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GROWTH OF KTN SINGLE CRYSTALS

Jack A. Rubin

Ceradyne, Incorporated

Prepared for:

Air Force Cambridge Research Laboratories

May 1973

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by

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Nadik Industries
(now identified as CERADYNE, INC.)
8948 Fullbright Avenue
Chatsworth, California 91311

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Contract Monitor: Charles Sahagian
Solid State Sciences Laboratory

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The best KTN crystals were grown at 1230°C * from a 200 cc melt prepared from 343 g K_2CO_3 , 358 g Ta_2O_5 , 358 g Nb_2O_5 , and 0.61 g SnO_2 (i.e., 53.5 m/o K_2O ; 17.4 m/o Ta_2O_5 ; 29.1 m/o Nb_2O_5 ; and 0.1 m/o SnO_2 or $\text{K}(\text{Ta}_{0.38}\text{Nb}_{0.62}\text{Sn}_{0.001})\text{O}_3$ + 15% excess K_2O) using a top-seeded, steady-state-gradient flux technique.

Crystals as large as 50mm x 50mm x 10mm were grown. The crystals were pale blue when grown in Pt-3.5Rh crucibles and colorless when grown in Pt crucibles. Oxygen, air, or argon atmospheres had no significant effect on the crystal color. KTN grown in this study contained large clear areas and were reproducible in quality, but still suffered from flux inclusions and striations.

It was recommended that (1) the K-Ta-Nb-O system be studied; (2) incremental pulling be investigated; (3) a controlled composition nutrient should be employed; (4) further use of additives should be looked into to eliminate flux inclusions; and (5) possibly other compositions in the KTaO_3 - KNbO_3 system should be investigated.

* Furnace temperature

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I. INTRODUCTION

KTN is a single crystal ferroelectric consisting of a particular solid solution of potassium tantalate, KTaO_3 , and potassium niobate, KNbO_3 . The specific composition for KTN is 65 mole per cent KTaO_3 and 35 mole per cent KNbO_3 which can be expressed as $\text{KTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$.¹ The abbreviated form for this specific composition, KTN, is derived from the first letter of the chemical symbols of each metallic element in the composition. Thus the K for kalium, i.e., potassium (K), the T for tantalum (Ta), and the N for niobium (Nb).

The solid solution composition, KTN, has a curie point near room temperature. Since the room temperature dielectric constant of KTN is very large ($\epsilon > 10^4$), it has a very large room temperature electro-optic effect. It also exhibits low electrical losses and a large saturation polarization. These factors coupled with the very large room temperature electro-optic effect allow many applications possible which were previously not feasible.¹

Since the electro-optic effect in KTN is quadratic (Kerr effect), a dc bias can be used to produce an effective linear transverse electro-optic effect that can easily be made several hundred times larger than that in a material such as ADP (ammonium dihydrogen phosphate).¹

Some of the outstanding potential applications for KTN are:

- . Polarization modulator¹
- . Amplitude modulator¹
- . Digital light deflector¹

- . Baseband light modulator¹
- . Light scanner¹
- . Microwave modulator²
- . Beam deflector^{3,4}
- . Light modulator^{3,4}
- . Optical polarization switch⁵
- . Variable delay line^{6,7}
- . Parametric amplifier^{6,7}
- . Energy storage device^{8,9}
- . Laser beam modulators^{10,11,12,13}
- . Prism deflectors¹⁴
- . Gradient light beam deflector¹⁵
- . Holographic electro-optic modulators
and beam deflectors¹⁶

These applications all require large, optically perfect, homogeneous single crystals of KTN. The growth and perfection of KTN is the subject of this program. This phase of the study examined the mechanism of the growth of KTN single crystals from melts containing excess K_2O and looked into the variables that effect the growth process and the perfection of the crystals.

II. PREVIOUS WORK

Many investigations have been carried out on the growth of KTN single crystals. Triebwasser^{17,18}; Bonner, Dearborn, and Van Uitert^{19,20}; Wilcox and Fullmer²¹; Denton⁶; Sal'nikov and Zhelankin²²; Gentile and Andres^{23,24}; Smakula²⁵; Fay and Alford²⁶; and Fukuda, Hirano and Koide²⁷

have reported on attempts to grow KTN single crystals from a melt. Hill, Harker and Chang^{28,29}; Shternberg, Lapsker and Kuznetsov³⁰; and Marshall and Laudise^{31,32} have reported on attempts to grow KTN single crystals hydrothermally.

However, very little information on detailed growth techniques is available. None of the previous investigations seemed to be aimed at providing a reproducible method of growing KTN single crystals with specific, well characterized properties.

The greatest variability which is reported in the above literature is the color of the crystals. Completely colorless crystals and crystals which contain uniform, zoned, striated, patchy, banded, shaded, and distinctly separated regions of color have been observed. The colors most frequently mentioned are "water white" (i.e., colorless), white, yellow, blue, and brown. The color ranged in shade from very pale to very intense, and from clear to opaque.

This investigation was undertaken in order to investigate a reproducible method for producing KTN single crystals and to explore the variables which affected the color and other properties of KTN.

III. EXPERIMENTAL PROCEDURE

A. Preparation of the Melt

The charge for the growth of the KTN single crystals was prepared by carefully weighing out the following powdered ingredients:

K_2CO_3 (J.T.Baker, Reagent No.3012)....343 g.

Ta_2O_5 (Kawecki Chem. optical grade)...358 g.

Nb_2O_5 (Kawecki Chem. optical grade)...358 g.

This batch yielded approximately 950g of melt which was empirically determined to fill a 200 cc platinum or platinum alloy crucible (Englehard Type 202, reinforced rim and bottom).

This method of preparing the mix was chosen as it eliminated the possibility of being off-composition due to poor mechanical mixing of the starting ingredients. It also allows very small amounts of additives to be added to the melt in precisely known quantities, e.g., 0.61g of SnO_2 to 950g of mix.

The weighed powders were added to the crucible in small increments. The crucible, with its contents, was then placed in a silicon carbide resistor-element box-furnace held at approximately 1250°C and containing a flowing oxygen atmosphere (5 cfh) until the H_2O and CO_2 were eliminated from the charge producing a homogeneous melt. This procedure was repeated until all of the batch was melted. The furnace was then shut off allowing the melt to solidify in the furnace under flowing O_2 . If any additives were to be used, e.g., SnO_2 , they were carefully weighed out and then placed on the top of the frozen melt. If the melt was not going to be used immediately it was stored in a desiccator to avoid pickup of CO_2 and H_2O by the K_2O formed during the decomposition of potassium carbonate.

B. Growth of Crystals

1. Apparatus

The crystal growing apparatus is shown diagrammatically in Figure 1.

