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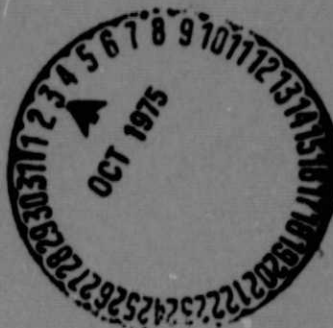
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**ALKALI OXIDE-TANTALUM, NIOBIUM AND ANTIMONY OXIDE IONIC CONDUCTORS**

by

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## SUMMARY

This report summarizes work carried out between January 1, 1974 and December 31, 1974 under an agreement with the National Aeronautics and Space Administration, Lewis Research Center (Interagency Agreement PR545160) to study the phase equilibria of alkali oxide-tantalum, niobium and antimony oxide systems and synthesis of phases which might have interesting ionic conductivity. It also includes work performed since the last contract (Interagency Order C-29933-C [1]) which ended in October 1973, as well as that done since the formal ending of the present contract and the issuance of this summary report.

In addition to the six systems reported in the previous contract (Interagency Order C-29933-C [1]) the phase equilibrium relations of four additional systems were investigated in detail. These consisted of sodium and potassium antimonates with antimony oxide and tantalum and niobium oxide with rubidium oxide as far as the ratio  $4\text{Rb}_2\text{O}:\text{11B}_2\text{O}_5$  ( $\text{B}=\text{Nb}, \text{Ta}$ ). The ternary system  $\text{NaSbO}_3\text{-Sb}_2\text{O}_5\text{-NaF}$  was also investigated extensively to determine the actual composition of the body centered cubic sodium antimonate. In addition, various other binary and ternary oxide systems involving alkali oxides were examined in lesser detail. The phases synthesized were screened by ion exchange methods to determine mobility of the alkali ion within the niobium, tantalum or antimony oxide (fluoride) structural framework.

Five structure types were found to be of sufficient interest to warrant further investigation. These structure types are (1) hexagonal tungsten bronze (HTB) (2) pyrochlore (3) the hybrid HTB-pyrochlore hexagonal ordered phases (4) body centered cubic antimonates and (5)  $2\text{K}_2\text{O}:\text{3Nb}_2\text{O}_5$ . Although all of these phases exhibit good ion exchange properties only the pyrochlore in the  $\text{Sb}_2\text{O}_5\text{-NaSbO}_3$  system has so far been prepared with  $\text{Na}^+$  ions as an equilibrium phase and as a low porosity

ceramic. Unfortunately  $\text{Sb}^{+3}$  in the channel apparently interferes with ionic conductivity in this case, although relatively good ionic conductivity was found for the metastable  $\text{Na}^+$  ion exchanged analogs of  $\text{RbTa}_2\text{O}_5\text{F}$  and  $\text{KTaWO}_6$  pyrochlore phases. Small crystals of the other phases can generally be prepared by flux techniques and ion exchanged with  $\text{Na}^+$ . However, in the one case where congruency allows large crystals to be pulled from the melt ( $4\text{Rb}_2\text{O}:\text{11Nb}_2\text{O}_5$ ) ion exchange techniques up to  $\sim 450^\circ\text{C}$  are not sufficient to accomplish replacement with  $\text{Na}^+$  ions.

## 1.0 INTRODUCTION

The program described in the present report involves the preparation of single crystals and ceramic specimens of materials which have passed some preliminary screening tests and appear to be potential candidates as solid ionic conductors. Much of the preliminary screening was done under previous work order (No. C-29933-C) [1]. Furthermore the phase equilibrium diagrams have been studied for some systems in which promising candidates have been discovered but for which no phase data existed.

Crystals and ceramic specimens were prepared or synthesis attempted for various different structure types and compositions, including the hexagonal tungsten bronze and pyrochlore phases in the system  $K_2O-Ta_2O_5-WO_3$ , the  $2K_2O:3Nb_2O_5$  type phase and the phases in the system  $Rb_2O-Nb_2O_5$ . In addition specimens of the pyrochlore phase and the body centered cubic phase of the  $NaSbO_3-Sb_2O_4-NaF$  system were examined.

