NASA CR-120949
ISO-5166-72

SINGLE CRYSTALS OF SELECTED TITANATES AND TUNGSTATES

by G. M. Loiacono

ISOMET CORPORATION

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS3-15327

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
CR-120949		

4. Title and Subtitle	5. Report Date
SINGLE CRYSTALS OF SELECTED TITANATES AND TUNGSTATES	June 6, 1972
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
G. M. Loiacono	ISO-5166-72
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
Isomet Corporation 103 Bauer Drive Oakland, N.J., 07436	NAS3-15327
	13. Type of Report and Period Covered

12. Sponsoring Agency Name and Address	13. Type of Report and Period Covered
	Final Report
NASA Lewis Research Center 21,000 Brookpark Road Cleveland, Ohio, 44135	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The compound preparation and crystal growth of a number of mixed titanate compositions was investigated. None of the compounds studied were found to melt congruently and therefore, crystal growth was extremely difficult. Various single crystal preparation methods always resulted in mixed phases from which 1-2 mm size crystals could be separated.

It is concluded from this study that before successful single crystal growth can be accomplished, a detailed study of the phase diagrams in each of the systems of interest must be completed.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Hollandite Type Materials Crystal Growth	

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
		50	

TABLE OF CONTENTS

1.0 Summary

The objective of this study was to prepare single crystals of $BaMgTi_7O_{16}$; $K_2MgTi_7O_{16}$; $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$; $Na_2Ti_6O_{13}$ and $K_2W_4O_{13}$ for investigation of their potential use in ionic conductor applications.

The original program was modified after seven months, to a study of the preparation and confirmation of single phase materials of $BaMgTi_7O_{16}$; $K_{1.75}Mg_{0.875}Ti_{7.125}$ and $Na_2Ti_6O_{13}$.

The basis for the materials examined was the fact that the hollandite group minerals were potentially useful in solid state battery applications. Selection of individual compounds was made by NASA together with suggestions on compound synthesis.

The study was hindered by the lack of information published on these compounds and in many cases the inaccurate data presented in the references available. Under the conditions described in detail in this report, none of the compounds studied were found to melt congruently as had been reported in the literature. Duplication of published experimental methods did not result in confirmation of cited data.

The growth of $BaMgTi_7O_{16}$ from a flux system could be accomplished if solubility data were available. The same is probably true for the potassium analogs. Growth of large single crystals of $Na_2Ti_6O_{13}$ by a melt method does not appear feasible.

It is concluded from this study that before successful single growth can be accomplished, a detailed study of the phase diagrams in each of the systems of interest must be completed.

2.0 Introduction

The original objective of this study was to prepare single crystals of $BaMgTi_7O_{16}$; $K_2MgTi_7O_{16}$; $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$; $Na_2Ti_6O_{13}$ and $K_2W_4O_{13}$. The principal crystal growth methods to be used were the Czochralski, Sealed Bridgman, Flux, and Flame Fusion techniques. Very little published literature exists on the growth of single crystals of mixed titanates and tungstates.[1-8] The program was divided into five tasks each consisting of compound preparation, characterization and crystal growth.

The original program was modified, after seven months, to a study of the preparation and confirmation of single phase materials of $BaMgTi_7O_{16}$; $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$ and $Na_2Ti_6O_{13}$. This report will discuss the results obtained both during the original program and the modified program.

The compounds investigated were selected by NASA to represent a crystallographic structure type known to be potentially useful in solid state battery device applications. The best known compounds are the hollandite group minerals.[9] They are represented by the formula

$$A_xMn_8O_{16}, \quad \text{where } A = Ba^{+2}, K^{+} \text{ or } Pb^{+2}$$

The compounds $BaMgTi_7O_{16}$, $K_2MgTi_7O_{16}$, and $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$, are a special form of the above formula where Mg and Ti both replace Mn.

3.0 Experimental Data

The single crystal growth techniques used in this study are described below. Only those methods of single crystal growth which appear appropriate for the compounds of interest are discussed.

Bridgman Technique

In general, the cooling of a melt in a crucible is controlled in a manner that permits the isothermal surface near the melting point to pass from the bottom of the curcible to its top. When this process is carried out in an ordinary crucible (i.e., flat bottom, cylinder type), many nuclei are formed which grow independently and at random until the entire melt is solidified. This type of process usually yields several crystals, but proper control and design of the apparatus can yield a large single crystal. Figure 1 illustrates a typical apparatus used in the growth of single crystals by the Bridgman method. The apparatus consists of two furnaces in a vertical position, each controlled so that the upper one is above the melting point of the material to be grown, while the lower furnace is below the melting point. Between the two furnaces, a polished platinum baffle provides thermal shielding so that the crucible when slowly lowered, passes through a non-linear large temperature gradient. The melt is contained in a thin walled platinum with a conical bottom placed on a metal seat supported by a metal elevator rod. The crucible can also

be made from high purity graphite or any other material not reactive with the compound to be grown. Figure 2 illustrates some of the crucibles used at Isomet for Bridgman growth. The elevator rod leads to a mechanism designed to lower the crucible at variable speeds. The rod is milled to a diameter of a few millimeters at the upper end which projects through a seal, in order to cool the crucible apex selectively during the initial solidification. Crystallization thus starts at the apex of the cone, and a single crystal is produced, provided the temperature gradient and the lowering speed of the crucible are properly controlled. Crystals grown by this method are usually randomly oriented. For crystals of a preferred orientation, seeds can be placed in the bottom of the crucible at the apex and growth carried out as previously described.

Czochralski Technique

One disadvantage of the Stockbarger method of crystal growth results from the fact that the crystal is growing in a restrained state because the crystal is solidifed in the crucible. All crucible restraint can be removed if the growing crystal is not permitted to come in contact with the walls of the crucible which contains the melt. This can be achieved by starting crystallization at the top and near the center of the crucible, and then raising the crystal at a sufficient speed so that it never grows out to the crucible walls. In this way the complete crystal-melt interface does

not contact the crucible walls. For single crystal growth, orientation of the crystal is controlled by use of a seed of desired crystallographic orientation. In addition, the melt can be easily stirred to give good mixing, by rotating the growing crystal with respect to the crucible. The growing crystal is controlled by adjustment of the temperature and pulling rate. As the temperature of the system is lowered or pulling rate reduced, the crystal diameter increases and if either of these parameters are increased, the crystal diameter will decrease.

Usually only the temperature is varied to control the crystal size because a slow constant pull rate is desirable for high optical quality single crystals. Together with the above parameters, rotation of the crystal while growing permits control of the impurity content of the single crystal. An important consideration in pulling from a crucible is the problem of the latent heat of fusion. This heat flow must be accounted for in order to obtain good single crystals. Usually the latent heat of fusion is conducted away from the solid-liquid interface by the crystal. The efficiency by which this heat is dissipated depends largely on the thermal conductivity of the material being grown. In the Bridgman method, the latent heat of fusion is of no consequence because the crucible and holder conduct all the heat away from the solid-liquid interface very efficiently.

A typical apparatus used in the Czochralski growth of oxides, fluorides and other halides is illustrated in Figure 3. A brief description of the process follows. A suitable crucible to contain the molten material is selected (i.e. one not reactive with the material). The contents of the crucible are melted by either R.F. induction or resistance heating. Once thermal equilibrium is attained, a seed crystal is immersed into the upper portion of the melt and after proper temperature adjustments have been made, it is slowly withdrawn by use of a system of lead screws, gears, and motors. The crystal may be rotated and pulled at variable rates depending on the apparatus design. Temperature control is maintained by use of a temperature sensing element and suitable electronic controls. Single crystals of some materials have been grown in sizes of 50 mm diameter by 30 cm lengths using the above techniques at Isomet.

Flux Technique

The method of growth from a flux has been extensively used when materials have very high melting points, decompose upon melting or undergo phase transitions. The most outstanding feature of this type growth is that very low temperatures can be used in the preparation of single crystals. One major problem is the inclusion of the flux material in the grown crystal. This problem is not too serious in the growth of most materials. Figure 4 illustrates a typical flux growth system. Once a suitable solvent has been obtained for the

material to be grown, crystal growth proceeds completely unattended. The only parameter which is controlled is the rate of temperature decrease. This method is very similar to growth from aqueous solutions except that the solvents in all cases are low melting inorganic or organic compounds. For example, the desired compound has a large solubility in NaCl. A charge is melted in a suitable crucible which contains an excess of the compound - usually enough to supersaturate the solvent at a temperature slightly above the melting point of the solvent. After allowing the molten mass to attain equilibrium and uniform mix, the temperature of the system is lowered at a rate suitable for single crystal growth. This rate of temperature decrease must be experimentally determined for each specific material/solvent combination, but usually falls into the 1^{o} to 15^{o}C per hour range.

