{30}$, where A is one of the following: Ba, Sr, Pb, Ca, Na and K; and B can be either Nb or Ta. Currently, leading SAW substrate materials are lithium niobate and α-quartz. But they have some serious drawbacks as well. For example, lithium niobate has a poor temperature coefficient, which restricts its applications in many ways; and α-quartz has relatively poor electromechanical coupling, which makes it unsuitable for large bandwidth devices [2]. However, PKN, particularly that composition in which $x = 0.2$, is considered to be an excellent SAW material because it is a temperature compensated ferroelectric having high values of piezoelectric [3] and electromechanical coefficients [4]. But for a PKN to succeed as a truly device material single crystals of high quality and of large size must be made available. For the last many years, many attempts were made to grow large, crack-free, single crystals of PKN [5,6,7]. None of these efforts produced the crystals to meet the stringent requirements of device engineering. For lack of high quality and crack-free samples, this material has neither been characterized fully nor have devices been fabricated using PKN. All the previous attempts of crystal growth were limited to the Czochralski technique using charges of stoichiometric composition. But PKN melts incongruently and loss of PbO due to evaporation is common at high temperatures (above 1200°C). These two inherent properties of the melt make the standard Czochralski method of crystal growth inappropriate for the synthesis of PKN crystals. However, PKN with $x = 0.2$ was successfully grown with high transparency and no cracks for the first time using the self-fluxing technique [8]. We have refined this technique now to synthesize large, crack-free crystals of PKN with $x = 0.2, 0.23, 0.34, 0.43$ and 0.5. All these compositions exhibit well defined ferroelectric transitions and high values of relative dielectric constant.

The partial phase diagram of PKN [7] indicates that PKN can also be grown by high temperature solution growth (HTSG) and top seeded solution growth methods. The charges for crystal growth experiments were prepared by mixing appropriate amounts of PbO, K_2CO_3 and Nb_2O_5 of high purity grades in a clean platinum crucible and subjecting them subsequently to the standard methods of solid state reactions and sintering between 1100 to 1200°C in air for many days. The details of the charge preparation can be found in references [8] and [9].

First of all, various compositions of PKN were grown by slow cooling of the melt in the range of 1300 to 900°C at the rate of $2°\ Ch^{-1}$. These trials were purely static in nature, i.e., no stirring of melt was accomplished by adopting any special technique (ACRT or crucible rotation). The crucibles were covered with tightly fitting lids in order to minimize the compositional changes in the bulk of the crystals because of the evaporation of melt components at high temperatures during prolonged periods.

The results of static growth are summarized in Table I.

Table I

Results of Self Fluxed Static Growth of PKN
Crystallization Range = 1300 to 900°C; $\Delta T/\Delta t = 2^\circ\ \mathrm{Ch}^{-1}$

Charge composition (x)	Expected crystal composition (x)	Results and comments
0.4	0.23*	Large number of yellow long crystals; multiple cracks, best yield.
0.5	0.34*	Extensive cracking, yellow color. Good yield.
0.6	0.43*	Largest and excellent optical quality crystals. Extensive cracking. Good yield.
0.7	0.5*	Good size and good optical quality crystals. Extensive cracking. Good yield.
0.87	0.62	Mica-like platelet crystals. Easily cleaved along surface. Light color, opaque Yield moderate.

* Birefringence and Ferroelectric Domains Present

The results obtained in this experiment became important in our efforts to grow large PKN crystals of different compositions without cracks. For this, crystal growth was achieved using the top seeded solution growth (TSSG) technique using an induction heater operational at 2MHz. Range of growth temperature was limited to 1250 to 1350°C depending upon the value of x present in the specific charge. Twisted platinum wire was used to initiate heterogenous nucleation and attainment of proper sized seed for the growth of large crystals. In our previous experiments [8] we had observed that cracking problem was virtually eliminated when the top surface of the PKN melt was covered with a thick layer of boron oxide, B_2O_3. This also helped in minimizing the evaporation loss of melt components of desired composition. Analysis had shown that B_2O_3 does not introduce any perceptible amount of impurities in the PKN crystals synthesized.

In the TSSG experiments the charges along with the encapsulent were melted well above the individual melting points and subsequently the molten charges were retained at these high temperatures for several hours to achieve complete melt homogenization as well as thermal equilibrium. Then the nucleating platinum wire was introduced a few mm below the melt surface. The actual growth was initiated by slowly reducing the melt temperature-1 to 2°Ch^{-1}. After a suitable seed was obtained, both in size and quality, the crystal was slowly withdrawn, 2 to 3 mm per hour, from the melt while continuing the slow cooling process throughout the duration of the experiment. With this method, five different compositions of PKN were synthesized. The results are shown in Table II.

Table II

Growth of PKN Crystals using TSSG Method

Composition Charge in x	Nominal Composition of crystal	Size in mm	Color	Weight in gm	Comments
0.3	0.18	L=20 d=8-10	Greenish	16.64	Polycrystalline
0.4	0.23	L=35 d=5-15	Greenish yellow	16.6	Best grown crystal
0.5	0.34	L=20 d=12	Yellow	14.3	Good growth and good yield
0.6	0.43	L=35 d=5-12	Yellow	15.2	Good growth and high yield
0.7	0.5	L=20 d=20	Light yellow	15.3	Good growth

All the crystals obtained were initially opaque, perhaps due to the frozen encapsulent. Once the outer layers were dissolved in hot HNO_3 and crystals were annealed in oxygen environment for several hours between 900 to 1000°C, they became almost transparent. None of these samples developed cracks on cooling to room temperature. Cracking of the PKN crystals had been a serious problem encountered by all investigators. In order to prevent cracks while bringing the crystals from high temperatures to room temperature the following cooling program was used: i) from 1250 to 500°C at the rate of 10°Ch^{-1}; ii) from 500-200°C at the rate of 5°Ch^{-1}, this temperature regime corresponds to the transition points of the crystals from ferroelectric to paramagnetic state; and iii) from 200 to 25°Ch^{-1} at the rate of 50°Ch^{-1}.