The phase equilibria diagrams of the  $Rb_2O-Nb_2O_5$  and  $Rb_2O-Ta_2O_5$  systems were examined as well as those of the  $Sb_2O_4-NaSbO_3$  and  $Sb_2O_4-KSbO_3$ . In addition the equilibria in the system  $Sb_2O_4-NaSbO_3-NaF$  were investigated. Other compositions examined included the alkali rare earth oxide systems and alkali oxide-bismuth oxide systems although no high temperature equilibrium phases were found in any of these systems.

The method of flux synthesis was used to prepare small single crystals for the first time of the pyrochlore phase  $RbTa_2O_5F$  and the body centered cubic phases of  $F^-$  stabilized potassium and sodium antimonates.

In the following discussion all ratios (1:3, 3:5, etc.) refer to the alkali/metal ratio rather than to the particular starting material that may have been used.

## 2.0 DISCUSSION OF RESULTS

### 2.1 The System $\text{Nb}_2\text{O}_5$ - $4\text{Rb}_2\text{O}$ : $11\text{Nb}_2\text{O}_5$

The system  $\text{Rb}_2\text{O}$ - $\text{Nb}_2\text{O}_5$  was investigated from the region of about 27 mole %  $\text{Rb}_2\text{O}$  to the  $\text{Nb}_2\text{O}_5$  end member. Ten compositions were prepared by dry mixing stoichiometric amounts of  $\text{Rb}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  and calcining in open Pt crucibles at  $500^\circ\text{C}$  and  $600^\circ\text{C}$  for extended periods of time with intermediate grindings. The specimens were heated at higher temperatures in sealed Pt tubes in resistance wound quench-type furnaces (Table 1). The x-ray diffraction patterns of these quenched specimens were used to establish the phase equilibrium diagram shown in Figure 1.

Single crystals of the eleven layer (11-L) ( $4\text{Rb}_2\text{O}$ : $11\text{Nb}_2\text{O}_5$ ), hexagonal tungsten bronze (HTB) ( $21.75\text{Rb}_2\text{O}$ : $78.25\text{Nb}_2\text{O}_5$ ) and Gatehouse tungsten bronze (GTB) ( $11.5\text{Rb}_2\text{O}$ : $88.5\text{Nb}_2\text{O}_5$ ) phases (see reference [1] for nomenclature of phases) were grown from the melt by modified Czochralski techniques. Single crystal fragments of the 11-L phase were used in ion exchange experiments but did not provide better results than isostatically pressed pellets prepared from calcined powder.

Unit cell dimensions for all phases are given in the summary table of x-ray data at the end of this report (Table 12). They were determined from both single crystal precession patterns and x-ray powder diffraction patterns ( $\text{CuK}\alpha$  radiation, Ni filtered) with the aid of a computer least squares program. Only the phase occurring at low temperatures at about 15 mole %  $\text{Rb}_2\text{O}$  has not been indexed, as no single crystals were obtained.

### 2.2 The System $\text{Ta}_2\text{O}_5$ - $4\text{Rb}_2\text{O}$ : $11\text{Ta}_2\text{O}_5$

The system  $\text{Rb}_2\text{O}$ - $\text{Ta}_2\text{O}_5$  was investigated from 26.67 mole %  $\text{Rb}_2\text{O}$  to 100 mole %  $\text{Ta}_2\text{O}_5$ . Eight compositions were prepared and the system was investigated by conventional quenching methods. The samples were heated in open Pt trays at  $500^\circ$  and  $600^\circ\text{C}$  and then heated in sealed



Pt tubes at higher temperatures. The phases were identified by comparison with known structures in the  $K_2O-Ta_2O_5$  and  $Rb_2O-Nb_2O_5$  systems. Equilibria was assumed to have been established when successive heat treatments showed no change in the x-ray diffraction patterns. As in the  $K_2O-Ta_2O_5$  [1,2] and  $Rb_2O-Nb_2O_5$  systems a layer sequence 9-L, 16-L, 11-L (in order of increasing alkali content) was found to be present. The HTB and GTB-like phases [1] were also found to be present. The results of the experiments are given in Table 2 and the phase equilibrium diagram interpreted from this data is shown in Figure 2.