The platinum crucible is situated in the furnace and is held by a McDanel AP 35, alumina ceramic support. (Note: The ceramic support was found necessary because the high specific gravity of the melt caused the platinum crucible to deform or "stretch", the liquid level to drop in the crucible, and the seed to actually leave the melt). The furnace is a Marshall unit with a Kanthal A-1 resistance heating coil. The furnace is 5" ID x 14" OD x 20" in length. The power is supplied by a West Model PSCR-27-240, 6.5 KVA, 240v AC SCR (silicon control rectifier). It is delivered to the crystal growing furnace through a Crittenden (Div. of Teledyne) 4 KVA step-down transformer (240v to 77v AC). The temperature is controlled by a West digital proportioning unit (Model Y) which drives the SCR. The furnace temperature is sensed by a Pt/Pt-10 Rh thermocouple (T/C) located in the center of the furnace. The temperature elsewhere in the furnace and in the melt is sensed by a manually held Pt/Pt-10 Rh T/C swedged in MgO and contained in a 0.060" dia Pt sheath (T/C manufactured by SEMCO, 11505 Vanowen Street, North Hollywood, California). The output of the T/C is read on a portable potentiometer.

The seed crystal is held in jaws formed from the split ends of a Pt-10 Rh rod (1/8" in dia x 13 1/8" long). The seed crystal is fastened to the rod by winding .020" Pt wire around the top of the seed, which has been grooved in two places to correspond with two grooves in the split end of the rod. The typical size of the seed is 5mm wide x 3mm deep x 17mm long. The Pt alloy rod is held by slipping it into a hole drilled into the end of a 12 1/8" long x 3/8" dia stainless steel rod. The stain-

less steel rod is securely held in place by a Jacobs chuck (Model 633c, capacity 0-1/2") on a modified Clausing (Model 1763) 15" floor model drill press. (The drill press was modified by attaching the spline shaft to a Bodine motor (Model NSH-12R) through an elastic coupling. The direction of rotation and speed of the motor were controlled by a Minarik Electric Co. (Model No. SH-12) unit.) Aluminum radiation shields were placed between the chuck and the furnace to prevent overheating of the rotating mechanism. No other coolant was used. The top of the furnace was closed with plates and bars of Korundal XD refractory, (Harbison-Walker Co.), to yield a Vee-shaped opening approximately 110mm long and 30mm wide (this opening was reproduced in every run).

2. Method

As will be explained later, this procedure must be explicitly followed to insure reproducible growth conditions.

a. The seed is placed in the cold furnace and rotated at 50 rpm at approximately 1-1/2" above the surface of the frozen melt which is contained in the platinum crucible.

b. The power is turned on and the furnace brought up to temperature in approximately 2-1/2 hours.

c. The furnace temperature is held at 1260°C for 24 hours to: (1) allow thermal equilibrium to be reached, and (2) to insure that a homogeneous melt is formed.

d. The furnace temperature is then reduced

to approximately 1230°C and allowed to soak for 1/2 to 1 hour to reach equilibrium.

e. The seed is then inserted in the melt whereupon growth takes place.

f. The crystal is then allowed to grow for normally 4 to 10 days.

g. At the end of the growth period the crystal is slowly removed from the melt while it is still rotating at 50 rpm until it is approximately 1-1/2" from the top of the melt.

h. The furnace power is then turned off and the crystal allowed to cool in the furnace while still rotating at 50 rpm.

i. The cool crystal is then removed from the Pt alloy rod and washed in distilled H₂O to remove any adhering melt.

If the same composition of melt is to be used for the next run, then all that is necessary is to weigh the resulting crystal and then add back to the melt ingredients equal to the amount of KTN removed. It must be emphasized here that the material added back is equivalent to KTN and not equal to the weight ratios of the starting batch. A typical amount of material to be added back to the melt after a typical 50g crystal has been formed is:

	<u>Batch</u>	<u>Result</u>
K ₂ CO ₃	14.60	- -
K ₂ O	- -	9.93
Ta ₂ O ₅	30.28	30.28
Nb ₂ O ₅	<u>9.81</u>	<u>9.81</u>
TOTAL	54.69	50.02

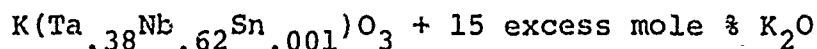
IV. RESULTS

A. Melt Stoichiometry

The best batch composition was:

<u>Material</u>	<u>Mole %</u>
K_2CO_3	53.5
Ta_2O_5	17.4
Nb_2O_5	29.1
SnO_2	0.1

Which corresponds to a liquid of composition:



At approximately 1185°C this should yield a solid composition of approximately "KTN" or $K(Ta_{.65}Nb_{.35})O_3$ (See Figure 4) and a system containing approximately 18% solid and 82% liquid (See Figure 4). This is true, of course, only if the binary system KT-KN is considered. This point will be discussed later.

B. Physical Appearance of Crystals

A typical crystal obtained in this work is shown in Figure 2. The crystals were either square or rectangular in outline with a rectangular or trapezoidal cross section. The crystals were always "blocky" in appearance with occasional square to rectangular protrusions. The edges of the crystals were frequently composed of a series of large right angle steps. The crystals ranged in size up to a maximum of 50mm in width and 10mm in thickness. The width of the crystal was limited by the diameter of the crucible. Diagonal lines were observed in all crystals running from the seed to the corners of the

crystal. At approximately 45° to these diagonals and parallel to the edges of the crystals (001 planes) parallel lines of flux inclusions were found which joined along the diagonal to form a chevron effect. The inclusions, which appeared opaque white to greyish green, were always associated with the diagonals or the "root" of a protrusion. The crystals were transparent pale blue to colorless as grown (except as noted below).

C. Color of Crystals

Crystals which were grown in Pt-3.5% Rh crucibles were pale blue in color, while those grown in pure Pt crucibles were colorless. Also, when a pale blue or colorless seed was used, it always turned golden yellow during the crystal growth period. A freshly grown pale blue crystal could be turned golden yellow by simply allowing it to cool extremely slow in the crystal growing furnace. Bars cut from pale blue crystals could be turned golden yellow by annealing them for approximately 100 hours at 1100°C . This color change phenomenon was independent of atmosphere, as the same effect was obtainable in air, oxygen, or argon. Both pale blue and colorless crystals turned golden yellow upon rapid heating, but returned to their original colors when immediately cooled back to room temperature.

D. Effects of Atmosphere

Crystals were grown in oxygen, air, and argon. No significant differences could be observed in the appearance of the crystals in going from an oxidizing to neutral atmosphere. However, it should be noted that the clearest, most inclusion-free crystal obtained in this study was grown in an argon atmosphere.

E. Cloudy Crystals

During the initial stages of this research, crystals were formed which, although clear and transparent when warm, became cloudy when cooled to room temperature or below. A cloudy crystal of this type would become clear just by allowing it to warm up by grasping it in ones hand. This type of crystal was formed by growing in the temperature range 1100 to 1150°C, especially with niobium-rich systems.