For dielectric measurements, 1 to 2 mm thick wafers were cut from the crystal boules along the direction perpendicular to the longitudinal direction of growth. After polishing etc. gold electrodes were affixed to the flat faces to obtain good ohmic contacts for dielectric measurements. The results of the temperature dependence of the relative dielectric constant, ϵ_r, is shown in Figure 1. Here we observe that as x increases in $Pb_{1-x}K_{2x}Nb_2O_6$ samples, so does the ferroelectric Curie point and the magnitude of the transition. In Figure 2, the compositional dependence of the Curie point (T_c) and dielectric constant at room temperature and at the transition point are presented. In Table III the absolute values of T_c and ϵ_r for each composition is given.

Table III

T_c and ϵ_r of $Pb_{1-x}K_{2x}Nb_2O_6$ Crystals

Nominal x in Crystal	Formula	Curie Point, °C	ϵ_r at 25°C	ϵ_r at T_c	$\epsilon_r,T_c/\epsilon_r,25$
0.20	$Pb_{0.8}K_{0.4}Nb_2O_6$	478	1250	10,000	8.00
0.23	$Pb_{0.77}K_{0.46}Nb_2O_6$	367	5208	7184	1.38
0.34	$Pb_{0.66}K_{0.68}Nb_2O_6$	258	4433	5653	1.28
0.43	$Pb_{0.57}K_{0.86}Nb_2O_6$	228	3713	4808	1.29
0.50	$Pb_{0.50}KNb_2O_6$	185	3397	4392	1.29

Notes

- ϵ_r measured parallel to the longitudinal growth axis at 1KHz.
- $XT_c^{0.83}$ = constant for x = 0.23 - 0.50

A thorough dielectric characterization of PKN with x=0.2 has been done from room temperature to about 600°C and in the frequency range from 100Hz to 100KHz [10]. Results and interpretations of this study will be presented separately at a later date. In photographs I & II the samples of PKN are shown.

II.2 KTN, $KTa_{1-x}Nb_xO_3$

The KTN is one of the most interesting members of the ferroelectric solid solution systems. It is perhaps the only truly solid solution ferroelectric. The end members of this system, $KNbO_3$ ($T_c \approx 708K$) and $KTaO_3$ ($T_c \approx 13K$), are completely soluble in each other yielding ferroelectric solid solutions of any desired composition of the type $KTa_{1-x}Nb_xO_3$

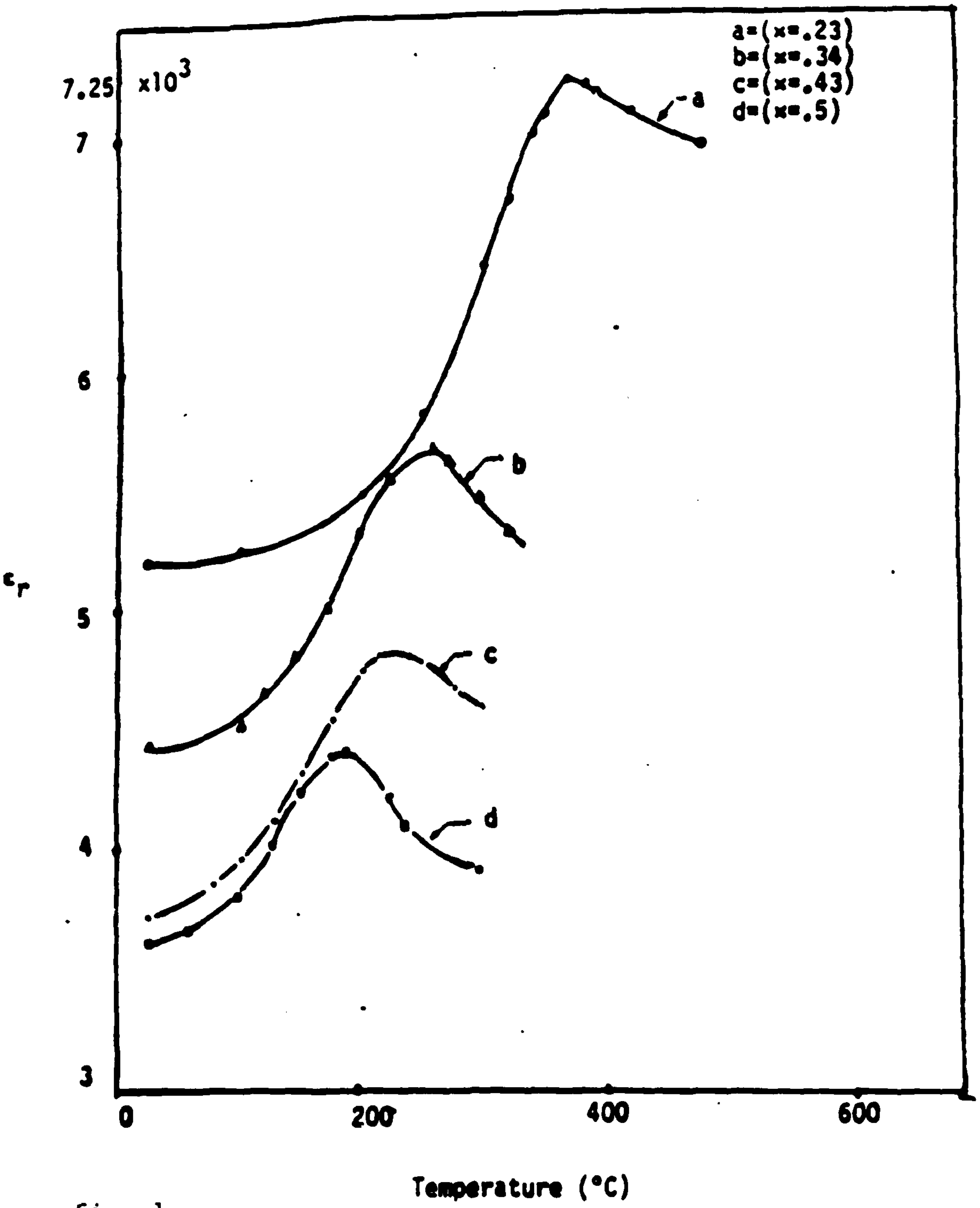


Fig. 1
Temperature dependence of the dielectric constant for Pb-K-Niobate crystals; Sample Orientation: Arbitrary.