### 2.3 The System $Sb_2O_4-NaSbO_3$

The system between the compositional limits of  $NaSbO_3$  and  $Sb_2O_4$  has been examined in detail. Thirteen compositions were studied by air by conventional quenching techniques and the materials were examined by single crystal, powder, and high temperature x-ray diffraction techniques. The phase equilibrium diagram, Figure 3, has been constructed from the data given in Table 3. When  $Sb_2O_4$  is reacted at low temperature ( $\sim 750-1000^\circ C$ ) with alkali carbonate it generally loses the  $CO_2$  and picks up oxygen from the atmosphere to satisfy equilibrium conditions of the phases formed, which may involve oxidation of the antimony ions. Therefore the antimonate systems reported here are not strictly binary.

The compound  $NaSbO_3$  (ilmenite-type) was found in this work to melt at about  $1555 \pm 5^\circ C$ . An intermediate pyrochlore solid solution exists from about 37.5 mole %  $Na_2O$ :62.5 mole %  $Sb_2O_4$  to 24 mole %  $Na_2O$ :76 mole %  $Sb_2O_4$  at  $1350^\circ C$ . The 1:3 composition probably does not really correspond structurally to  $[NaSb^{+3}]Sb_2^{+5}O_7$  although the 3:5 composition may be written as  $[Na_{1.5}Sb_{.5}^{+3}]Sb_2^{+5}O_{6.5}$  see Section 3.2. The  $3Na_2O:5Sb_2O_4$  composition apparently melts congruently at  $1490 \pm 5^\circ C$ . The solidus curve falls from this temperature to about  $1340 \pm 5^\circ C$  at 24 mole %  $Na_2O$ :76 mole %  $Sb_2O_4$ . A two phase region exists between the pyrochlore solid solution and  $Sb_2O_4$ . An unknown phase was found to occur in the system which could

be made approximately single phase by calcining the composition 15 mole %  $\text{Na}_2\text{O}$ :85 mole %  $\text{Sb}_2\text{O}_4$  at  $750^\circ\text{C}$  and reheating in a sealed Pt tube to  $1000^\circ\text{C}$  for 64 hours in the presence of  $\text{PtO}_2$ . This phase has an as yet unindexed x-ray diffraction pattern with the four strongest lines occurring at  $d$  values equal to 3.283, 2.798, 3.453, 8.23A.<sup>1/</sup>

### 2.3.1 $\text{NaSbO}_3$

The compound  $\text{Na}_2\text{O}:\text{Sb}_2\text{O}_5$  was first reported to occur by Schrewelius [4] and to be hexagonal with  $a=5.316$  and  $c=15.95\text{\AA}$  and an ilmenite structure. This compound was found in the present work to melt congruently at about  $1555\pm 5^\circ\text{C}$ . No other stable polymorphs were encountered.

### 2.3.2 Pyrochlore Solid Solution

One intermediate phase, a cubic pyrochlore solid solution mentioned by Stewart and Knop [5], was characterized in the system. The compositional varies from approximately  $\text{Na}_2\text{O}:\text{Sb}_2\text{O}_4$  to  $3\text{Na}_2\text{O}:\text{Sb}_2\text{O}_4$  with unit cell dimensions varying from 10.289 to 10.286A respectively. Since the pyrochlore is a tunnel structure and since this pyrochlore is the only one reported that contains sodium that can be formulated by direct synthesis it was worthy of further study as a possible ionic conductor. For ionic conductivity measurements dense materials were needed and several experiments were conducted with  $\text{Na}_2\text{O}:\text{Sb}_2\text{O}_4$  (1:2) in an effort to determine its stability under high pressure and temperature. In the first experiment, 2.25 g of single phase pyrochlore material were prepressed at 10,000 psi,<sup>2/</sup> packed into a Pt cylinder 3/8 O.D. x 1 1/2" long with  $\text{PtO}_2$  and sealed. This sealed crucible was heated to  $1000^\circ\text{C}$  and 69,800 psi with catastrophic results. Apparently this phase is not completely stable in this temperature-pressure range and some of the material reacted with the Pt container resulting in a melting of the Pt. The remaining

<sup>1/</sup> 10A = 1.0 nanometers

<sup>2/</sup> The use of psi, bar, and kbar follows the current common practice of workers in the field. Note that 1 bar =  $10^5 \text{ N/m}^2$  (or pascal) =  $10^6 \text{ dyn/cm}^2$  = 0.9869 atm = 14.504 psi. The accepted international standard (SI) unit of pressure is the pascal or newton per meter squared.

specimen, slightly depleted in antimony oxide, was found by x-ray diffraction to contain a pyrochlore phase plus ilmenite (1:1).