Unlike the other two methods of crystal growth described above, this method does not require high precision temperature control during the entire process because crystal growth normally occurs over a temperature range of a few hundred degrees. Once the solvent solidifies, crystal growth has terminated and the system is lowered at rates of 50^{o} to 100^{o}C down to room temperature. The grown single crystals are removed from the flux by dissolving the flux with a solvent which is inert to the single crystal.

Flame Fusion

Basically this method envolves the melting of a powder in an oxygen-nydrogen flame with subsequent build-up of a single crystal. The powdered sample is placed in a hopper and then fed continuously into an oxygen stream which enters the gas burner. Here it is mixed with hydrogen and is ignited. The oxyhydrogen flame is directed on a ceramic rod, composed of the same composition as the material to be grown, and adjusted so the top part of the rod melts. The powder which is fed into the flame melts and impinges on the rod. The rod is slowly rotated and lowered out of the small melting zone. Using careful adjustments of flame temperature, lowering and rotation rates, a single crystal boule will grow. A large number of oxide materials have been prepared by this method including spinels, garnets, etc. Figure 5 illustrates the process.

3.1 $BaMgTi_7O_{16}$

3.1.1 Preparation of Compound

The initial synthesis of $BaMgTi_7O_{16}$ was accomplished by solid state reaction according to the equation:

$$BaCO_3 + MgCO_3 + 7TiO_2 \rightarrow BaMgTi_7O_{16}$$

The compound was mixed, ground, isostatically pressed at 1.37×10^8 N/m^2 and calcined in air at 950°-1000°C for 30 minutes. After this initial firing, the preparation was again ball-milled, compacted and fired at 1200°C, in air, for 2 hours. The starting materials used in the above preparation were Fisher "Reagent Grade" chemicals and had the analysis shown in Table 1.

The final reacted powder was examined by differential thermal analysis (D.T.A.). The data obtained was measured on a R.L. Stone Model LB202 machine. The sample was measured against an alumina reference in air at atmospheric pressure. Pertinent experimental parameters were:

Heating/Cooling Rate - 20°/min.
Sensitivity - 80 μV
Crucible - Pt
Chart Speed - 1.15 cm/min.

Both heating and cooling curves were made on the same sample from room temperature to 1442.7°C (the melting point). No phase transitions were detected. A considerable amount of hysteresis was observed (85°C) upon cooling; indictive of a large degree of supercooling. This type behavior is not conducive to crystal growth by the Bridgman method and makes Czochralski growth quite difficult. The sample used in the

D.T.A. run was examined microscopically in reflected and polarized light. The solidified melt was easily removed from the platinum crucible leaving a bright surface at the contact point. This indicated the absence of reaction between these two materials under the conditions described above. Microscopic examination showed the solidified melt was composed of long columnar crystals, which were transparent and colorless, imbedded in a polycrystalline matrix.

X-ray powder diffraction of both the initial and final $BaMgTi_7O_{16}$ firings are given in Table 2. The data was obtained on a Siemens Diffractometer, Kristalloflex 4, using Mo, Kα radiation at 40KV and 18 ma. A ZrO_2 filter was used. The data obtained were compared with the literature values and the correlation of lines and intensities were extremely poor.[7] The reference cited indicated that the Ba-priderite was prepared by flame fusion but gave no details as to the specific procedure. In view of these findings, a review of the preparation procedure used for this compound was made. Our procedure called for first firing at 1000°C for 1/2 hour followed by a second firing at 1200°C for 2 hours. The use of $BaCO_3$ and $MgCO_3$, as specified in the task outline, was then examined. In the preparation of $BaMgTi_7O_{16}$, we are assuming that the components are reacting at some finite rate and furthermore, we are assuming that the compounds $BaCO_3$ and $MgCO_3$ lose CO_2 at the firing temperatures. This is not

the case, only $MgCO_3$ loses CO_2 at 900°C, while $BaCO_3$ does not decompose until the temperature reaches about 1450°C. This may account for the differences between our x-ray data and that previously published.

Two alternative methods of preparation were attempted. The first method involved high temperature calcination. The components were mixed as previously described, calcined in a platinum crucible, in air, at 1200°C for 15 hours followed by re-mixing and a final firing at 1400°C for 8 hours. The final firing was performed in an oxygen atmosphere. The x-ray powder diffraction data for these samples are given in Table 3 together with the data from the cited reference.[7] Based on calculations performed prior to preparation, a total weight loss, due to the evolution of CO_2, of 10.74 gms. was expected. The actual losses measured were:

1st Firing at 1200°C for 15 hours:

$$0.41 \text{ gms. or } \frac{0.41}{10.74} \times 100 = 4\%$$

2nd Firing at 1400°C for 8 hours:

$$0.66 \text{ gms. or } \frac{0.66}{10.74} \times 100 = 6\%$$

These data indicate that only 10% of the theoretical loss due to CO_2 was observed and that complete compound formation

probably did not occur. Examination of the x-ray data in Table 3 confirms this conclusion.

A second method of preparation was performed as follows:

1. Dissolve 270.12 g. oxalic acid in distilled H_2O. Use only enough water to completely dissolve the acid. After all the acid is dissolved, add 400 ml. of distilled H_2O. The H_2O should be at 70-75°C before the addition of the acid is made.

2. Dissolve 654.9 ml. of $TiCl_4$ in 1310 ml. of distilled H_2O. The H_2O should be cooled so that the temperature rise does not exceed 30°C. The solution should be clear (no hydrolyzed TiO_2 present).

3. Add the $TiCl_4$ solution to the oxalic acid solution. Keep stirring. This will result in the formation of 540 gms. of $Ti_2(C_2O_4)_3 \cdot 10H_2O$.

4. Prepare a solution of $BaCl_2 \cdot 2H_2O$ in distilled H_2O by dissolving 69.6 gms. of $BaCl_2 \cdot 2H_2O$ in 150 ml. of H_2O.

5. Prepare a solution of $MgCl_2 \cdot 6H_2O$ in distilled H_2O by dissolving 57.6 gms. of $MgCl_2 \cdot 6H_2O$ in 100 ml. of H_2O.

6. Mix the Ba and Mg solutions together.

7. Heat the solution of $Ti_2(C_2O_4)_3 \cdot 10H_2O$ to 80^oC and stir well. Add the mixed Ba and Mg solution rapidly. A heavy white precipitate will form. Stir for 1/2 hour.

8. Filter the precipitate, wash twice with distilled H_2O. Air dry the cake for 4 hours then fire at 1000^oC for 5 hours.

This procedure follows what we assumed to be the method of preparation of $BaMgTi_7O_{16}$ by use of $TiCl_4$ as described in the literature, although no process details were stated.[1] The published data did indicate agreement of the x-ray data with that of Norrish.[7]

Table 4 lists the x-ray data obtained for the chemical preparation of $BaMgTi_7O_{16}$ together with that of a flame fusion boule grown from the same material. The match between the reference data and that obtained from chemical preparation agrees quite well.

3.1.2 $BaMgTi_7O_{16}$ Crystal Growth

Three methods of crystal growth were attempted with material prepared by the chemical reaction procedure. Crystal growth by the flame fusion technique was attempted using an oxidizing flame and the chemically prepared powder with

100 mesh size particles. Two dark blue boules were grown by the powder cone method of seeding. Both boules were polycrystalline and measured approximately 5 mm^2 x 10 mm long. One of the boules was annealed in oxygen at 1300°C for 10 hours and resulted in partial re-oxidation. Microscopic examination showed that the outer skin of the boule, to a depth of about 1 mm, was colorless and transparent. Both samples consisted of at least two phases and very possibly three. X-ray data on the grown boule is given in Table 4. Repeated attempts at growth by this method by variations in O_2/H_2 ratios did not result in single phase growth nor improvement over the original two crystals.