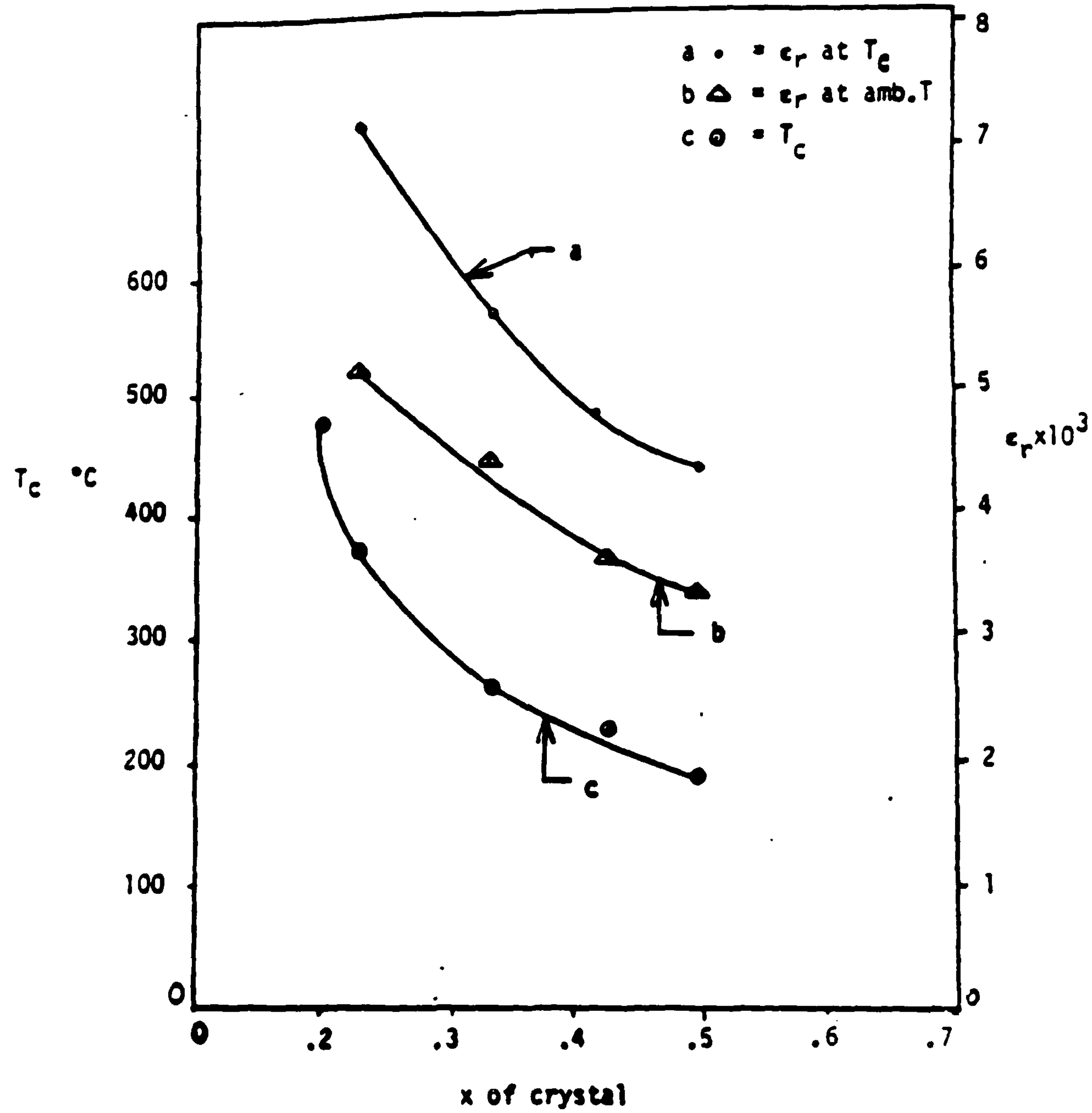
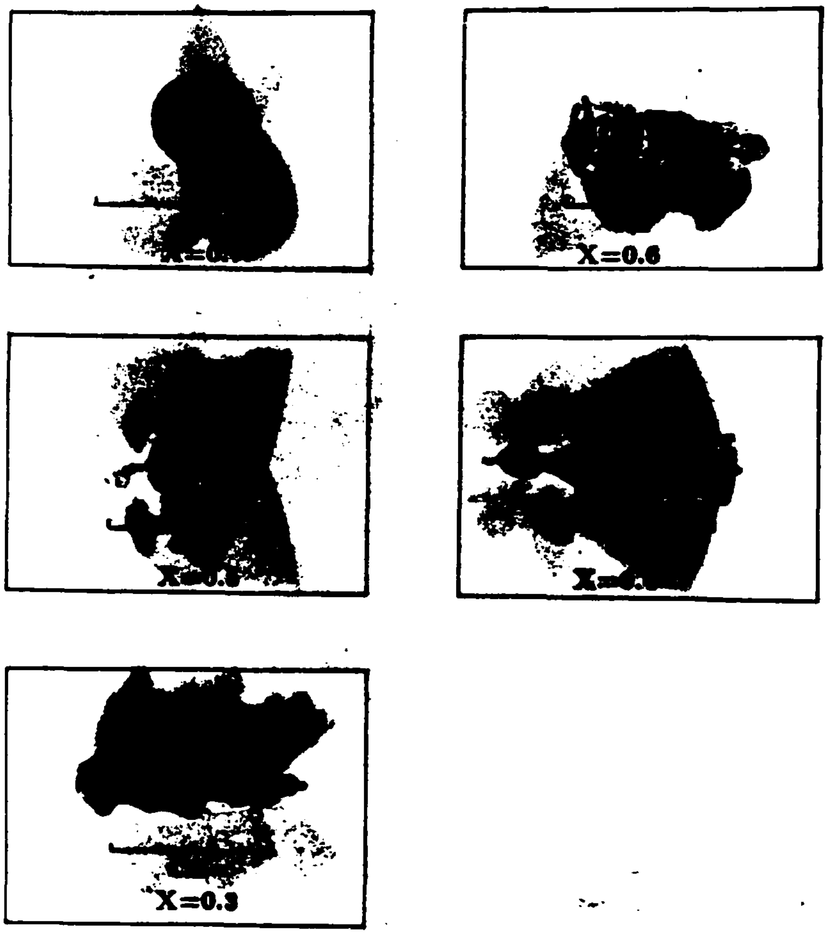
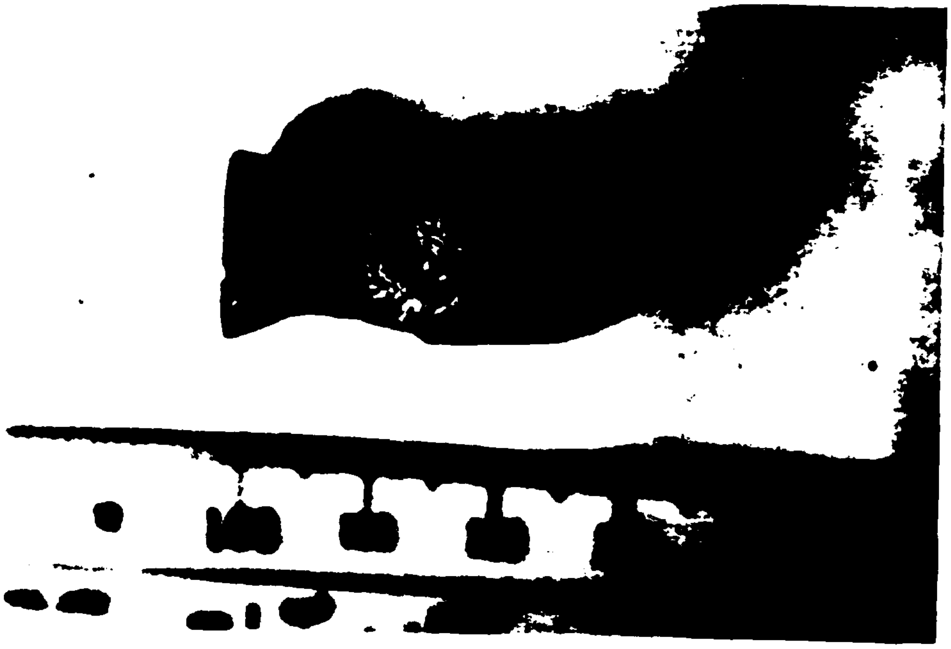