The next experiment was scaled down in amount of material and pressure. A few milligrams of material were sealed in a 3 mm diameter Pt tube and heated to 700°C and 4,000 psi for 1 hour in the presence of  $\text{PtO}_2$ . The material remained 1:2 (pyrochlore) with slight sintering. A similar experiment was conducted at 1000°C and 4,000 psi for 2 hours. The  $\text{PtO}_2$  was decomposed and there was grain growth. The x-ray pattern was of 1:2 pyrochlore. In the next experiment, two samples in sealed platinum tubes were heated at 1100°C and 5,000 psi for 3 hours. Platinum oxide was added to only one of the tubes before sealing. The specimen without  $\text{PtO}_2$  was a single phase pyrochlore which appeared to be a very dense material. The measured density was  $5.21 \text{ g/cm}^3$ . The specimen containing  $\text{PtO}_2$  was not dense.

In the last experiment two 5 mm diameter x 1 1/4" long tubes were flattened (to a rectangular shaped cross section, 1.5 mm thick) packed with material, sealed and heated to 1100°C and 4,000 psi. After heating, this specimen was very thin and brittle and the specimen fragmented when the Pt was mechanically removed. Again the specimen was quite hard with a measured density of 5.26 to  $5.29 \text{ g/cm}^3$ . The average density of four measured fragments was  $5.26 \pm 0.05 \text{ g/cm}^3$ .

For ionic conductivity measurements, pellets of  $\text{Na}_2\text{O}:2\text{Sb}_2\text{O}_4$  (3/4" in diameter) were placed in sealed platinum foil envelopes and hot pressed by a commercial company at 1100°C and 5,000 psi. The pellets were well formed single phase material with a density of 96% theoretical (See Section on Mechanisms of Non-stoichiometry 3.2). The ionic conductivity of these pellets was measured at NASA Lewis Research Center (LeRC) [6] and they were found to be essentially insulators.

The distribution of the various ions (i.e.  $\text{Na}^+$ ,  $\text{Sb}^{+3}$ ,  $\text{Sb}^{+5}$ ,  $\text{O}^{-2}$ ) in the  $\text{Na}_2\text{O}:2\text{Sb}_2\text{O}_4$  has not as yet been determined from single crystal structure analysis. The structure of this material is currently

being determined at NBS. Until the results of this analysis are forthcoming it may be assumed that the "lone pair" electrons associated with  $\text{Sb}^{+3}$  will not allow the passage of  $\text{Na}^+$  through the channels.

### 2.3.3 Polymorphism of $\text{Sb}_2\text{O}_4$ <sup>3/</sup>

Two stable polymorphs of  $\text{Sb}_2\text{O}_4$  have been reported in the literature. They are  $\alpha\text{-Sb}_2\text{O}_4$  which is orthorhombic [7]  $a=5.436$ ,  $b=11.76$ ,  $c=4.810\text{\AA}$  and  $\beta\text{-Sb}_2\text{O}_4$  which is monoclinic [8]  $a=11.905$ ,  $b=4.834$ ,  $c=5.383\text{\AA}$  and  $\beta=101^\circ 22'$ . From Table 4(a) it can readily be seen that specimens quenched from a temperature composition region represented on the phase diagram, Figure 3, as  $\text{Sb}_2\text{O}_4$  + pyrochlore may contain either  $\alpha\text{-Sb}_2\text{O}_4$  and/or  $\beta\text{-Sb}_2\text{O}_4$  when quenched from high temperatures and ambient pressures and examined at room temperature. From this seemingly inconsistent data it would appear that the  $\alpha\text{-Sb}_2\text{O}_4$  form and  $\beta\text{-Sb}_2\text{O}_4$  form have a polytypic relationship. To help resolve this problem a high resolution electron microscope study should be done.