F. Red Deposit

During the early stages of most runs, a red to red-brown solid would form on the cooler parts of the Pt-alloy support rod. This material was extremely soluble in water forming an intense yellow solution. A spectrographic analysis of a typical sample of the material indicated that its composition was approximately:

<u>Element</u>	<u>Wt%</u>
K	50
Pt	7
Ir	3
Na	2
Cr	2
B	2
Rh	.5
Si	.1
Fe	.07
Sn	.06

V. DISCUSSION OF RESULTS

A. Growth Mechanism

The mechanism of growth was believed by some investigators^{17,18,19,20} to be that which is found in the Kyropoulos method, i.e., where the molten liquid is forced to crystallize on a seed which acts as a heat sink and is quite frequently force cooled. (The Kyropoulos method has been used with stoichiometric melts and quite frequently, slow cooling of the melt was also employed. In the Kyropoulos method, it is assumed that the liquid portion is pure liquid and does not contain any solid; the seed crystal and the subsequent new growth representing the solid phase.) However, in this study, probing the melt with a platinum sheathed Pt-10Rh thermocouple, it was learned that the bottom portion of the crucible was filled with solid. The distribution of this crystalline mass is shown in Figure 1. These crystals are believed to be those in equilibrium with the melt at any specified temperature. Because of the high specific gravity of these crystals, they sink in the melt and assume a shape equal to the isotherm of the liquidus curve and a volume equal to the percent solid-liquid obtainable at any specified temperature and composition. This crystalline mass then becomes the "nutrient" for growth of the crystal upon the seed which is at a lower temperature. The mechanism for growth, therefore, becomes the transfer of material from the nutrient through the liquid to the cooler seed by mass transport. This method can best be described as a top-seeded steady-state-gradient flux growth. The composition of the crystal will remain

approximately constant during the growth period except for changes in temperature due to (i) radial and vertical thermal gradients in the furnace, (ii) convection currents in the liquid, (iii) fluctuations in the temperature control circuitry, (iv) change in the geometry of the heat sink as the crystal grows, and (v) change in the stirring action as the crystal changes in shape.

B. Melt Stoichiometry

Since all of the above parameters are dependent on the phase diagram of the system involved, it is important at this time to review the equilibrium system. Figure 3 is a phase diagram obtained by compiling all of the information available in the literature^{33,34,35,36} and combining it into the diagram. It is interesting to note that, according to the solid miscibility gap reported by workers at Tem-Pres Research, Inc.^{28,29}, the composition KTN is not stable below about 800°C, but rather, two solutions are reported to be in equilibrium with each other, therefore, making KTN a metastable phase at room temperature (See Figure 3). A more detailed drawing of the "loop" portion of the diagram is shown in Figure 4. Any composition along the isotherm L_1 -S will yield solid of composition KTN (S) in equilibrium with liquid of composition (L_1). For this work the composition at $\underline{X}$ was used. As stated earlier, this corresponds to the composition 38 mole % KTaO_3 (KT) and 62 mole % KNbO_3 (KN) plus a 15 mole % excess of K_2O (K) (plus a small amount of tin) assuming that phase relations in the binary KN-KT hold. Unfortunately, this may not be altogether true because of the excess alkali in the system. Therefore, the system

$\text{KTaO}_3\text{-KNbO}_3\text{-K}_2\text{O}$ (i.e., KT-KN-K), would best describe the phase relations during crystal growth. The hypothetical $\text{KTaO}_3\text{-KNbO}_3\text{-K}_2$ prism in the system $\text{Ta}_2\text{O}_5\text{-Nb}_2\text{O}_5\text{-K}_2\text{O}$ is shown in Figure 5. A vertical slice through this hypothetical prism at the KTN composition is shown in Figure 6. The letters L_2 and S in Figure 6 correspond approximately to the same letters in Figure 4. It can be seen from Figure 6 that the addition of excess K_2O (i.e., K) to the KT-KN system would most probably extend the liquid-plus-solid region and increase the temperature range over which crystals could be grown. This condition most likely modifies the compositions of the solid solutions shown in Figure 4, so that only an approximate composition can be initially deduced from the published diagrams.

C. Physical Appearance of Crystals

The flux inclusions observed along the diagonals of the approximately square crystals probably occur when the melt is trapped on the large growth steps of the crystal and covered over by the rapidly growing (100) faces.

The large amount of birefringence observed at the striations of the crystal when observed under crossed polarizers is most likely due to interference of the light by areas of varying indices of refraction and Ta/Nb ratios^{12,23,26,37}. These changes in composition are normally related to small cyclical variations in temperature at the growth site. This change in temperature is most likely caused by convection currents formed in the melt because of the impressed temperature gradients. Separation of two immiscible solid phases may also be considered as a source of the areas of variable composition and

indices of refraction^{28,29}.

D. Color of Crystals

Since the pale blue color was only observed in the crystals grown in the Pt-3.5 Rh crucible, it is assumed that the coloration is due to the substitution of rhodium for either tantalum or niobium in the perovskite lattice. Rh^{3+} has an ionic radius ($.68\text{\AA}$) approximately the same as Nb^{5+} ($.69\text{\AA}$) and Ta^{5+} ($.68\text{\AA}$). The uncompensated substitution of Rh^{3+} in a Nb^{5+} or Ta^{5+} site would result in a defect structure, probably causing the pale blue coloration. (Other platinum group ions, e.g., Ir^{4+} ($.68\text{\AA}$), Ru^{4+} ($.67\text{\AA}$), Pd^{4+} ($.65\text{\AA}$), and Pt^{4+} ($.65\text{\AA}$)³⁸ could also substitute for Nb^{5+} and Ta^{5+} .)

Upon annealing at high temperature, the change in color from colorless or pale blue to golden yellow is probably the rearrangement of the electronic configuration within the lattice. However, the role of impurity ions and tin oxide on this color change cannot be overlooked. The cause for the reversible change in color of KTN from either pale blue or colorless to golden yellow upon heating is not known at this time.

The reported formation of blue and brown crystals in melts containing excess potassium probably may be explained by the solubility of platinum and other noble metal impurities (especially rhodium and iridium) in K_2O and their eventual incorporation into the crystal. A gradation in color might be explained by an initial high solubility which is then greatly reduced as K_2O is volatilized from the melt or a depletion of rhodium and

other platinum group impurities from the surface of the crucible in contact with the melt.

E. Effect of Atmosphere

The literature presents a rather confusing picture on the effect of atmospheres on KTN. Most previous investigators have stated that the presence of an oxygen-containing atmosphere is absolutely vital to obtain a transparent crystal^{19,23,24}. The oxygen-containing atmosphere is claimed essential by the previous workers whether a tin oxide additive has or has not been employed^{19,23,24}. However, this work has shown that any atmosphere from oxidizing to neutral or inert will produce transparent crystals. The lack or presence of tin oxide in the melt did not seem to materially change the appearance of the crystal.

The formation of crystals relatively free of inclusions and other internal defects when grown in an argon atmosphere, may simply be related to the good thermal conductivity of the gas. The higher thermal conductivity would aid in heat transfer and have a tendency to decrease thermal gradients in the growth environment, thus reducing convection currents and other phenomena which are deleterious to crystal growth.

F. Cloudy Crystals

Since crystals which become cloudy at room temperature were those either grown at low temperature or from niobium-rich melts, it follows that these crystals were not "KTN" in composition, but a composition richer in niobium. An examination of Figure 3 indicates that

these compositions would have a curie temperature above room temperature. Therefore, at room temperature, these crystals would exist in the tetragonal ferroelectric form instead of the paraelectric cubic phase. The random formation of ferroelectric domain walls, as the cubic phase transforms into the tetragonal phase, is most likely responsible for the "milky" or cloudy appearance of the crystals. When the crystal is heated above the curie temperature, the domain boundaries disappear and the crystal again becomes transparent.