Fig. 2 Dependence of the Curie point (T_c) and dielectric constant (ϵ_r) on the composition (x) for Pb-K-Niobate crystals



Pb-K-Niobate Single Crystals

I. Pb-K-Niobate Single Crystals, Values of x correspond to the charge composition.



II. Pb-K-Niobate crystal with x = 0.4 (charge) where x = 0 to 1. The compositional dependence of the ferroelectric Curie point is almost linear [11] and it is extremely sensitive to Ta/Nb ratio. The T_c increases with the increase of Nb and it decreases when the Ta content in the solid solution is decreased. Like $KNbO_3$ and $KTaO_3$ all compositions in the $KTa_{1-x}Nb_xO_3$ synthesize in perovskite structure, i.e. they can be represented by ABO_3.

The KTN crystals are extremely important both for fundamental research and novel device applications. Samples having very low temperature Curie points are being studied for quantum field effects whereas those samples which have the Curie points close to room temperature are appropriate for a large number of applications in the fields of radiation detection, electro-optics, signal processing etc.

Solid solutions of $KTa_{1-x}Nb_xO_3$ with x=0.35 have a large dielectric constant ($\epsilon_r > 10^4$) and, therefore, a very large electro-optic effect at room temperature. The nature of this effect is quadratic (Kerr effect) in KTN. An extremely large effective linear electro-optic effect (> 100 times that in materials like ADP and KDP) can be achieved by applying a transverse field.

KTN shows high saturation polarization and very low dielectric losses. Therefore, it is an attractive material for the following applications: 1. electro-optic and acousto-optic light modulators and deflectors; 2. second harmonic generation; 3. parametric oscillators; 4. variable delay lines; 5. holographic data storage; 6. pyroelectric detectors and 7. photorefractive devices.

Since its discovery [11,12] various efforts were made for the synthesis of KTN single crystal using techniques such as Kyropoulos, Pfann, TSSG and ACRT. All these efforts failed to produce optical quality KTN crystals. The crystals invariably possessed observable striations which are detrimental for the fabrication of efficient electro-optical devices. Here the challenge is to synthesize optically transparent, striations free large single crystals having no compositional gradient. Moreover, the ferroelectric Curie point should be around room temperature (i.e. 25-35°C) so that the maximum value of the dielectric constant, which is available in ferroelectrics at the Curie point, can be utilized. In general, the higher the value of the dielectric constant, the higher is the electro-optical coefficient as well as the amplification factor of a radiation detector.