From the data in Table 4(b) it appears that the  $\beta$  form is the equilibrium high pressure form of  $\text{Sb}_2\text{O}_4$ . Insufficient data has been collected to establish if an equilibrium boundary curve exists between  $\alpha\text{-Sb}_2\text{O}_4$  and  $\beta\text{-Sb}_2\text{O}_4$  at various temperatures and pressures. When specimens are sealed and heated under pressure in the presence of  $\text{PtO}_2$  in either Pt or Au tubes single phase  $\beta\text{-Sb}_2\text{O}_4$  is obtained. However when heated under pressure without the  $\text{PtO}_2$ , a two phase specimen results,  $\beta\text{-Sb}_2\text{O}_4$  and the dense high pressure form of  $\text{Sb}_2\text{O}_3$  (valentinite). A similar polytypic relationship probably exists for the two polymorphs of  $\text{Sb}_2\text{O}_3$ .

Some samples of  $\text{Sb}_2\text{O}_4$  will be sent out of house for electron diffraction studies in an attempt to establish the polytypic relationship of  $\alpha\text{-Sb}_2\text{O}_4$  and  $\beta\text{-Sb}_2\text{O}_4$ . Some additional experiments will be conducted to establish the high pressure boundary curve between  $\alpha$  and  $\beta\text{-Sb}_2\text{O}_4$ .

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<sup>3/</sup> Most of the polymorphism study of  $\text{Sb}_2\text{O}_4$  was conducted prior to the issuance of Interagency Agreement PR545160, and is included in this report for the sake of completeness.

## 2.4 The System $\text{Sb}_2\text{O}_4$ - $\text{KSbO}_3$

This system has been examined between the compositional limits of  $\text{KSbO}_3$  and  $\text{Sb}_2\text{O}_4$ . Sixteen compositions were studied by conventional quenching techniques and the materials were examined by powder and by single crystal x-ray diffraction techniques. Compositions which were initially calcined at 500 and 700°C for 60 hrs, were dried at 230°C for 1 hr, sealed in Pt tubes and reheated. The results of the experiments are given in the data presented in Table 5 from which the subsolidus relationships have been established as shown in Figure 4. The compound  $\text{KSbO}_3$  with an ilmenite structure has been previously reported [9]. A body centered cubic solid solution phase originally reported as  $\text{KSbO}_3$  [9] has been found to occur metastably at about 47.5%  $\text{K}_2\text{O}$ . The  $3\text{K}_2\text{O}:5\text{Sb}_2\text{O}_5$  compound reported previously [10,11] was found in this work to melt congruently at about 1400°C. The  $\text{K}_2\text{O}:2\text{Sb}_2\text{O}_5$  compound reported previously [11] was found in this work to have a phase transition at about 1000°C and to dissociate to pyrochlore plus  $3\text{K}_2\text{O}:5\text{Sb}_2\text{O}_5$  at about 1150°C. The low temperature form of this compound labeled  $\text{P2}_1/\text{c}$  represents a monoclinic phase with  $a=7.178\text{\AA}$ ,  $b=13.378\text{\AA}$ ,  $c=11.985\text{\AA}$  and  $\beta=124^\circ 10'$ . Single crystals of this phase were grown by flux evaporation from the composition  $50\text{K}_2\text{O}:5\text{Sb}_2\text{O}_4:45\text{MoO}_3$ . The unit cell and space group were determined from these crystals and confirmed by least square indexing of the powder diffraction pattern of the low temperature form of the compound  $\text{K}_2\text{O}:2\text{Sb}_2\text{O}_5$ . The pyrochlore solid solution exists at 1150°C from about 15 mole %  $\text{K}_2\text{O}$ :85 mole %  $\text{Sb}_2\text{O}_4$  to greater than 30 mole %  $\text{K}_2\text{O}$ :70 mole %  $\text{Sb}_2\text{O}_4$ . The melting characteristics of these phases have been partially determined and are currently being reported.

### 2.4.1 Hydroxyl Ion Stabilization of Cubic Potassium Antimonate

The compound  $\text{KSbO}_3$  was reported previously [12] as being cubic at ambient conditions when previously subjected to high temperatures and pressures. In this work two experiments were conducted, heating single

phase  $\text{KSbO}_3$  ilmenite in sealed platinum tubes at about  $750^\circ\text{C}$  and 20,000 psi, utilizing argon as a pressure medium. The first of these, a two-hour run, showed only one small cubic line in the x-ray pattern but the specimen quickly reacted with atmospheric moisture. This experiment was then repeated for a longer time, 7 hours. In this time the material apparently reacted with the sealed Pt tube. The specimen was ground, mixed with petroleum jelly, and subjected to x-ray diffraction analysis before too much hydration could take place. The x-ray pattern showed lines of a material not seen by us previously. It may be concluded that this is a somewhat reducing environment and some of the material has transformed to  $\text{K}_2\text{O}$  and  $\text{Sb}_2\text{O}_3$  which in turn melted and reacted with the Pt container.