G. Red Deposits

The yellow to brown to red-brown deposits which form on the seed holder rod were originally believed to be a "complex, higher tantalate-niobate of potassium, possibly the 3:1 ratio"³⁹. However, as the spectrographic analyses performed during the research indicated, no tantalum or niobium was detected in the deposit. The main constituent of the deposit, potassium, has been shown by x-ray powder diffraction to be present as a mixture of KOH, K_2CO_3 , and $K_2CO_3 \cdot xH_2O$. These compounds form by the absorption of H_2O and CO_2 by K_2O which volatilizes from the melt and is probably the first material to condense on the rod. The platinum group metals volatilize from the crucible as either their volatile oxides or some volatile alkali "platinates". It is interesting to note the concentration of iridium in the deposit. Iridium occurs only as an impurity in the crucibles but is preferentially lost because of the high volatility of its oxide. The iron and chromium are probably from the Kanthal heating element. The furnace refractories are probably the source

of silicon, boron, and sodium. However, some of the sodium may have come from sodium impurities in the potassium carbonate starting material. The tin originated as an additive in the melt.

It is interesting to speculate that some of this deposit falling from the rod and back into the melt may be the source of the non-reproducible colors obtained by previous investigators.

Another interesting facet of this deposit is that it shows that an appreciable amount of platinum and other platinum group metals are lost by volatilization from the crucible during crystal growth. This would tend to indicate that the loss in weight of the system attributed to the volatilization of K_2O by others is more likely due to a combined loss of $K_2O + Pt$. In fact, one of the crucibles used in this investigation lost 10% of its initial weight.

VI. CONCLUSIONS

1. The method of growth described herein can best be described as a top-seeded, steady-state-gradient flux growth (rather than modified-Kyropoulos as described in the literature).
2. By carefully controlling the pre-treatment of the melt and the composition of the melt, reproducible KTN crystals can be grown.
3. The KTN crystals grown in this study, even though reproducible in quality, still suffer from problems of inclusions and compositional inhomogeneities.

4. KTN crystals can be grown in atmospheres ranging from oxidizing to neutral.

5. The pale blue produced in this study are attributed to the substitution of rhodium (derived from impurities or Pt-3.5Rh crucibles) for niobium and tantalum in the KTN crystal lattice.

6. The addition of tin oxide to the melt is not important for the growth of KTN.

VII. RECOMMENDATIONS

1. A more detailed phase study should be done on the K-Ta-Nb-O system in order to resolve some of the important questions which plague anyone attempting to grow KTN. For example; What are the thermal anomalies observed when the system $K_2O-Ta_2O_5$ was investigated by IBM?³⁵ Does the large subsolidus miscibility exist in the system $KTaO_3-KNbO_3$ as reported by Tem-Pres?^{28,29}

2. Since the material which initially grows from the seeds contains less imperfections and inclusions than the bulk of the crystal, a growth technique should be investigated where "pure" single crystal material is constantly used as a "new" seed and the crystal raised periodically to produce a bar-shaped crystal rather than the plate-shaped one which is presently grown.

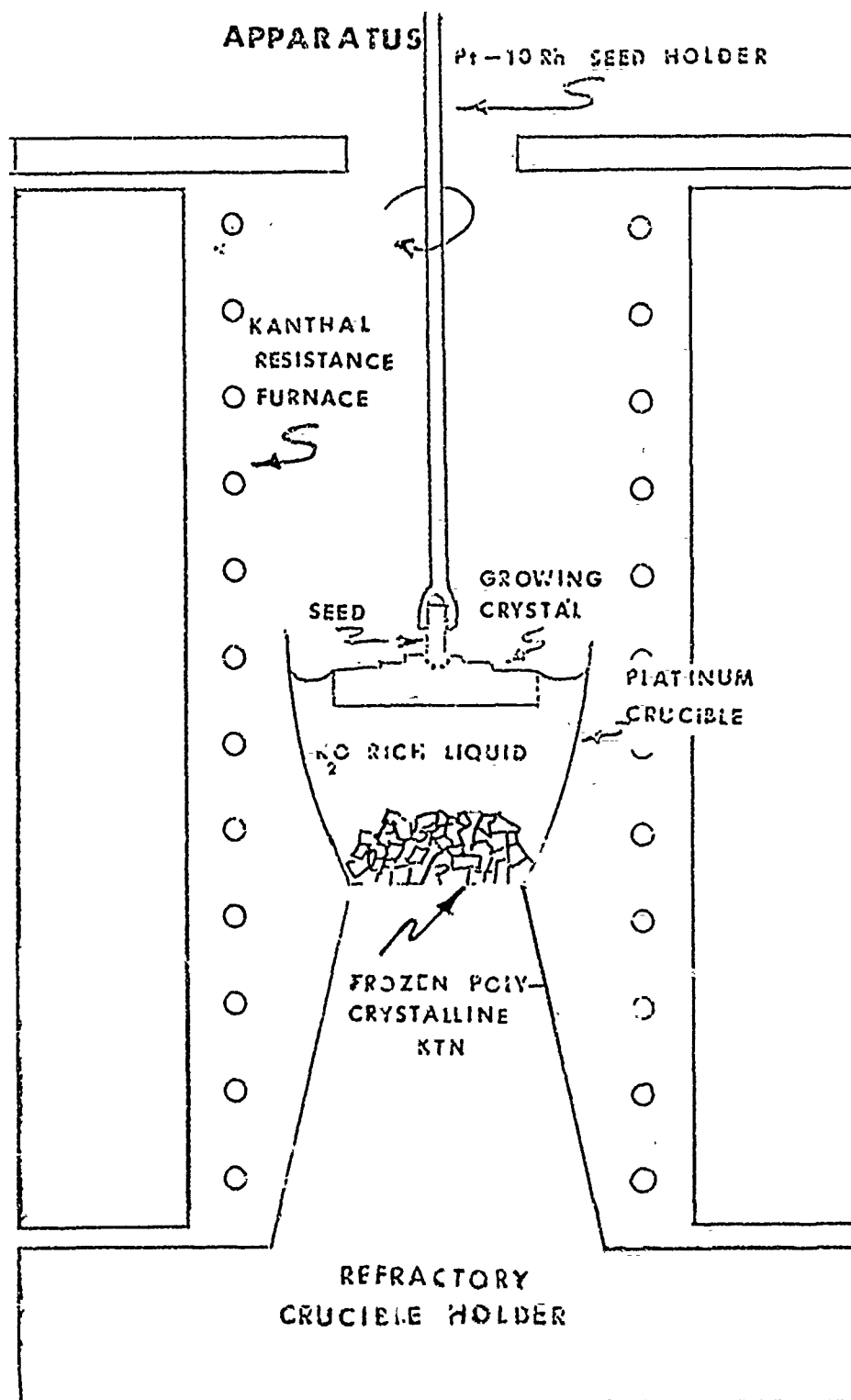
3. Ceramics of KTN composition should be investigated as the nutrient for crystal growth rather than forming the nutrient by the precipitation of KTN from the melt. This should reduce the preparation time and guarantee a more controlled-composition nutrient.

4. A study should be made to investigate the effect of various additives on the elimination of flux inclusions in the crystal.