Czochralski growth (pulling from the melt) was tried both in argon, air and under oxygen pressure. The first crucible we used was fabricated from platinum based on the relatively low melting point of this compound. Heating under R.F. conditions caused the crucible to melt. Repeated attempts resulted in the same behavior. We then selected an iridium crucible which proved to be suitable for containing molten $BaMgTi_7O_{16}$. Initially nucleation on an Ir wire was attempted to produce seed crystals, but always resulted in polycrystalline boules. Observation of the melt surface during these growth attempts resulted in the identification of an unknown phase being formed which had a different melting point than the bulk melt. Although the phase was removed by

the dipping technique, additional material was constantly being generated from the melt. We attempted to eliminate this behavior by confining the melt under gas pressure. Both argon and pure oxygen were used at pressures up to 3.4×10^5 N/m^2 without success. In all experiments, at least two major phases were formed. It is interesting to note that under an argon atmosphere, colorless to pale yellow crystals were formed the same as in our oxygen experiments. We therefore concluded, based on the x-ray data and growth experiments that under the experimental conditions employed, $BaMgTi_7O_{16}$ does not form a single phase and is not congruently melting. Therefore Czochralski growth cannot be performed.

The last growth method attempted was a modified Bridgman technique using sealed Pt-40% Rh ampules. Use of pure Pt sealed ampules always resulted in reptures regardless of the method of heating employed (R.F. or resistance). Several crystal growth runs were also made using partially sealed small bore Pt/Rh tubes under an atmosphere of pure oxygen at 2.1×10^5 N/m^2. Typically, the furnace was raised to about 1700°C with the ampule being supported by a Pt wire. After a soak period of two hours, the ampule was lowered out of the furnace at a rate between 0.025 mm to 12 mm per hour. In no case was pure single phase $BaMgTi_7O_{16}$ obtained which is consistent with the results of our pulling experiments.

3.2 $K_2MgTi_7O_{16}$

3.2.1 Compound Preparation

The preparation of $K_2MgTi_7O_{16}$ and $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$ will be discussed together with $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$, which was the composition specified in the change in the programs technical direction.

Initially, the preparation of the composition $K_2MgTi_7O_{16}$ was attempted by solid state reaction of the components according to the equation:

$$K_2CO_3 + MgCO_3 + 7TiO_2 \rightarrow K_2MgTi_7O_{16}$$

The components were mixed and processed as described in Section 3.1.1. The reaction temperatures for this compound were 950°-1000° for 1/2 hour for the initial calcination stage followed by a final firing at 1200°C for 2 hours. Air was the ambient atmosphere. Table 5 gives the x-ray diffraction data obtained for this material together with the standard pattern.[8] If one examines the melting points of the individual components used in this preparation, it is apparent that K_2CO_3 melts well below 1000°C, therefore loss of K_2O is very probable. Although this would increase the rate of reaction, the danger of non-uniformity in composition is apparent. An additional preparation technique was formulated which involved an initial calcination at 500°C for 15 hrs. followed by two firings at 1000°C for 15 hrs. and 1200°C for 15 hrs. This process was

performed in air. Table 6 lists the x-ray diffraction data obtained for this preparation. Examination of both Tables 5 and 6 show that neither preparation duplicates the standard reference pattern.

Weight loss measurements of CO_2 were also obtained on the modified preparation method. Theoretically, a total of 15.6 gms. of CO_2 should have been evolved during the process. The actual weight losses measured were:

1st Firing 500°C: 3.17 g. (20.3%)
2nd Firing 1000°C: 4.16 g. (47.0% total)
3rd Firing 1200°C: 0.45 g. (49.9% total)

It is apparent that only 50% of the total CO_2 content was evolved during the firing sequence - assuming all losses were due to CO_2 and Not K_2O evolution. Of this, it can be further assumed that only 33% was due to CO_2 loss from K_2CO_3. Again it is apparent that $MgCO_3$ does not completely react. Both the x-ray data and weight loss data indicate that complete formation of single phase $K_2MgTi_7O_{16}$ did not occur.

The re-direction of the programs technical effort specified only one composition need be prepared, $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$. The preparation was attempted by

two methods. First, the components, K_2CO_3, $MgCO_3$ and TiO_2 were mixed and sieved through a 200 mesh screen. This was followed by a.) calcination at 1000°C for 1/2 hr.

b.) regrind and sieve

c.) isostatically pressed into balls at 1.37×10^8 N/m^2

d.) fired in packing powder at 1200°C for 2 hrs. in air in a closed crucible (Pt)

e.) regrind, resieve, repack and refire.

The packing powder was prepared by mixing the components by the technique described above and adding 5% excess K to the mixture. Samples were taken after each firing and analyzed by x-ray and chemical methods. A modification to this method was also used which involved the same initial processing, as described above, except the firing cycle was:

a.) 1100°C for 16 hrs.

b.) 1150°C for 4 hrs.

c.) 1200°C for 1 hr.

The results will be discussed later in this report.

The second method of preparation involved the initial synthesis of $K_2Ti_6O_{13}$ and $MgTiO_3$. These components were then mixed according to:

$$K_2Ti_6O_{13} + MgTiO_3 \rightarrow K_2MgTi_7O_{16}$$

The following processing procedures were examined:

1a. Mix and sieve both components (200 mesh)
1b. Calcine at 1000°C for 1/2 hr.
1c. Regrind, sieve
1d. Isostatically press at 1.37×10^8 N/m^2
1e. Fire at 1200°C for 2 hrs. in packing powder (of same material).
1f. Regrind, sieve, press
1g. Fire at 1200°C for 2 hrs. in packing powder.

2a. Mix and process as in 1a - 1g except firing temperatures are:

a. 1100°C - 16 hrs.
b. 1150°C - 4 hrs.
c. 1200°C - 1 hr.

3a. The same procedure used in 1 and 2 except packing powder contained 3% excess K.

The chemical analysis and x-ray data for these preparations will be discussed later.

3.2.2 Crystal Growth

A large number of crystal growth runs were made by the flame fusion and Czochralski methods. Neither of these methods produced a single phase product. The flame fusion process resulted in boules of at least three phases - probably due to the loss of K_2O during growth. Both oxidizing and reducing flames were used. We attempted the growth of seed material by nucleation of a Pt/Rh wire by the pulling method. Growth was performed at 30 RPM with a pulling speed of 0.25 cm/hr. The growth chamber was kept at an oxygen pressure of two atmospheres. All boules grown consisted of at least two phases. Table 9 lists the typical composition found by analysis for material prepared by this method. Attempts at growth under one atmosphere of K_2O pressure had no effect on the crystal growth but did result in a third phase being generated. Long needles of a single crystal can be found in all samples. One sample obtained, which contained the largest crystals produced, was essentially a flux grown sample. Upon slow cooling of the melt, long needle-like crystals were formed. Attempts to remove these from the solid matrix were not successful. There is a difference in melting between the matrix material and needle-like crystals of at least 150°C, this permitted the removal of some samples by melting the matrix and quickly dipping out the floating needles with a platinum rod. The two major phases present in this material appear as greenish colored crystals and light grey to colorless needles. We believe that a large series of compositions exist in the K_2CO_3 - $MgCO_3$ - TiO_2 system with considerable solid solubility ranges and therefore growth of single crystals by a melt method will be extremely difficult,

and only small samples would be obtained. Table 7 lists the x-ray diffraction data for the light grey to colorless needles. We could not separate enough of the greenish crystals from the matrix for analysis.

Several growth runs were made by sealing various compositions of $K_2MgTi_7O_{16}$ to $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$ in Pt/40% Rh ampules and using the Bridgman method of growth. Two runs were made at elevated pressure by sealing the components in the presence of 3% and 5% excess KO_2 and two runs were made with 3% and 5% excess K_2CO_3 mixed with the $K_2MgTi_7O_{16}$ composition. These runs resulted in the formation of the identical phases obtained by the pulling method. Here again, we conclude that crystal growth in this system will not be possible until the phase diagram of this system is examined.

3.3 $Na_2Ti_6O_{13}$

3.3.1 Material Preparation

The compound was prepared by reacting Na_2CO_3 and TiO_2 according to the equation:

$$Na_2CO_3 + 6TiO_2 \rightarrow Na_2Ti_6O_{13}$$

The same ceramic processing methods described previously were employed. The initial calcination was at 750°C for 14 hrs. followed by re-mixing and firing at 1150°C for 10 hrs. in air. Table 8 lists the x-ray diffraction data obtained.