The charge compositions for the crystal growth experiments were based on the following two factors: 1. the method of growth and 2. the desired crystal composition. Both these parameters are dictated by the well established phase diagram of the $KNbO_3$-$KTaO_3$ system [11]. By adopting the usual practice of charge preparation–appropriate mass ratio of K_2CO_3:Nb_2O_5:Ta_2O_5, grinding, solid state reaction, sintering etc.–initially the crystals of various compositions were grown by the methods like HTSG, ACRT, slow cooling etc. All these crystals exhibited compositional gradient as well as colors ranging from black, blue to green. These colors are caused by the reduction of pentavalent Nb and Ta. In subsequent experiments these colors could be eliminated by adding a small amount ($< 1\%$ by weight) of SnO_2 in the charge. The crystals grown by the mass transport method at a constant temperature show no compositional gradients and only a few striations. They are amber colored and usually they are 2 cm x 1 cm x 0.5 cm. The principle of this growth technique can be outlined as follows: first of all the charge containing excess of K_2O is melted and then held at a temperature about 50 to 100°C higher than its melting point for several hours to achieve complete homogeneity of the melt. Also, a positive O_2-pressure of 6 to 10 psi was maintained in the growth chamber to prevent the loss of charge composition due to evaporation. The next step was to reduce the temperature of the melt slowly so that crystallization took place in the bottom of the platinum crucible. Naturally, for this to occur one must introduce a small temperature gradient between the bottom and the top of the melt. Once a good size crystal was precipitated in the bottom of the crucible, the temperature was raised to that temperature which would allow, according to the phase diagram, the crystallization of a desired composition isothermally. At this stage, an oriented seed is introduced and the crystal is allowed to grow. The inital crystal precipitated at the bottom of the crucible acts as the nutrient material for the growth of the oriented crystal with one unique composition. A good size crystal is grown in about three to four days.

By this method we have been able to synthesize excellent crystals of three different compositions of KTN, i.e. with $x=0.66$, 0.77 and 0.95 in the $KTa_{1-x}Nb_xO_3$ series. The temperature dependence of relative dielectric constant is shown in Figure 3. Here we observe two things: 1. at the respective Curie points the values of the dielectric constant is very high in these crystals, their range is between 10,700 to 14,457; and 2. the Curie point increases as x in charge increases. In this figure, the values of x represent the original charge compositions. The important parameters for our KTN crystals are presented in Table IV. Photograph III shows one of our KTN crystals.

Table IV

Some Ferroelectric Properties of KTN Crystals

Growth Temperature [°C]	**Charge Composition**	**Crystal Composition** (estimated)	**Curie Point,** T_c[K]	$\epsilon_{r,amb}$	ϵ_{r,T_c}
1211	x=0.6	x=0.95	198	1.586	14,457
1185	x=0.7	x=0.77	249	4.153	10.700
1165	x=0.725	x=0.66	328	5,916	14,100

II.3 K-doped Pb-niobate, $Pb_3Nb_4O_{13}$

This is one of the members of the $PbO{\cdot}Nb_2O_5$ series [13]. Its stoichiometric composition can also be expressed as $3PbO{\cdot}2Nb_2O_5$. Though it has been known to exist for a long time, this composition was neither synthesized previously in single crystals nor ferroelectricity was found in this material. During the search of suitable thermal conditions for the growth of PKN with x = 0.2 using the self fluxing technique, we could synthesize the single crystals of $Pb_3Nb_4O_{13}$. When the initial charge has the following compositions, this material precipitates in single crystals both by static and dynamic slow cooling techniques:

$$PbO : Nb_2O_5 \ = \ 1.5 : 1 \quad \text{by mole}$$

$$K_2CO_3 : Nb_2O_5 \ = \ 1.5 : 1 \quad \text{by mole}$$

That is,

$PbO : K_2CO_3 : Nb_2O_5 = 46.57{:}7.21{:}46.22$ by weight.

The melting point of this material is about 1235°C and it solidifies at approximately 1220°C. When slow cooling is done at the rate of 1-2°Ch^{-1}, single crystals synthesize by spontaneous nucleation.

The crystals can be recovered by dissolving the flux in dilute HNO_3. The crystals are transparent and yellow, but they are rarely larger than 0.5 x 0.5 x 0.5 cm^3 in size. However,