The body centered cubic phase was not formed at the above stated conditions. However, occasionally small amounts of a cubic phase were seen in the x-ray powder diffraction pattern of  $\text{KSbO}_3$  ilmenite heated at ambient pressure. For these reasons specimens of 1:1 and 3:5 mole ratios  $\text{K}_2\text{O}:\text{Sb}_2\text{O}_5$  were equilibrated in air at  $750^\circ\text{C}$  for 60 hours and picked up oxygen to form the phases  $\text{KSbO}_3$  and  $\text{K}_3\text{Sb}_5\text{O}_{18}$  and then were reheated for one hour at  $1200^\circ\text{C}$  to drive off all excess moisture. X-ray diffraction patterns of these specimens showed single phase ilmenite and the  $3\text{K}_2\text{O}:5\text{Sb}_2\text{O}_5$  compound. Portions of these  $1200^\circ\text{C}$  calcines were then weighed and mixed in acetone in the appropriate ratios to yield compositions of 46, 47, 47.5, 48 and 49 mole %  $\text{K}_2\text{O}$ . Each of these specimens was dried at  $240^\circ\text{C}$  for one hour and heated in open Pt tubes at  $1200^\circ\text{C}$  for one hour. Only the x-ray pattern of the 46% specimen showed a little  $3\text{K}_2\text{O}:5\text{Sb}_2\text{O}_5$ , the others contained only the cubic phase. A new specimen of 48 mole %  $\text{K}_2\text{O}$  was prepared in the same way except the Pt tube was sealed. After one hour at  $1200^\circ\text{C}$ , the x-ray pattern of the specimen showed only about 50% cubic. A new specimen of 48% was prepared by weighing the 1:1 and 3:5 phases immediately after removal from the

1200°C furnace and sealing the material in a flattened Pt tube within 1-2 minutes. This tube was then inflated at 1200° for a few minutes and the material mixed by shaking in a "wobble-bug". The sealed specimen was then heated for 64 hours at 1200°C. The resultant specimen had exceedingly large grain growth indicating considerable solid state recrystallization but showed no cubic phase. The conclusion is inescapable that access to atmospheric moisture is probably necessary for the formation of the cubic phase at atmospheric pressure.

A paper entitled "Flux Synthesis of Cubic Antimonates" was published by the present authors during the course of this work [13]. In addition to the discovery that the  $F^-$  ion stabilized the formation of the body centered cubic phase of potassium antimonate it was disclosed that the cubic antimonate could also be obtained by reacting  $KSbO_3$  with a small amount of other cations with small radii like  $B^{+3}$ ,  $Si^{+4}$ , etc. It now appears obvious that in this reaction the boron or silicon (etc.) actually ties up some of the  $K^+$  ion in a second phase and allows the  $K^+$  deficient antimonate to react with atmospheric moisture to form the cubic antimonate previously thought to be " $KSbO_3$ ".

## 2.5 The System $Sb_2O_4$ - $NaSbO_3$ - $NaF$

### 2.5.1 The System $NaSbO_3$ - $NaF$

To determine if  $NaF$  additions will stabilize the body-centered cubic phase similar to the  $6KSbO_3:KF$ -phase,  $NaF$  was added to  $NaSbO_3$  in the ratio of  $3NaSbO_3:NaF$ ,  $4NaSbO_3:NaF$ ,  $5NaSbO_3:NaF$ , and  $6NaSbO_3:NaF$ . The x-ray diffraction patterns of these specimens contained varying amounts of body centered cubic phase, ilmenite, and  $NaF$ . After heating at 750°C and 1000°C in sealed Pt tubes, the x-ray patterns showed only ilmenite and  $NaF$ , however at ~1150°C all the compositions contained some body centered cubic-type phase. The compositions  $3NaSbO_3:NaF$  and  $4NaSbO_3:NaF$ , when heated in sealed Pt tubes at ~1250°C, did not contain ilmenite and