3.3.2 Crystal Growth

Pulling experiments using a Pt crucible were not successful due to the presence of multi-phases. Nucleation of seed material was attempted on a Pt wire by the "necking" technique. Several of these were separated from the matrix for further study. The needles were used as seeds, but only polycrystalline boules were produced at 20 RPM and a pulling speed of 0.25 cm/hr. Two distinct types of crystals are obtained. Figures 6 and 7 illustrate the x-ray powder diffraction data obtained from the A and B type $Na_2Ti_6O_{13}$. Several major reflections are missing in the A type pattern. There is the possibility of considerable line splitting in both power patterns. There was no standard pattern available for comparison. Essentially no volatilization was observed during growth. A sample was dipped from the melt for analysis. During this process, we observed rapid growth of one crystalline phase. This would indicate that this phase is being crystallized from a supersaturated solution. We therefore tried to grow at fast pulling rates, on the order of 7.6 to 12.7 cm/hr. at rotation rates between 0-60 RPM. In no case did we obtain single phase growth.

The growth of $Na_2Ti_6O_{13}$ was attempted by the flux method. Growth of $K_2Ti_6O_{13}$ from a KCl flux has been described and therefore a NaCl flux was used for $Na_2Ti_6O_{13}$. A charge containing 100 gms. of NaCl plus 10 gms. TiO_2 was loaded into a platinum crucible and sealed. This mixture was heated to 1150°C and allowed to soak for four hours. At this point, the temperature programmer was turned on and

the furnace temperature lowered at 1^{o}/hr. Very small plate-like crystals, which are transparent, were removed from the flux by dissolution of the flux in hot H_2O. X-ray diffraction and chemical analysis data are discussed below.

3.4 $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$ and $K_2W_4O_{13}$

These two compositions were removed from this program when the change in technical direction was received. A few growth experiments in the $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$ system resulted in multi-phase products by both the Bridgman and pulling techniques. The phases formed are similar to those obtained with $K_2MgTi_7O_{16}$. One flux run was attempted with $K_2W_4O_{13}$ by dissolving the compound in excess WO_3. Excessive volatilization of the flux and the lack of crystal formation indicated that growth in this system was unlikely.

4.0 Discussion of Results

4.1 $BaCO_3$, $MgCO_3$, TiO_2 System

Tables 2 and 3 compare the x-ray diffraction data obtained for the preparation of $BaMgTi_7O_{16}$. Table 4 gives the x-ray data for $BaMgTi_7O_{16}$ prepared by chemical reaction and a boule grown by flame fusion. Agreement with the literature reference is poor in almost all cases. These samples have been shown to consist of at least two major phases and a third minor phase. One of these phases (85% by volume) is of the hollandite type structure. The other two phases have not been identified but indications are that one is probably $MgTiO_3$. It is apparent that $BaMgTi_7O_{16}$ is <u>not</u> congruently melting and therefore, pulling, flame fusion or Bridgman growth will not produce a single phase crystal. The only growth method which could possibly yield a single phase crystal would be the flux technique. This would involve about a six months effort of intensive study of the phase relationships in the $BaCO_3$-$MgCO_3$-TiO_2 system and the solubility of $BaMgTi_7O_{16}$ in various solvent systems. This is obviously beyond the scope of this present program. The composition of the grown boule is given in Table 9. From this analysis a composition corresponding to the formula $Ba_{0.96}Mg_{0.57}Ti_{6.98}O_{16}$ is apparent (based on complete oxidation).

Table 10 is presented to identify the remaining samples which were analyzed by chemical and x-ray diffraction techniques. Table 11 lists the formulas corresponding to

the compositions determined for "$BaMgTi_7O_{16}$". It is obvious from this data that only the high temperature firing at 1200°C, which gives a formula of $Ba_{1.00}Mg_{1.04}Ti_{6.80}O_{16}$, approaches the desired stoichiometry of $BaMgTi_7O_{16}$. We must also consider the fact that this does not specify a single phase but an average composition of all phases present in the sample analyzed. A sealed Bridgman run on this material resulted in two phases; a large amount of "black" crystalline material and a minor amount of clear crystals. It was not possible to chemically analyze these phases. Phase determination was accomplished by orthoscopic examination at 10X in polarized light. X-ray powder diffraction data identified the phases as $BaMgTi_7O_{16}$ and $MgTiO_3$. The samples were also checked by X-ray methods for the presence of unreacted starting components. Within the limits of x-ray detection no unreacted components were found.

4.2 $K_2CO_3 + MgCO_3 + TiO_2$ System

Tables 10 and 11 give the compositions and preparation of samples examined in this system (Nos. 1-5). The composition which we had tried to prepared was $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$. The chemical analysis clearly shows that the preparation procedure did not result in this composition. The data also indicates a loss of K as the firing temperature increases. A sealed Bridgman run was not made with this material because none of the compositions were close to $K_{1.75}Mg_{0.875}Ti_{7.125}O_{16}$.

4.3 $K_2Ti_6O_{13}$ + $MgTiO_3$ System

A large number of samples (Nos. 6-15) were prepared by the direct reaction of $K_2Ti_6O_{13}$ with $MgTiO_3$. The preparation details and formulas of the resulting products are given in Tables 10 and 11.

The first series (Nos. 6-8) were prepared and individually fired once, in closed Pt ampules at 1100°, 1150°, and 1200°C. The results indicate that the composition approached $K_2MgTi_7O_{16}$, within experimental error. A Bridgman run in a sealed Pt ampule was made with composition $K_{2.16}Mg_{1.04}Ti_{7.05}O_{16}$. The x-ray powder diffraction data showed a single phase in excellent agreement with the published data. Orthoscopic examination of the same indicated large amounts of yellow and black crystals. The black crystals are probably just oxygen deficient. A small amount of clear microcrystals with high birefringence were also observed.

The next series of samples were prepared and fired with packing powder containing 3% excess K (Nos. 9-11). Again, the desired composition was not obtained (See Table 11). The sample of composition $K_{2.09}Mg_{1.21}Ti_{7.05}O_{16}$ was Bridgman growth in two different environments. First, the powder was melted under six atmospheres of KO_2 pressure while the second sample was melted in a sealed (air) ampule. Neither process produced single phase material. The x-ray data showed two phases -

$K_2MgTi_7O_{16}$ (80%) and $K_2Ti_2O_5$ (20%); while microscopic observation showed yellowish and clear, colorless crystallites of high birefringence.

The final series of samples (Nos. 12-15) were prepared by initial calcination of 300 gms. of material and separate firings of this material at the conditions indicated in Table 10. None of these were found to correspond to the desired formula. Two of these compositions, $K_{2.14}Mg_{1.06}Ti_{7.19}O_{16}$ and $K_{2.06}Mg_{1.17}Ti_{7.00}O_{16}$ were melted by the Bridgman method in sealed ampules both with and without KO_2 present. In all cases, orthoscopic examination showed the presence of three phases: yellowish crystals, black crystals and transparent colorless crystals of very high birefringence. The x-ray data indicated two major phases - $K_2MgTi_7O_{16}$ and $K_2Ti_2O_5$.

We can conclude from the results stated above that single crystal growth in the potassium magnesium titanate system can not be done until an accurate phase diagram is prepared which resolves the stability regions of the various phases formed.

4.4 $Na_2Ti_6O_{13}$

The crystals grown from the NaCl flux, described previously, were examined by chemical and x-ray analysis.

While the chemical analysis resulted in a formula of $Na_{0.47}Ti_{6.36}O_{13}$ (Table 11), x-ray data showed $Na_2Ti_6O_{13}$ and NaCl phases were present with the $Na_2Ti_6O_{13}$ phase being highly crystalline. Figure 8 illustrates the crystals obtained. The x-ray data was checked against a powder pattern given for $K_2Ti_6O_{13}$.[10]

5.0 Conclusions and Recommendations

The data discussed above concludes that the methods of compound preparation do not result in the formation of single phase material, which would be suitable for single crystal growth. None of the systems studied have phase diagrams available and prior to any future work with these or similar systems, an accurate determination of the phase stability regions must be performed.

We feel that single crystal growth from a flux system is possible for $BaMgTi_7O_{16}$ but solubility data for this material would have to be obtained first. The same would apply to the potassium series of phases except that the large areas of solid solubility evident would have to be identified and their stability regions determined. Growth of large single crystals of $Na_2Ti_6O_{13}$ by a melt method does not appear feasible.