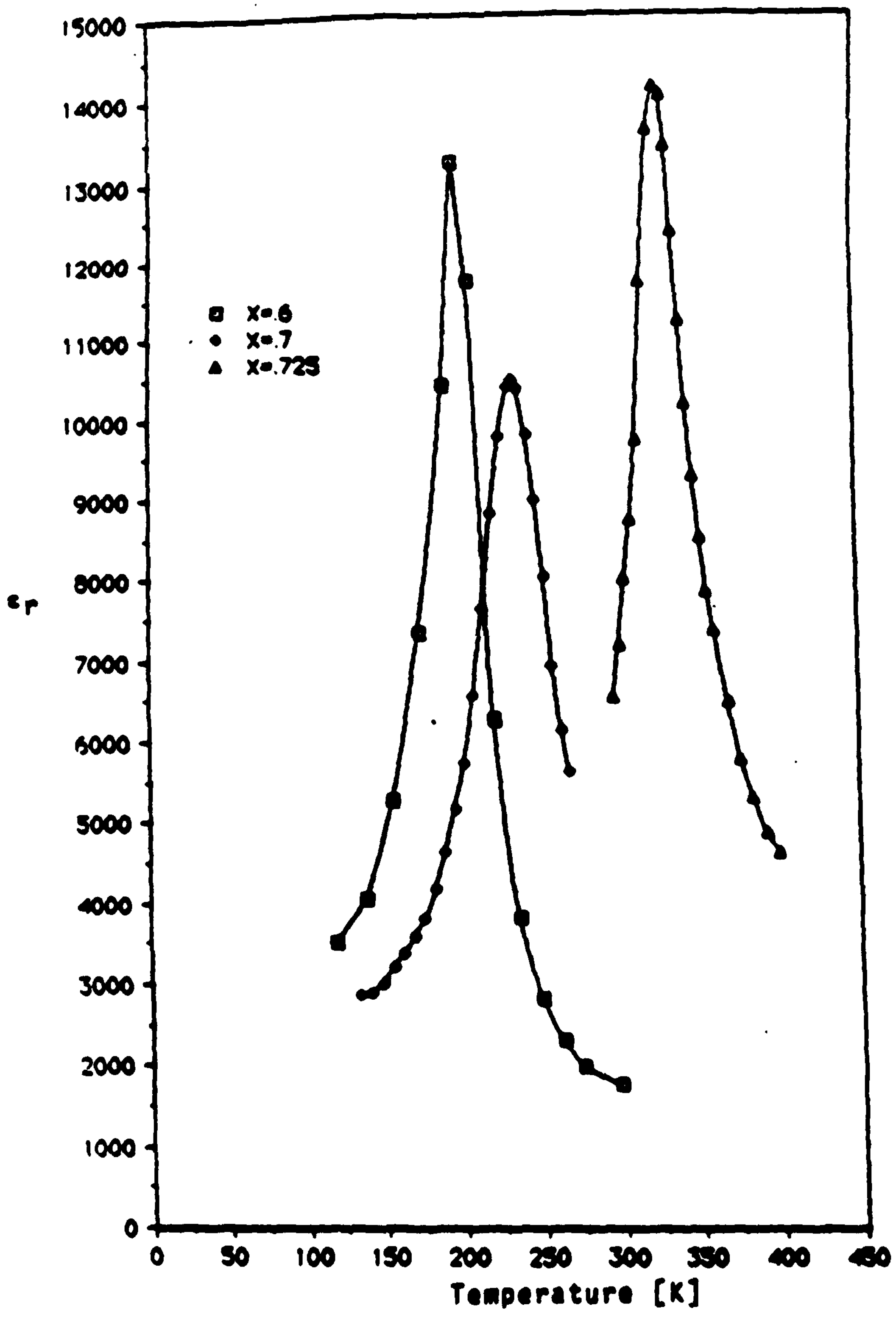
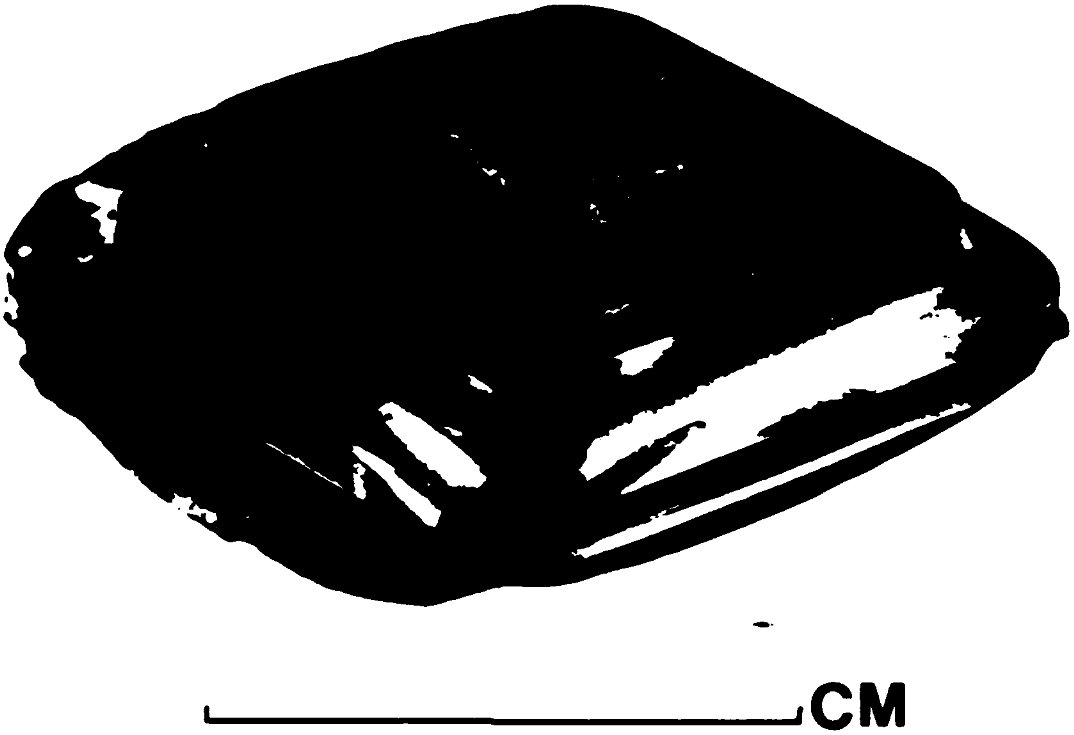


Fig. 3 Dielectric Constant (ε_r) vs Temperature of $KTa_{1-x}Nb_xO_3$



III. K-Ta-niobate, $KTa_{1-x}Nb_xO_3$, crystal both quality and the size show a remarkable improvement when the accelerated crucible rotation technique (ACRT) is employed in the growth process. In our experiments, the maximum rotation rate of 22 rmp and the period (for ACRT) of 3 minutes were found to be most effective. One of the ACRT grown $Pb_3Nb_4O_{13}$ crystals is shown in the photograph IV.

In the phase diagram of $PbO\cdot Nb_2O_5$ [13] one finds the $3PbO\cdot 2Nb_2O_5$ phase, which is pyrochlore in structure, to coexist in a wide range with other phases. But it precipitates as the single phase when the charge composition given above is used for the crystal growth.

So far as ferroelectricity is concerned in the $PbO\cdot Nb_2O_5$ system, only lead metaniobate ($PbNb_2O_6$) and $PbNb_4O_{11}$ are found to be ferroelectric, whereas antiferroelectricity is present in Pb-pyroniobate, $Pb_2Nb_2O_7$. But in the single crystalline sample of $Pb_3Nb_4O_{13}$ we have found conclusive proof of the existence of ferroelectricity. The results are now discussed here.