5. A review of the KTN composition, i.e., 65 m/o KTaO_3 -35 m/o KNbO_3 should be made. This composition was originally selected for use as an electro-optic material because it had a curie temperature at room temperature. This would maximize the electro-optic effect at room temperature. However, at the curie temperature the rate of change of various properties, e.g., dielectric constants, are also maximized. The difference in composition between the solid and liquid is also the greatest near the KTN composition. Therefore, it is recommended that the crystals richer in KTaO_3 for e.g. 80 m/o KTaO_3 -20 m/o KNbO_3 be studied in order to enhance the uniformity of the crystal, while at the same time improving their stability.

FIG. 1

KTN CRYSTAL GROWING



TYPICAL KIN CRYSTAL
(AFCRL KIN VI)

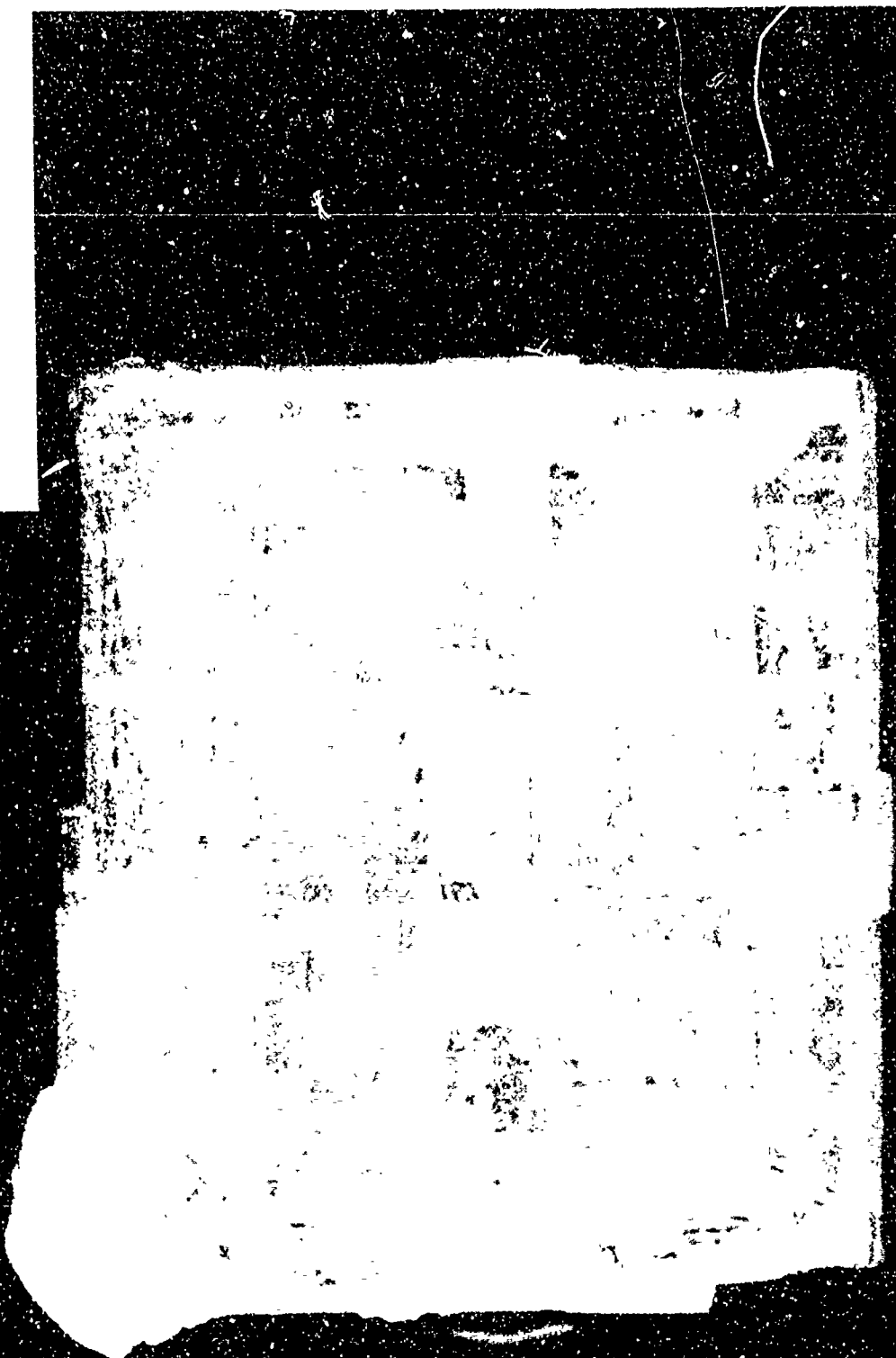
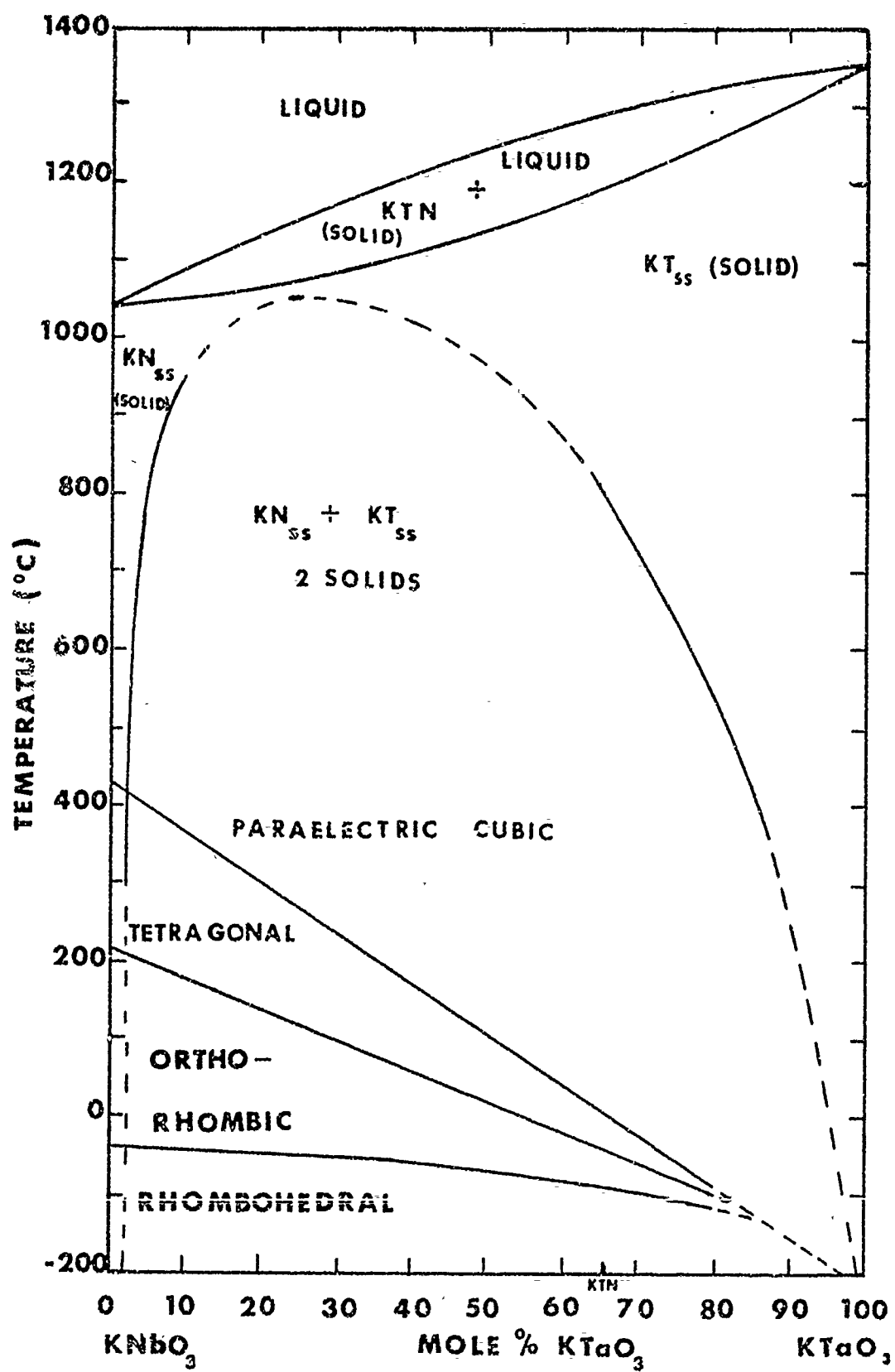