6.0 References

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7.0 List of Tables and Figures

Table 1

Analysis of Starting Materials*

Impurity	$BaCO_3$ #702854	TiO_2 #795250	$MgCO_3$ #775675	K_2CO_3 #773592
Ba	-	-	0.005	-
Ca	0.003	-	0.03	0.010
Fe	0.0007	0.01	0.001	0.0001
Cl	0.001	-	0.003	-
NO_3	0.005	-	0.003	0.0007
Pb	0.0005	0.0007	0.001	0.0003
Sr	0.3	-	-	-
As	-	0.0001	-	-
Zn	-	0.005	0.010	-
Na	-	-	-	0.003

*Concentrations given in %.

Table 2

Powder Diffraction Data for $BaMgTi_7O_{16}$

Line #	Relative Intensity 1st	Relative Intensity 2nd	1st Firing (1000° - 1/2 hr.) d	2nd Firing (1200° - 2 hrs.)
1	S	VS	5.2140	6.8675
2	MS	MS	3.4734	3.1423
3	W	W	3.2013	2.8139
4	W	W	2.5932	2.4744
5	W	M	2.3992	2.2086
6	W	W	2.1397	2.0026
7	S	W	1.7488	1.8120
7a	-	M	-	1.6727
8	MS	W	1.4537	1.5837
9	W	-	1.3596	-
10	M	S	1.3138	1.3320
11	MS	W	1.2486	1.2531
12	M	-	1.1538	-
13	W	W	1.0948	1.1038
14	W	W	1.0369	1.0270
15	W	-	0.94667	-
16	W	-	0.91135	-
17	W	W	0.89294	0.88088
18	W	W	0.84228	0.83289
18a	-	W	-	0.81657
19	W	-	0.74130	-

Table 3

X-Ray Powder Diffraction Data
$BaMgTi_7O_{16}$

Mo, K - Zr
40 KV; 18 ma.

Line #	I_R*	Std. Pattern[1] "Norrish"	I_R	1st Firing 1200°C, 15 hrs.	I_R	2nd Firing 1400°C, 8 hrs.
1	vwd	7.12	vs	6.60	vs	6.52
2	w	5.06	s	5.38		-
3	w	3.55		-		-
4	s	3.19	m	3.18	m	3.08
5	vwd	2.817	w	2.845	vw	2.739
6	m-s	2.470	m	2.463	m	2.416
7	vw	2.250		-		-
8	m	2.223	m	2.228	m	2.199
9	vwd	2.032	w	2.018		-
10	vw	1.977		-		-
11	w-m	1.884	w	1.875	m	1.859
12	m	1.683	m	1.673	w	1.695
					m	1.657
13	w-m	1.583	vvw	1.593	m	1.577
14	vw	1.475	vvw	1.466	vw	1.480
15	vw	1.446		-		-
16	vvw	1.415		-		-
17	w-m	1.390	vvw	1.398	w	1.383
18	w	1.340	w	1.349		-
19	vw	1.323	wd	1.265	vw	1.327
20	w	1.113	wd	1.090	w	1.176
21	vw	1.026	w	1.035	w	1.104
22	vw	1.007	w	1.035	vvw	1.017
23	vwd	0.886		-		-
24	w	0.873	vvwd	0.879		-
25	vw	0.864		-	w	0.869

*I_R = relative intensity
s = strong
m = medium
w = weak
vw = very weak, etc.
d = diffuse

Table 4

X-Ray Data for $BaMgTi_7O_{16}$

Chemically Prepared $BaMgTi_7O_{16}$		Flame Fusion Grown $BaMgTi_7O_{16}$	
d	Intensity	d	Intensity
5.029	vw	5.119	m
3.565	m	3.405	m
3.201	vs	3.188	s
2.825	m	2.475	w
2.458	s	2.346	w
2.250	w	2.305	m
2.228	m	2.105	s
2.011	vw	1.985	w
1.879	m	1.845	m
1.680	m	1.679	m
1.572	m	1.497	w
1.465	vvw	1.466	w
1.382	w	1.356	vw
1.342	w	1.347	vvw
1.325	vvw	1.329	vw
		1.258	m
		1.156	w

Table 5

X-Ray Powder Diffraction of $K_2MgTi_7O_{16}$

MoK - Zr
40 KV; 18 ma.

Line #	I * R	Standard Pattern(3)	I * R	1st Firing 1000°C, 1/2 hr.	I * R	2nd Firing 1200°C, 2 hrs.
1	m	7.16	s	7.11	s	6.91
2	m	5.08	s	5.16	s	5.11
3	w	3.592	w	3.427	w	3.546
4	vs	3.211		-	w	3.076
			w	2.986	w	2.717
5	w	2.538		-		-
6	s	2.487		-	s	2.463
7	w	2.391	w	2.355		-
8	w	2.271		-		-
9	ms	2.235		-		-
			w	2.171		
10	vvw	2.045	s	2.079		-
11	w	1.991		-		-
12	ms	1.896	s	1.859	w	1.859
13	vw	1.794		-		-
14	vw	1.740		-		-
15	m	1.691		-		-
16	w	1.696	s	1.673	w	1.667
17	ms	1.592		-	s	1.567
18	m	1.487		-		-
19	vw	1.457	ms	1.466	ms	1.466
20	vw	1.426		-		-
21	m	1.399		-	m	1.386
22	w	1.349		-		-
23	vw	1.333	s	1.320	w	1.335
24	vw	1.283		-		-
25	vw	1.263	ms	1.250	w	1.259
26	vw	1.196	m	1.159	w	1.164

*I_R = relative intensity
m = medium
w = weak
vs = very strong
s = strong
vw = very weak, etc.

Table 6

X-Ray Powder Diffraction of $K_2MgTi_7O_{16}$

Mo K - Zr
40 KV; 18 ma.

Line #	I R	Standard Pattern[3]	I R	1st Firing 500°C, 15 hrs.	I R	2nd Firing 1000°C, 15 hrs.	I R	3rd Firing 1200°C, 15 hrs.
1	m	7.16	vs	6.60	vs	6.52	vs	6.52
			s	5.50				
2	m	5.08		-		-	w	4.66
					vvw	4.07		
3	w	3.592	s	3.348	vw	3.546	vw	3.546
4	vs	3.211	w	2.986	m	3.058		-
					w	2.717	m	2.894
5	w	2.538		-		-	w	2.620
6	s	2.487		-	w	2.463	mw	2.439
7	w	2.391		-		-		-
8	w	2.271	ms	2.297		-		-
9	ms	2.235		-	w	2.200		-
10	vvw	2.045	w	2.071		-	w	2.181
11	w	1.991		-		-		-
12	ms	1.896	ms	1.852	m	1.875	w	1.859
13	vw	1.794		-		-		-
14	vw	1.740		-		-		-
15	m	1.691		-		-		-
16	w	1.676		-	w	1.673	w	1.673
			ms	1.646				
17	ms	1.592		-	m	1.577	w	1.562
18	m	1.487		-		-		-
19	vw	1.457		-	w	1.466	w	1.466
20	vw	1.426		-		-		-
21	m	1.399		-	w	1.379	w	1.370
22	w	1.349		-		-		-
23	vw	1.333	m	1.332	vvw	1.329	vvw	1.317
24	vw	1.283		-		-		-
25	vw	1.263		-	vvw	1.250		-
			m	1.246		-	vw	1.249
26	vw	1.196		-	vw	1.177	vvw	1.174
			w	1.154	vw	1.111	vvw	1.096

Table 7

X-Ray Diffraction Data For
Crystals Grown From $K_2MgTi_7O_{16}$

I (Relative)	d	I (Relative)	d
20	4.730	20	1.241
10	3.398	21	1.237
35	3.147	9	1.230
10	3.026	5	1.034
45	2.703	5	1.027
5	2.580	5	1.022
5	2.399	5	0.9537
10	2.337		
75	2.199		
45	2.185		
5	2.149		
45	1.950		
20	1.937		
5	1.859		
100	1.824		
20	1.655		
10	1.645		
38	1.611		
15	1.601		
9	1.583		
9	1.360		
50	1.291		
38	1.248		

Table 8

X-Ray Data for $Na_2Ti_6O_{13}$

Initial Prep.		Final Firing	
d	$I_{(Rel.)}$	d	$I_{(Rel.)}$
3.596	30	3.583	30
3.211	65	2.935	90
2.943	100	2.739	20
2.654	55	2.661	70
2.468	45	2.647	80
2.171	20	2.486	30
2.069	90	2.471	50
2.038	90	2.088	60
1.859	55	2.075	80
1.849	20	2.063	100
1.810	30	2.028	80
1.727	30	1.857	90
1.678	65	1.845	40
1.667	30	1.808	20
1.628	45	1.720	20
1.618	30	1.628	80
1.530	30	1.618	30
1.388	30	1.529	20
1.353	20		