Figures 4 and 5 present the thermal behavior of dielectric constant (ϵ_r) and a.c. conductivity (σ) of this material. The existence of two Curie points–first at 1°C and the other at 393°C–is extremely important. The presence of the lower Curie point is confirmed also by the σ vs temperature measurement. However, the higher transition point is not detected in the conductivity measurement. Nevertheless, the existence of ferroelectricity in this material is certainly important so far as the basic understanding of the phenomenon is concerned. As reported in reference [14], the structure of this compound is fcc with $a_o = 10.561Å$. This structure does not allow non-centro-symmetry which is a necessary condition for the occurrence of ferroelectricity. A thorough investigation of the determination of its structure has been undertaken (Prof. A. Clearfield, Chemistry Department, Texas A&M University). We have found the existence of superlattice which would allow the structure to be asymmetric. The investigations are being carried out presently and a complete understanding of the structure will be available in a month or two. Then only we will be able to understand the origin of ferroelectricity in $Pb_3Nb_4O_{13}$. It is believed that K^{+1} is responsible for superlattice. In our previous work on x-ray diffraction [14], the presence of K-ion in this material could not be detected. Subsequently, we could detect K in $Pb_3Nb_4O_{13}$ crystal by using EDAX analysis. However, we have not

IV. Pb-niobate, $Pb_3Nb_4O_{13}$ doped with K, crystal

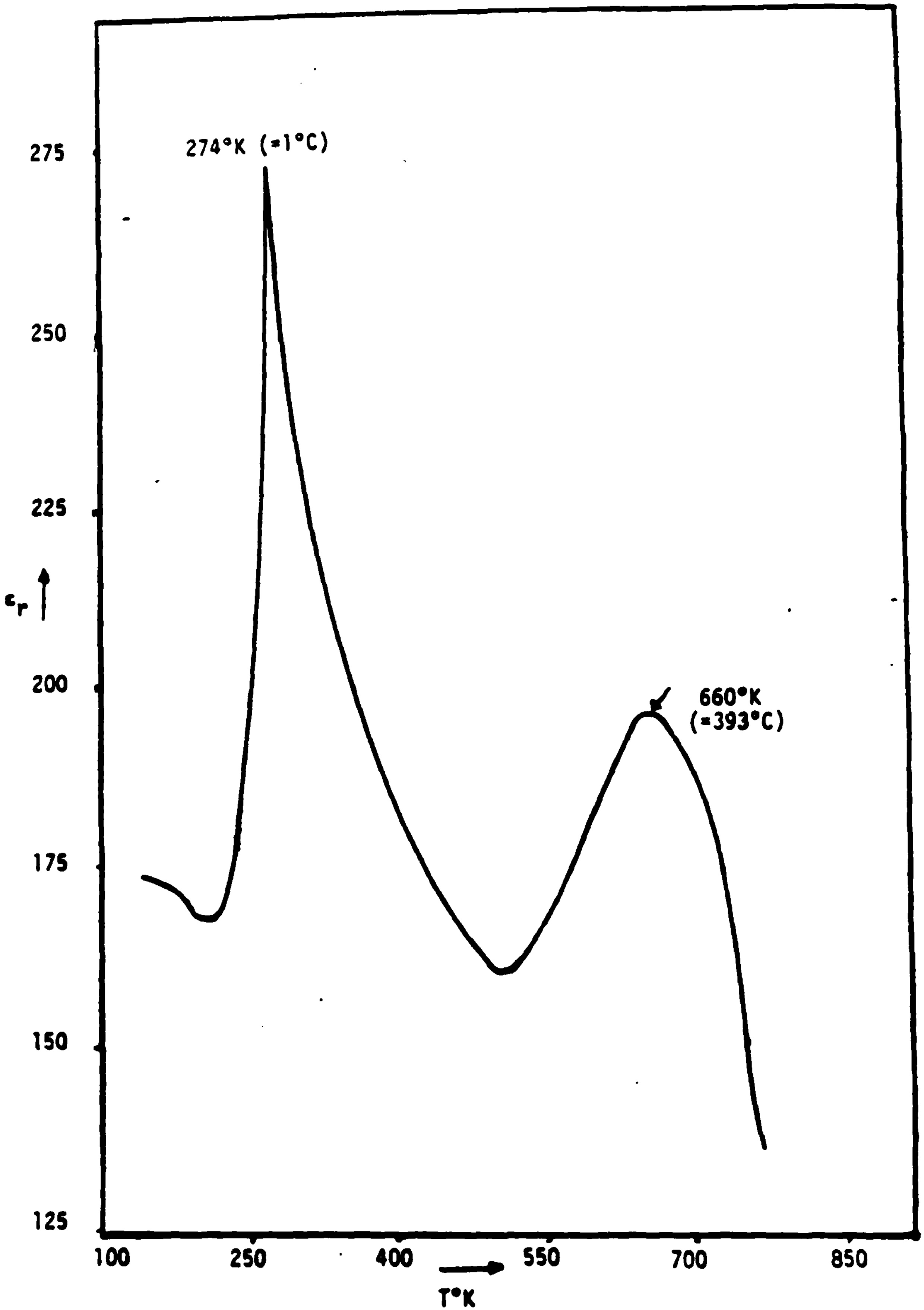


Fig. 4 DIELECTRIC CONSTANT VS. TEMPERATURE OF LEAD NIOBATE, $Pb_3Nb_4O_{13}$

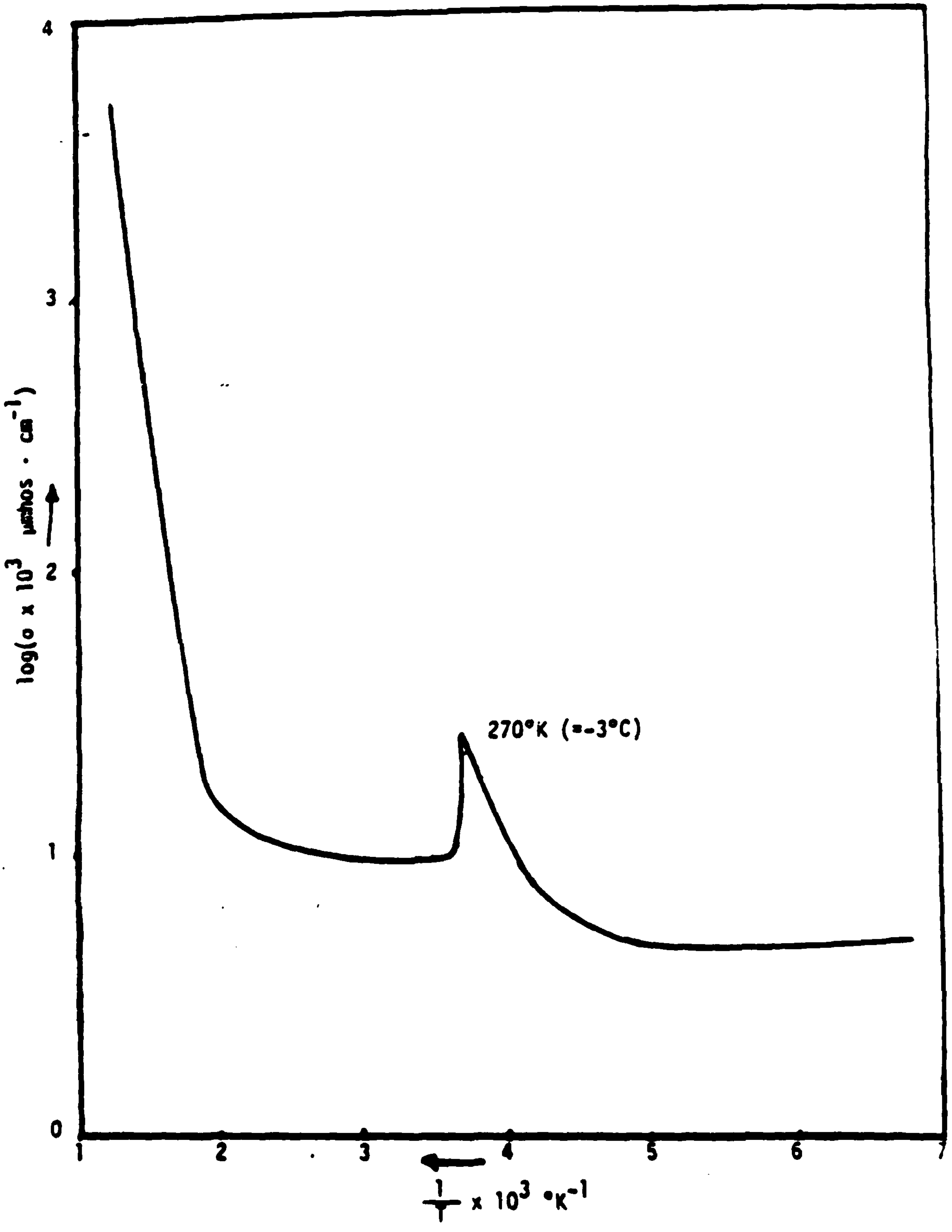


Fig. 5 ELECTRICAL CONDUCTIVITY VS. TEMPERATURE OF LEAD-NIOBATE, $Pb_3Nb_4O_{13}$

yet determined its amount. But it is believed that the crystal is uniformly doped with K^{+1}. This material appears to be an important material for further research. Its crystal quality, transparency and high dielectric constant could make it suitable for some applications. The steep rise in the conductivity at higher temperatures as shown in Fig. 5, leads one to believe that the onset of extrinsic semiconduction effect is perhaps responsible for overriding the ferroelectric effect in σ vs temperature behavior. In Table 4, we present the comparison of Pb-niobates with respect to structure and ferroelectricity.