FIG. 3

PHASE DIAGRAM OF THE SYSTEM $\text{KNbO}_3 - \text{KTaO}_3$



SOLID SOLUTION LOOP in SYSTEM KT - KN

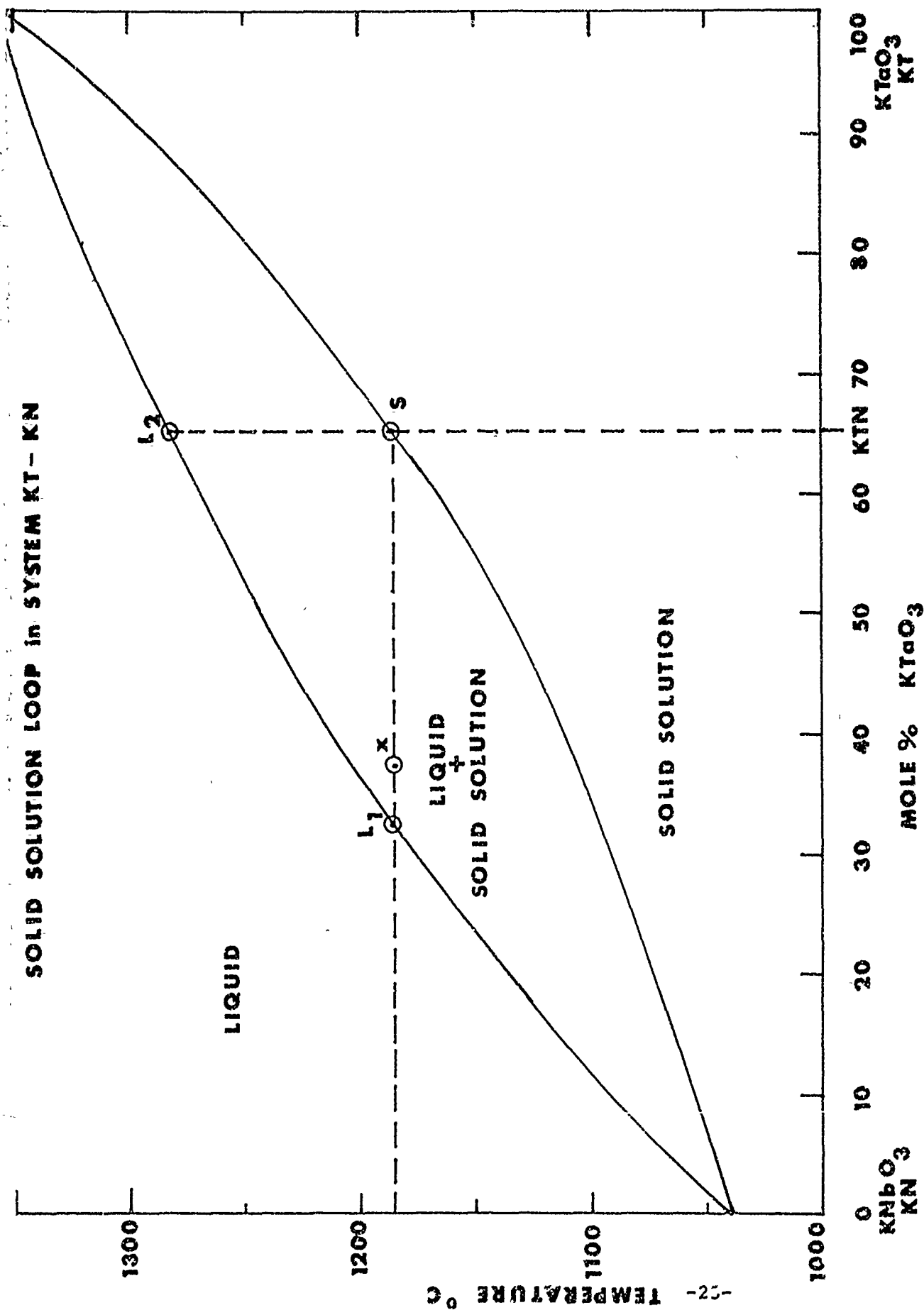
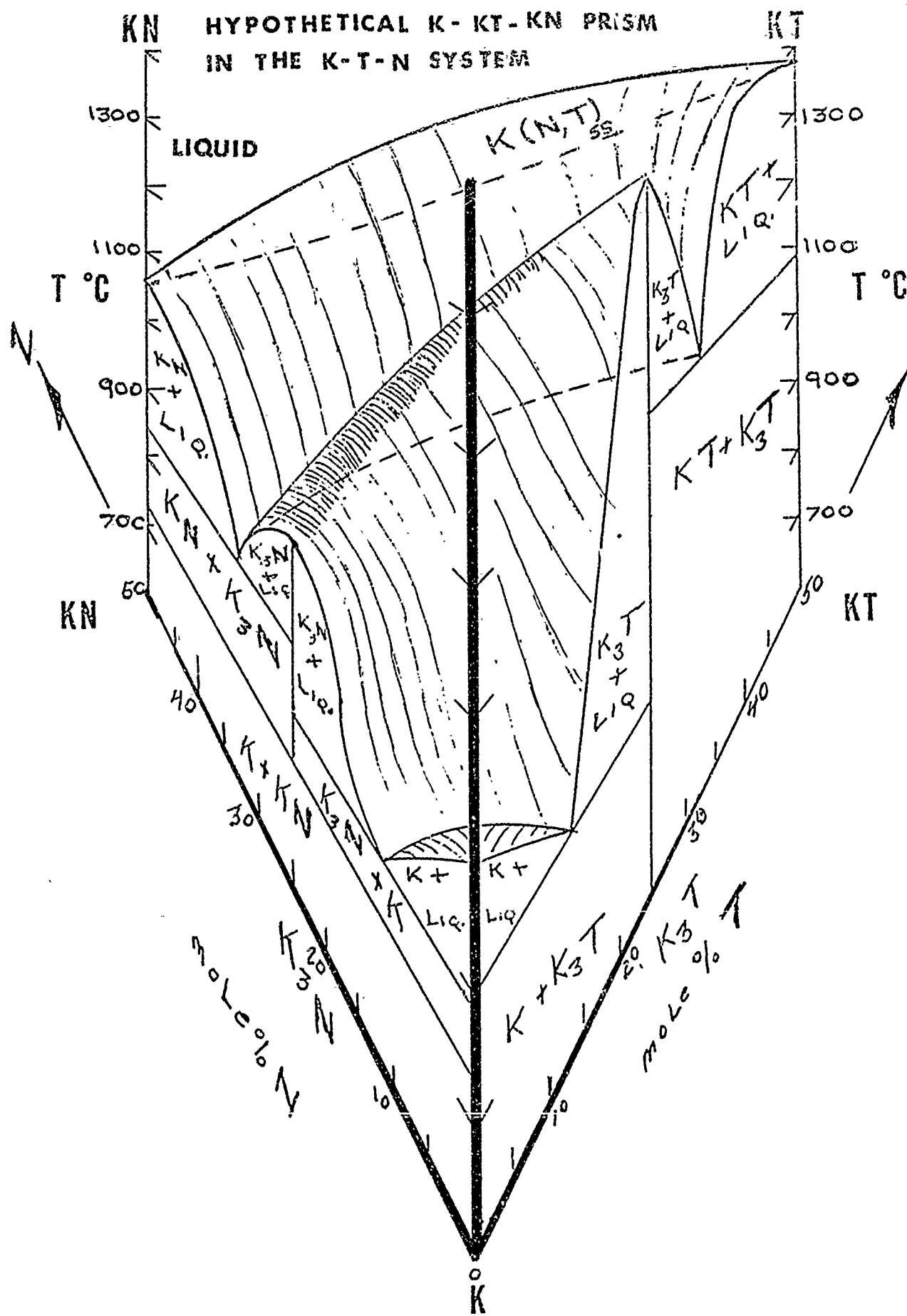
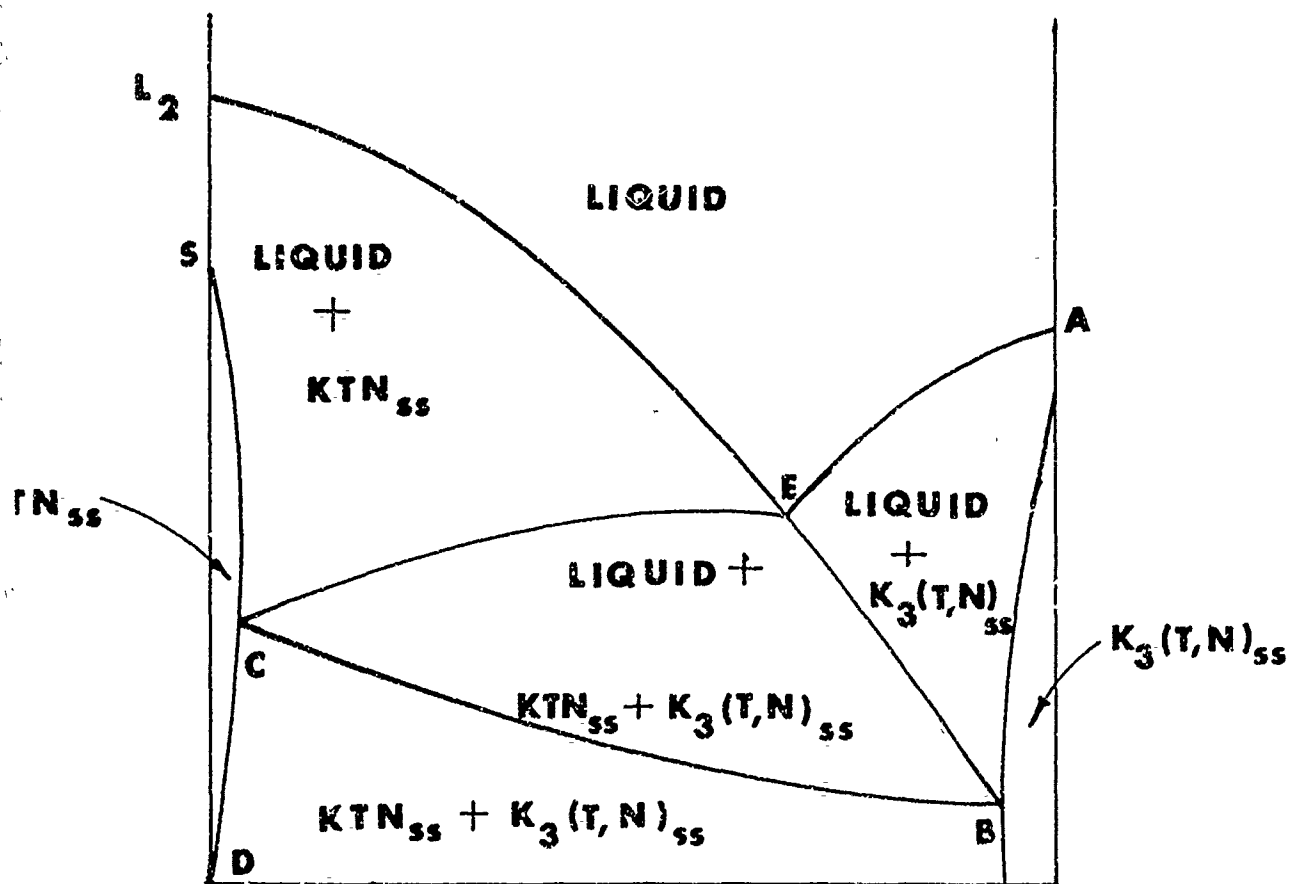