Table 9

Chemical Analysis of $K_2MgTi_7O_{16}$ and $BaMgTi_7O_{16}$ for Composition

$BaMgTi_7O_{16}$		$K_2MgTi_7O_{16}$	
Ti	45.47%	Ti	47.19%
Mg	1.90%	K	11.29%
Ba	17.83%	Mg	3.20%

Table 10

Identification of Samples

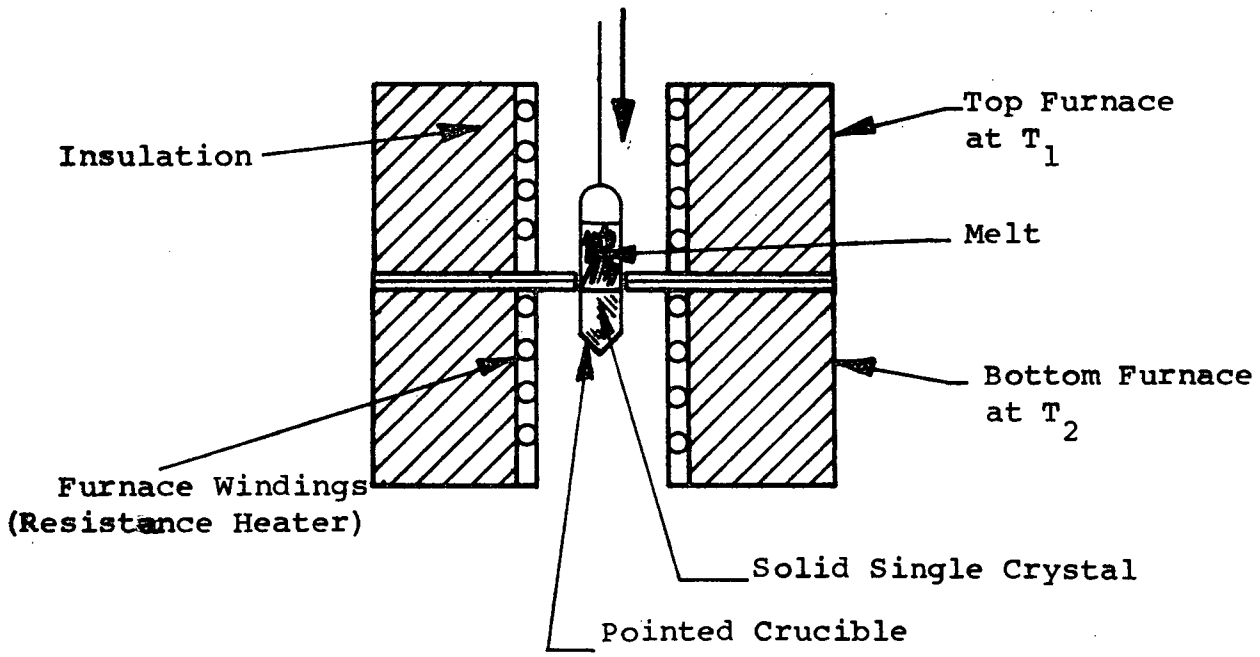
Sample #	Description and Firing Conditions
1	K_2CO_3 + $MgCO_3$ + TiO_2; calcined 1000°C, 1/2 hr.
2	" " " ; refired 1100°C, 16 hrs.
3	" " " ; " 1150°C, 4 hrs.
4	" " " ; " 1200°C, 1 hr.
5	" " " ; " 1200°C, 2 hrs.
6	$K_2Ti_6O_{13}$ + $MgTiO_3$ - Fired closed tube; 1100°C, 16 hrs.
7	" " " " " ; 1150°C, 4 hrs.
8	" " " " " ; 1200°C, 1 hr.
9	$K_2Ti_6O_{13}$ + $MgTiO_3$ - 3% excess K, in packing powder, calcined 1000°C, 1/2 hr.
10	$K_2Ti_6O_{13}$ + $MgTiO_3$ - 3% excess; refired 1200°C, 2 hrs.
11	" " - " " ; refired 1200°C, 2 hrs.
12	$K_2Ti_6O_{13}$ + $MgTiO_3$ - Calcined 1000°C, 1/2 hr.
13	" " - 1/3 fired 1100°C, 16 hrs.
14	" " - 1/3 fired 1150°C, 4 hrs.
15	" " - 1/3 fired 1200°C, 1 hr.
16	$BaCO_3$ + $MgCO_3$ + TiO_2 - Calcined 1000°C, 1/2 hr.
17	" " " - refired 1200°C, 2 hrs.
18	" " " - refired 1200°C, 2 hrs.
19	$Na_2Ti_6O_{13}$ - Flux grown crystals (NaCl flux)

Table 11

Formulas of Various Compositions
(by Chemical Analysis)

Sample #	Formula
1	$K_{2.09}Mg_{0.86}Ti_{7.08}O_{16}$
2	$K_{1.97}Mg_{0.97}Ti_{7.04}O_{16}$
3	$K_{1.47}Mg_{0.95}Ti_{7.19}O_{16}$
4	$K_{1.93}Mg_{0.92}Ti_{7.18}O_{16}$
5	$K_{1.89}Mg_{0.93}Ti_{7.33}O_{16}$
6	$K_{2.10}Mg_{1.04}Ti_{7.06}O_{16}$
7	$K_{2.18}Mg_{1.01}Ti_{7.05}O_{16}$
8	$K_{2.16}Mg_{1.04}Ti_{7.05}O_{16}$
9	$K_{2.10}Mg_{1.02}Ti_{6.97}O_{16}$
10	$K_{2.16}Mg_{1.17}Ti_{7.22}O_{16}$
11	$K_{2.09}Mg_{1.21}Ti_{7.05}O_{16}$
12	$K_{2.22}Mg_{0.99}Ti_{7.18}O_{16}$
13	$K_{2.14}Mg_{1.06}Ti_{7.19}O_{16}$
14	$K_{2.12}Mg_{0.97}Ti_{7.10}O_{16}$
15	$K_{2.06}Mg_{1.17}Ti_{7.00}O_{16}$
16	$Ba_{0.61}Mg_{0.68}Ti_{6.97}O_{16}$
17	$Ba_{0.83}Mg_{0.87}Ti_{7.08}O_{16}$
18	$Ba_{1.00}Mg_{1.04}Ti_{6.80}O_{16}$
19	$Na_{0.47}Ti_{6.36}O_{13}$