appeared to be the closest to single phase cubic. The small crystals of  $4\text{NaSbO}_3:\text{NaF}$  prepared by quenching in a small sealed tube appeared to be well formed truncated octahedrons. However, the room temperature x-ray diffraction pattern of the material had somewhat diffuse lines with the exception of the  $h00$  lines which were reasonably sharp, suggesting rhombohedral symmetry. This material was placed on a hot stage microscope slide and analyzed by x-ray diffraction from room temperature up to  $220^\circ\text{C}$ . At  $190^\circ\text{C}$  the material appeared to start to go cubic and by  $220^\circ\text{C}$  a good quality cubic x-ray diffraction pattern was obtained ( $a=9.353\text{\AA}$ ). When the material was cooled to room temperature the symmetry was again non-cubic. As the  $h00$  lines deteriorate somewhat on cooling, the true symmetry of the room temperature form is probably no higher than monoclinic or triclinic rather than rhombohedral. It was therefore not unreasonable to expect that a body centered cubic phase could be obtained by direct synthesis with NaF without the necessity for  $\text{Na}^+$  ion exchange.

### 2.5.2 The Ternary System

X-ray diffraction patterns (single crystal and powder) of selected NaF-flux synthesized (see Section 2.8.2.4) washed crystals show only a truly cubic bodycentered phase ( $a=9.334\text{\AA}$ ). It must be postulated that the composition formed by this technique is slightly different from that made essentially single phase at  $4\text{NaSbO}_3:\text{NaF}$  in a sealed tube. In an attempt to obtain a fluorine-substituted body centered cubic phase which exists at room temperature the compositions shown in Table 6 were prepared and show the reported phases when quenched from  $1250^\circ\text{C}$ . Equilibrium was not obtained in overnight heat treatments at  $1200^\circ\text{C}$ . At  $1350^\circ\text{C}$  the body centered cubic phase started to decompose. The composition  $68\text{NaSbO}_3:4\text{Sb}_2\text{O}_4:28\text{NaF}$  (mole percent) was chosen as the best composition for further studies on ceramic procedures (Section 2.7).



The phases found in the specimens heated at  $\sim 1250^{\circ}\text{C}$  are summarized in "equilibrium" diagrams for the quaternary system  $\text{NaSbO}_3\text{-Sb}_2\text{O}_3\text{-Sb}_2\text{O}_5\text{-NaF}$  (Figure 5) and the ternary plane of this system  $\text{NaSbO}_3\text{-Sb}_2\text{O}_4\text{-NaF}$  (Figure 6).

## 2.6 Other Systems

During the course of this study other alkali-oxide systems were surveyed, to decide whether interesting phases existed in these systems. Among those investigated were sodium and potassium bismuthates and sodium and potassium with several rare earth oxides,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ , and  $\text{Gd}_2\text{O}_3$  as well as with  $\text{Y}_2\text{O}_3$ .

### 2.6.1 Alkali Bismuthates

Samples of sodium bismuthates and potassium bismuthates were prepared from the respective alkali carbonates and  $\text{Bi}_2\text{O}_3$  and heated in open Pt tubes at  $500^{\circ}\text{C}$  for various periods of time (Table 7). X-ray diffraction patterns showed essentially single phase  $\text{Bi}_2\text{O}_3$  with several small unidentified peaks in the  $\text{Na}_2\text{O-Bi}_2\text{O}_3$  samples. These peaks did not correspond with those of commercial  $\text{NaBiO}_3$  (apparently prepared according to Scholder and Stobbe [14]), which decomposes to  $\text{Bi}_2\text{O}_3$ .

### 2.6.2 Alkali-Rare Earth Systems

Alkali carbonates were dry mixed with the respective rare earth oxides and heated as shown in Table 8. X-ray diffraction patterns were recorded with Ni filtered Cu radiation. A "?" indicates an unknown phase which is present as one or two small peaks in the pattern.

The only significant result of these studies appears to be the presence of the cubic rare earth structure in  $\text{Gd}_2\text{O}_3$  well above its equilibrium transition. Apparently the alkali ion enters the rare earth oxide lattice to some extent, altering the polymorphic conditions.