FIG. 5





DIAGRAMMATIC SLICE THRU KT-KN-K SYSTEM
FROM KTN TO $K_3(T,N)_{ss}$

FIG. 6

VIII. LIST OF REFERENCES

1. Geusic, J. E., Kurtz, S. K., Van Uitert, L. G., and Wemple, S. H., "Electro-Optic Properties of Some ABO_3 Perovskites in the Paraelectric Phase", Appl. Phys. Letters 4, 141 (1964).
2. Cohen, M. G. and Gordon, E. I., "Electro-Optic ($\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN)) Gratings for Light Beam Modulation and Deflection", Appl. Phys. Letters, 5, 181 (1964).
3. Chen, F. S., Geusic, J. E., Kurtz, S. K., Skinner, J. G., and Wemple, S. H., "The Use of Perovskite Paraelectrics in Beam Deflectors and Light Modulators", Proc. IEEE, 52, 1258 (1964).
4. Chen, F. S., Geusic, J. E., Kurtz, S. K., Skinner, J. G., and Wemple, S. H., "Light Modulation and Beam Deflection with Potassium Tantalate-Niobate Crystals", J. Appl. Phys., 37, 388 (1966).
5. Kurtz, S. K., "Design of an Electro-Optic Polarization Switch for a High-Capacity High-Speed Digital Light Deflection System", Bell System Tech. J., 45, 1209 (1966).
6. Denton, R. T., "Elastic Wave Devices Utilizing Mixed Crystals of Potassium Tantalate-Potassium Niobate", U. S. Patent No. 3,293,557, Dec. 20, 1966.
7. Kahng, D., Ligerza, J. R., Wemple, S. H., "Crystal Surface Oxidation", French Patent No. 1,460,259, Nov. 25, 1966 (CA 67: 6557S, 1967).
8. DiDomenico, Jr., M., and Wemple, S. H., "Paraelectric-Ferroelectric Phase Boundaries in Semiconducting Perovskite-Type Crystals", Phys. Rev., 155, 539 (1967).
9. Wemple, S. H., Kahng, D., Berglund, C. N., and Van Uitert, L. G., "Surface Barrier Junctions on Semiconducting Ferroelectrics", J. Appl. Phys., 38, 799 (1967).
10. Smakula, P. H. and Claspy, P. C., "The Electro-Optic Effect in LiNbO_3 and KTN", Trans. Met. Soc. AIME, 239, 421 (1967).

11. Van Raalte, John A., "Linear Electro-Optic Effect in Ferroelectric KTN", J. Optic Soc. Amer., 57, 671 (1967).
12. Fay, Homer, "Characterization of Potassium Tantalate-Niobate Crystals by Electro-optic Measurements", Mater. Res. Bull., 2, 679 (1967).
13. Chen, F. S., "A Laser-Induced, Inhomogeneity of Refractive Indexes in KTN", J. Appl. Phys., 38, 3418 (1967).
14. Haas, W. and Johannes, "Linear Electro-optic Effect in Potassium Tantalate Niobate Crystals", Appl. Optics, 6, 2007 (1967).
15. Dugan, A. F., Doyle, W. M., and Sutton, P. M., "KTN Concentration Gradient Light Beam Deflector", Appl. Optics, 7, 556 (1968).
16. Hulme, K. C., "Holographic Correction of Crystals for Electro-optic Modulators and Deflectors", IEEE J. Quantum Electron., 4, 243 (1968).
17. Triebwasser, S., "Study of Ferroelectric Transitions of Solid-Solution Single Crystals of KNbO_3 - KTaO_3 ", Phys. Rev., 114, 63 (1959).
18. Triebwasser, S., "Method of Preparation of Single Crystal Ferroelectrics", U. S. Patent No. 2,954,300, Sept. 27, 1960.
19. Bonner, W. A., Dearborn, E. F., Van Uitert, L. G., "Growth of Potassium Tantalate-Niobate Single Crystals for Optical Applications", Bull. Am. Cer. Soc., 44, 9 (1965).
20. Bonner, W. A., Dearborn, E. F., and Van Uitert, L. G., "Growth of $\text{K}(\text{Ta}, \text{Nb})\text{O}_3$ Single Crystals for Optical and Semiconductor Studies", J. Phys. Chem. Solids, Suppl. No. 1, 437 (1967).
21. Wilcox, W. R., and Fullmer, L. D., "Growth of KTaO_3 - KNbO_3 Mixed Crystals", J. Am. Cer. Soc., 49, 415 (1966).

22. Sal'nikov, V. D., Zhelankin, V. I., "Preparation of Single Crystals of $\text{KTaO}_3\text{-KNbO}_3$ Solid Solutions from a Solution in a Potash Melt", Tr., Vses. Nauch.-Issled. Inst. Khim. Reaktivov Osobo Chist. Khim. Veshchestv., 1967. (3), 415. (CA 69: 39318j, 1968).
23. Gentile, A. L. and Andres, F. H., "A Constant Temperature Method for the Growth of KTN Single Crystals", Mater. Res. Bull., 2, 853 (1967).
24. Andres, F. H., and Gentile, A. L., "Potassium Tantalate Niobate Crystal Growth from a Melt", U. S. Patent No. 3,428,438, Feb. 18, 1969.
25. Smakula, A., "A Study of the Physical Properties of High Temperature Single Crystals", Rept. No. AFCRL-67-0645, Sept. 30, 1967.
26. Fay, Homer and Alford, W. J., "Single Crystal Perovskites as Electro-optically Active Materials", Rept. No. AFML-TR-67-417, Dec. 1967.
27. Fukuda, T., Hirano, H., and Koide, S., "Growth and Electrical Properties of $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ Single Crystals", J. Phys. Soc. Japan, 24, 430 (1968).
28. Hill, V. G. and Harker, R. I., "Development of Hydrothermal Method for Growing Large, High Purity Single Crystals of Beryllium Oxide, and Initiate Research for Growing Single Crystals of 'KTN' and Chrysoberyl", Tech. Rept. No. AFML-TR-66-343, pp. 37-49, Oct. 1966.
29. Hill, V. G., Chang, L. L. Y., and Harker, R. I., "Subsolidus Stability Relations in the System $\text{KTaO}_3\text{-KNbO}_3$ ", J. Amer. Ceram. Soc., 51, 724 (1968).
30. Shternberg, A. A., Lapsker, Ya. E., and Kuznetsov, V. A., "Hydrothermal Synthesis of Potassium Niobate and Potassium Tantalate", Kristallografiya, 12, 957 (1967). English translation: Soviet Physics-Crystallography, Vol. 12, No. 5, March-April, 1968, pp. 838-9.
31. Marshall, D. J. and Laudise, R. A., "The Hydrothermal Phase Diagrams $\text{K}_2\text{O-Nb}_2\text{O}_5$ and $\text{K}_2\text{O-Ta}_2\text{O}_5$ and the Growth of Single Crystals of K(Ta, Nb)O_3 ", J. Phys. Chem. Solids, Suppl. No. 1, 557 (1967).

32. Laudise, Robert A., and Marshall, David J., "Hydrothermal Growth of Potassium Tantalate-Potassium Niobate Mixed Crystals", U. S. Patent No. 3,440,025, April 22, 1969.
33. Reisman, A. and Holtzberg, F., "Phase Equilibria in the System $K_2CO_3-Nb_2O_5$ by the Method of Differential Thermal Analysis", J. Am. Chem. Soc., 77, 2115 (1955).
34. Reisman, A., Triebwasser, S., and Holtzberg, F., "Phase Diagram of the System $KNbO_3-KTaO_3$ by the Methods of Differential Thermal and Resistance Analysis", J. Am. Chem. Soc., 77, 4228 (1955).
35. Reisman, A., Holtzberg, F., Berkenblit, M., and Berry, M., "Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. III. Thermal and X-Ray Phase Diagrams of the System K_2O or K_2CO_3 with Ta_2O_5 ", J. Am. Chem. Soc., 78, 4514 (1956).
36. Garn, P. D., and Flaschen, S. S., "Analytical Application of a Differential Thermal Analysis Apparatus", Anal. Chem., 29, 271 (1957).
37. Gashler, R., and Levy, S. A., "On the Origin of Lamellae in High Resistivity KTN", Mater. Res. Bull., 3, 417 (1968).
38. Green, Jack, "Geochemical Table of the Elements for 1959", Bull. Geol. Soc. Am., 70, 1127 (1959).
39. Andres, F. H., Personal communication.