FIGURE 1. BRIDGMAN CRYSTAL GROWTH



$T_1 > T_2$

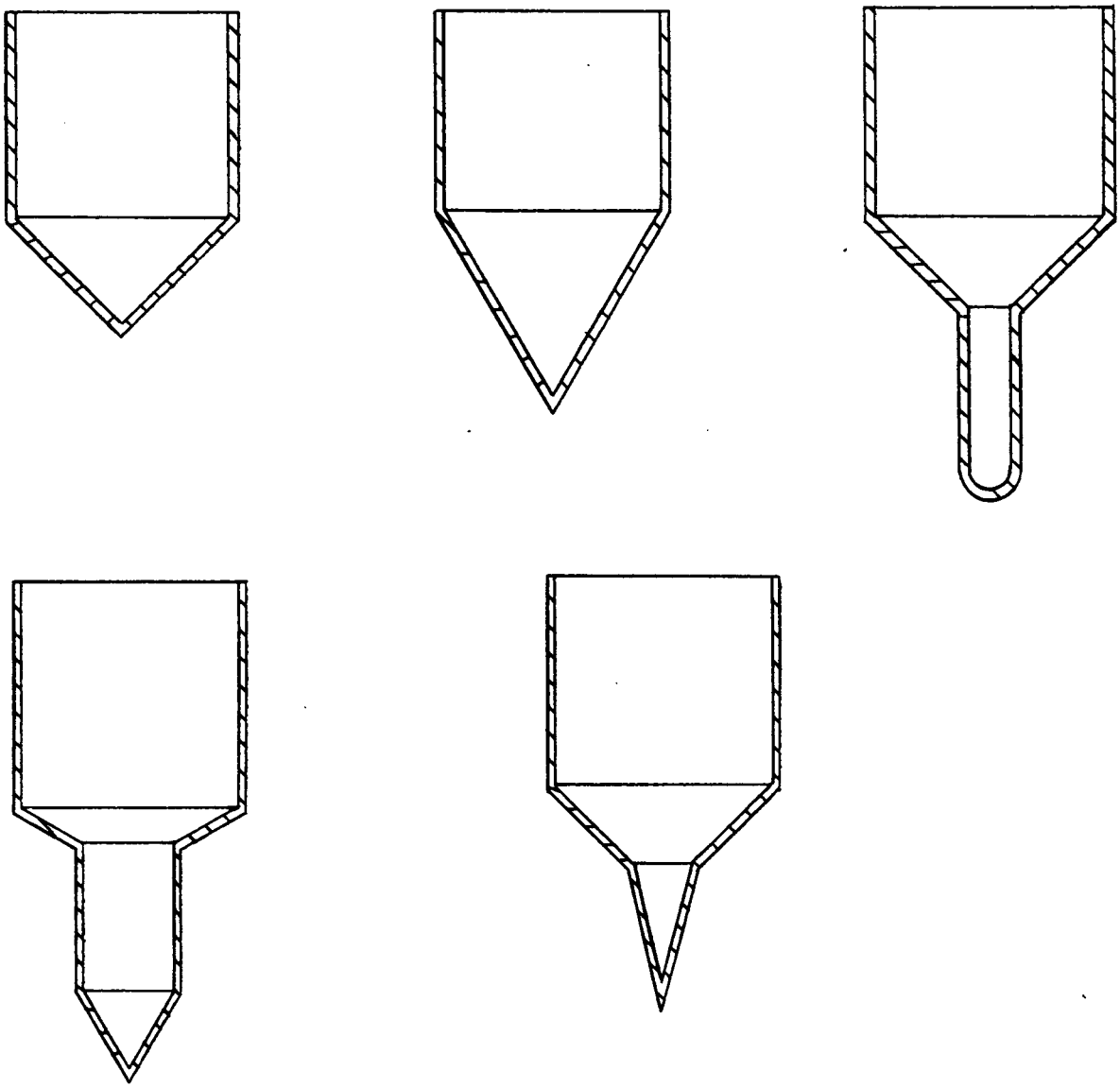


FIGURE - 2

CRUCIBLES USED IN GROWTH BY THE BRIDGMAN - STOCKBARGER METHOD.