Table V

Structure and Ferroelectricity of Pb-niobates

COMPOUND	STRUCTURE	NATURE	TRANSITION POINT°C
1. $PbNb_2O_6$	Orthorhombic, Tungsten Bronze	Metastable	560
2. $PbNb_4O_{11}$	Orthorhombic or Tetragonal	Ferroelectric	660
3. $Pb_2Nb_2O_7$	Rhombohedral, Pyrochlore	Antiferroelectric	-259
4. $Pb_3Nb_4O_{13}$	Pyrochlore Structure FCC; a_o=10.561Å Evidence of superlattice and K^{+1} doping	Ferroelectric	-1 and 393

III. SUMMARY

Important ferroelectric crystals like PKN and KTN can be grown to satisfy the requirements of device engineering. Pb-K-niobate crystals are very difficult to grow without multiple cracks in the boules. Here it has been shown how this serious problem can be prevented by adopting some new techniques for the crystal growth. We have not only succeeded in the synthesis of the well known PKN crystal of the type $Pb_{0.8}K_{0.4}Nb_2O_6$ rather we have also found four new ferroelectric members of the $Pb_{1-x}K_{2x}Nb_2O_6$ family: i.e. single crystals with x = 0.23, 0.34, 0.43 and 0.50. All these samples have fairly high values of dielectric constants. Temperature and composition dependence of some important properties have also been studied for all these crystals of PKN. The best quality single crystals of KTN have been synthesized using the isothermal mass transport technique and by maintaining a positive O_2-pressure in the growth chamber. Three different compositions of KTN crystals have been grown by this method. Their ferroelectric properties are also discussed in this report. This research is in progress in our laboratory and we are investigating the possibilities of: 1. growing optical quality PKN with no compositional gradient; and 2. synthesizing KTN crystal with the Curie point at 25°C. Besides PKN and KTN some amount of work was also done in growing single crystals of Pb-niobate pyrochlore of the type, $Pb_3Nb_4O_{13}$. By using self-fluxing charge single crystals of this material was grown by high temperature solution growth (HTSG) method. The best results were obtained using the ACRT (accelerated crucible rotation technique). When doped with K^{+1} this material exhibits ferroelectricity and it is believed that the formation of superlattice in the pyrochlore structure introduces asymmetricity in the lattice which in turn causes ferroelectricity in this material.

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