FIGURE 3. CZOCHRALSKI OR KYROPOULOS PULLING

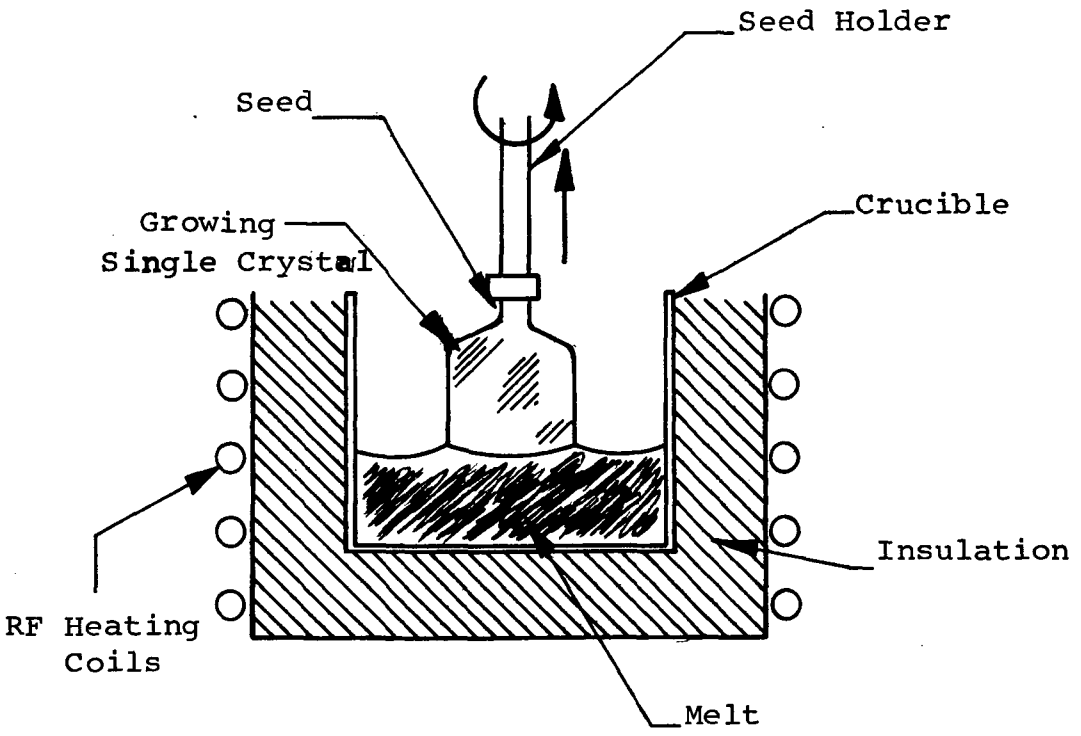


FIGURE 4. FLUX GROWTH

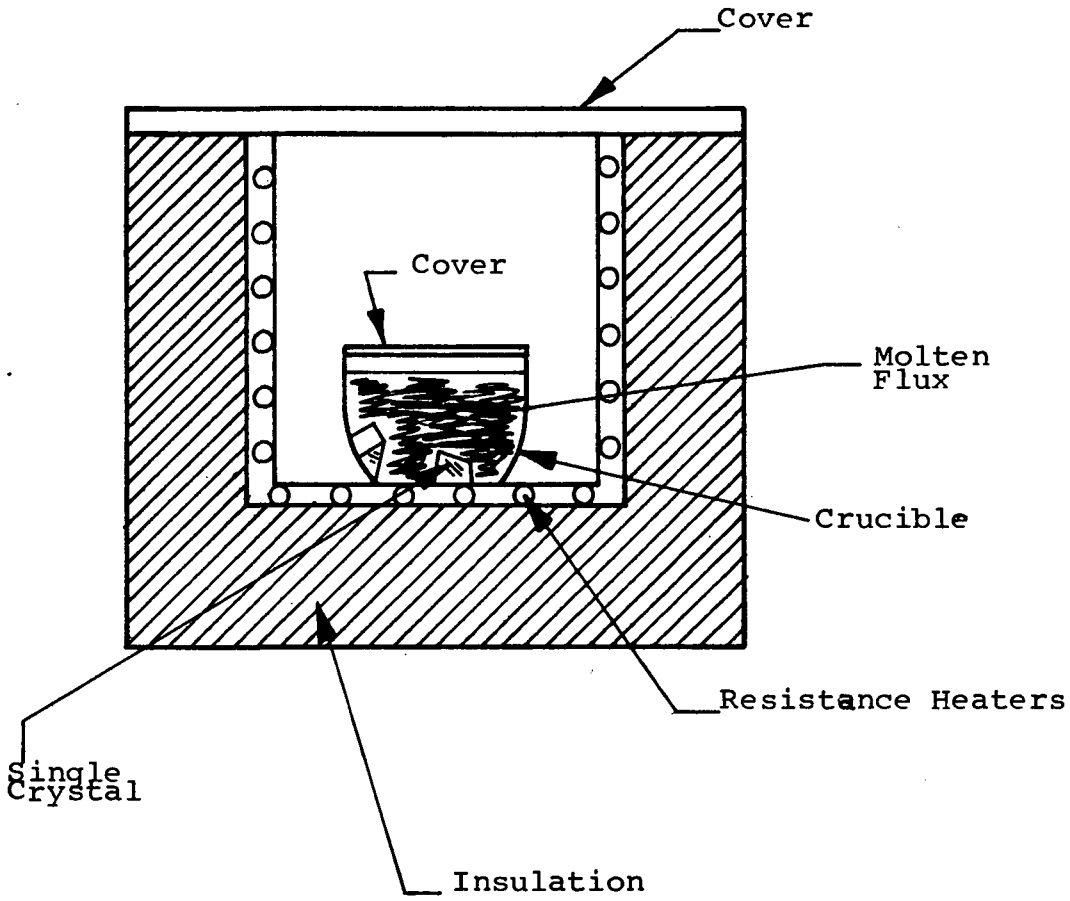
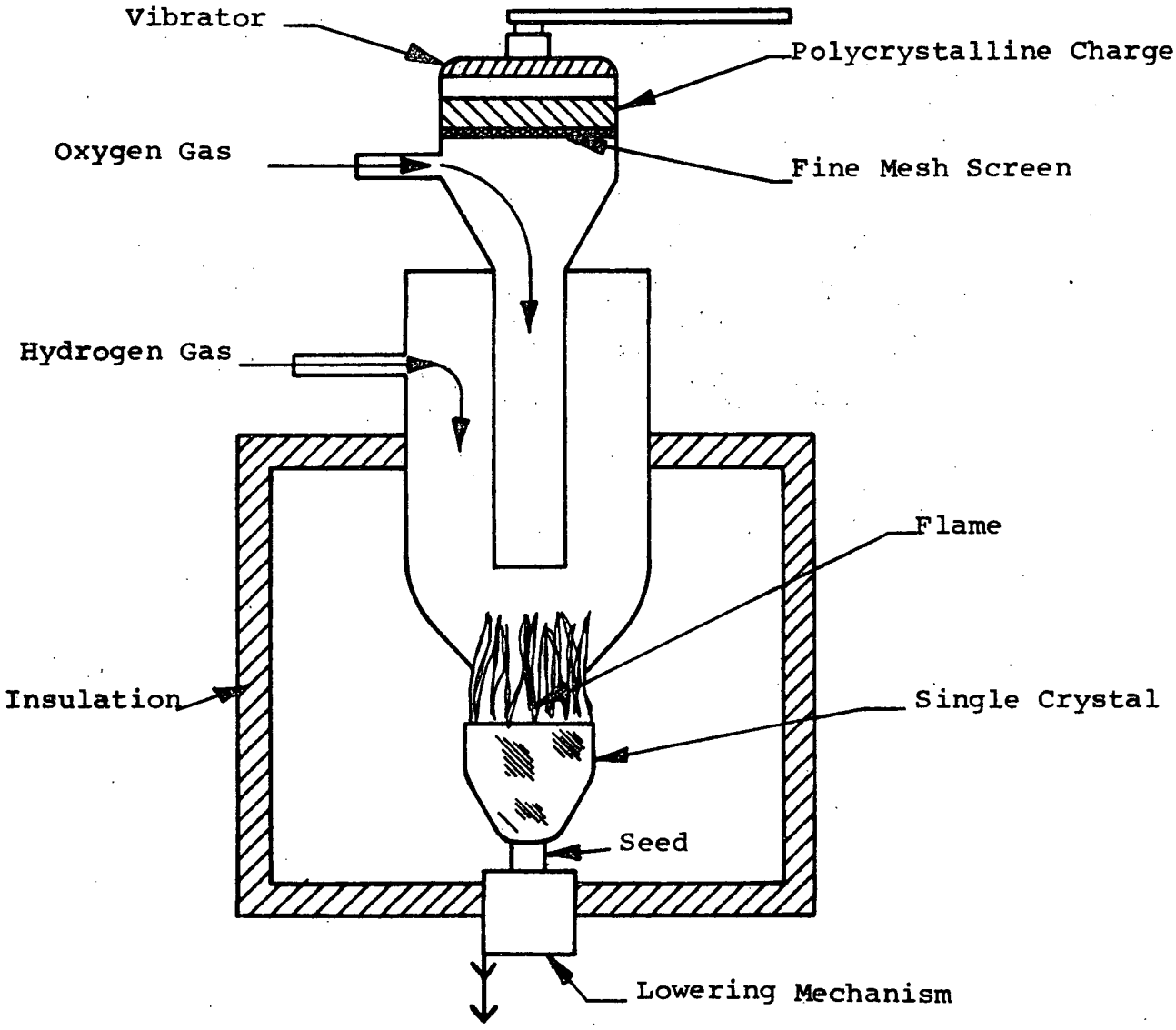


FIGURE 5. FLAME FUSION/VERNEUIL



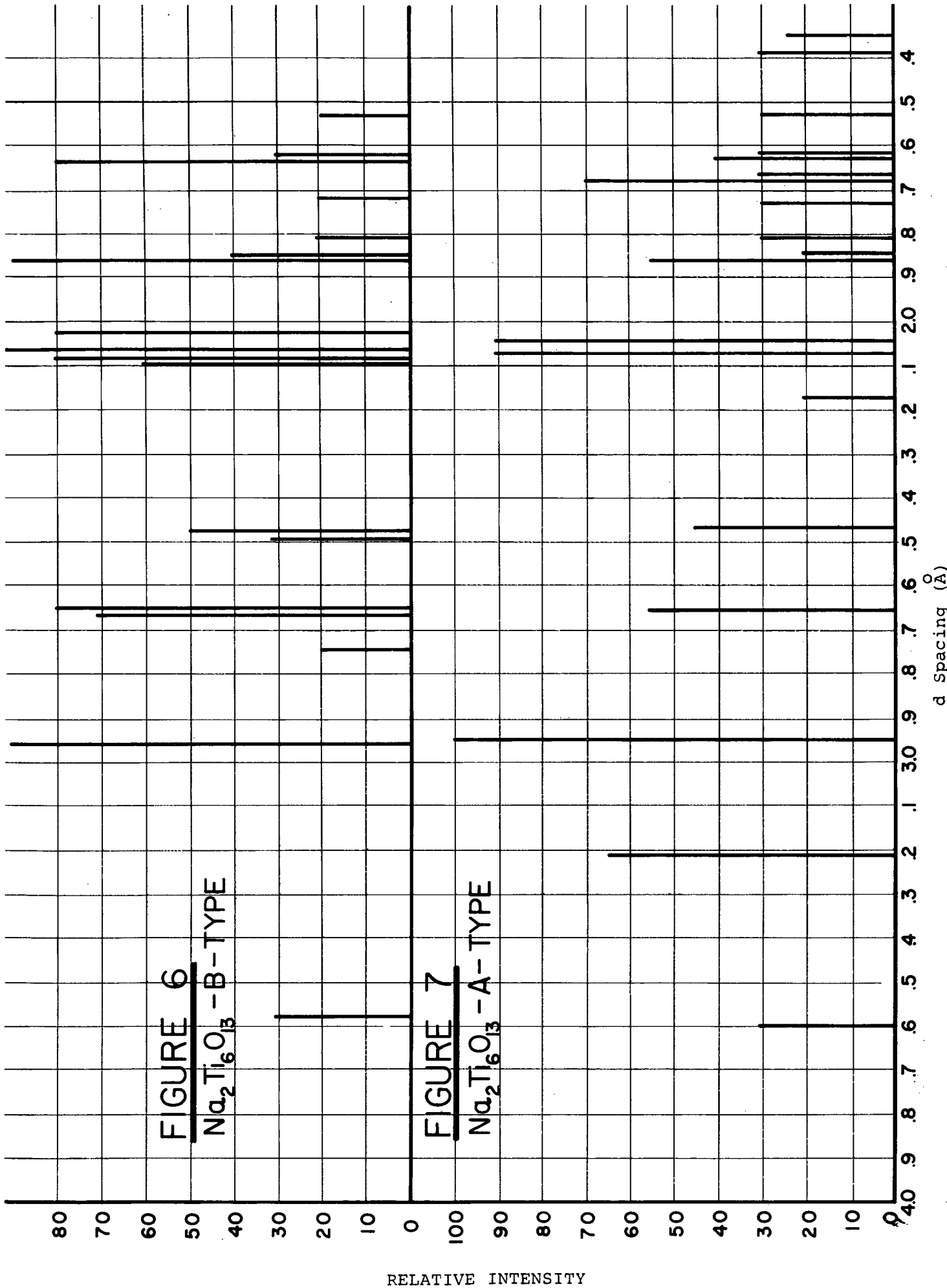


FIGURE 6
$Na_2Ti_6O_{13}$ -B- TYPE
FIGURE 7
$Na_2Ti_6O_{13}$ -A- TYPE
80 70 60 50 40 30 20 10 0
100 90 80 70 60 50 40 30 20 10 0
.4 .5 .6 .7 .8 .9 2.0 .1 .2 .3 .4 .5 .6 .7 .8 .9 3.0 .1 .2 .3 .4 .5 .6 .7 .8 .9 4.0
d Spacing (Å)
RELATIVE INTENSITY

$Na_2Ti_6O_{13}$ 100X

FIGURE 8

$Na_2Ti_6O_{13}$ Crystals 100X