### 2.6.3 Further Studies in the System $\text{Nb}_2\text{O}_5\text{:KNbO}_3$

During the interim between this contract and the previous one, it became apparent that the compound  $2\text{K}_2\text{O:3Nb}_2\text{O}_5$  might have interesting ionic conductivity. However, as the exact ratio  $40\text{K}_2\text{O:60Nb}_2\text{O}_5$  did not yield a single phase, new compositions were prepared (Table 9) and the composition  $41\text{K}_2\text{O:59Nb}_2\text{O}_5$  was further studied. The conclusion that this is probably a non-stoichiometric phase led to a revision of the  $\text{Nb}_2\text{O}_5\text{-KNbO}_3$  phase diagram (Figure 7).

### 2.7 Pellet Fabrication

#### 2.7.1 $41\text{K}_2\text{O:59Nb}_2\text{O}_5$ ("2:3", $\text{K}_4\text{Nb}_6\text{O}_{17}$ )

Evaluation by LeRC of the never-hydrated single crystal of  $\text{K}_4\text{Nb}_6\text{O}_{17}$  supplied by NBS resulted in a request for single phase, polycrystalline, never-hydrated pellets of this same composition.

The starting material was prepared by dry mixing  $\text{KNbO}_3$  and  $\text{Nb}_2\text{O}_5$  in appropriate amounts, followed by calcining at  $800^\circ\text{C}$  for 10 hours and  $1000^\circ\text{C}$  for 30 hours with intermediate grinding. Pellets were pressed without binder at 10,000 psi in a 5/8 inch diameter steel die. Sintering was done in air at  $1125^\circ\text{C}$  for 18 hours. The pellets were removed from the sintering furnace at temperature, immediately placed in a silica glass tube, evacuated to  $p \sim 2 \times 10^{-5}$  torr and sealed for transmittal.

The composition  $2\text{K}_2\text{O:3Nb}_2\text{O}_5$  ( $\text{K}_4\text{Nb}_6\text{O}_{17}$ ) was observed to contain a small amount of the tetragonal tungsten bronze (TTB) second phase. This second phase was completely eliminated by using a starting composition of  $41\text{K}_2\text{O:59Nb}_2\text{O}_5$ . A large batch of this 41:59 K/Nb composition was prepared and successfully exchanged as shown in Table 10. A pellet of the unexchanged 41:59 composition was prepared and sintered at  $1100^\circ\text{C}$  for 1 hour and subsequently exchanged. However, the problem of hydration with the 41:59 composition is much more severe than with the 2:3. It was necessary to maintain the sample at temperatures  $\sim 100^\circ - 150^\circ\text{C}$  to obtain a powder diffraction

pattern and to our dismay, the exchanged pellet hydrated and decrepitated while being x-rayed in laboratory air. More elaborate precautions were necessary to successfully characterize pellets of this composition. It is not known if the lack of the TTB second phase increased the susceptibility to hydration or if this is due to a slightly higher than stoichiometric amount of  $K^+$  ( $Na^+$  in the exchanged material) in the lattice.

A series of heating experiments was performed to determine the optimum sintering conditions for pellets of nominal composition  $41K_2O:59Nb_2O_5$ . At a temperature of  $1100^\circ C$  overfiring of the pellet was pronounced, as evidenced by the presence of a small amount of a liquid phase and marked reduction of niobium. Attempts to reoxidize the sample by annealing at lower temperatures were not completely successful. Temperatures of  $1000^\circ$  and  $1040^\circ C$  (the melting point of  $KNbO_3$ ) did not result in sintering sufficient to develop any mechanical strength. A temperature of  $1050^\circ$  and 2 hours time was found to result in sound pellets. X-ray characterization of the material after this heat treatment showed only single phase "2:3".

As stated above, the problem of hydration in this composition is severe at all stages of the fabrication and exchange. The following schedule was adopted in order to minimize the exposure to laboratory air, with each subsequent fabrication step performed with a minimum of delay.

Single phase $41K_2O:59Nb_2O_5$ powder	→	prepress 700 psi	→	isostatically press 20,000 psi	→	dry at $220^\circ C$ 0.5 hr	→
sinter at $1050^\circ C$ 2 hrs	→	place in fused quartz tube, evacuate to $p \leq 10^{-5}$ torr and seal off					

A similar procedure was used for the pellets to be exchanged, except that at the completion of sintering, the pellets were placed individually in

$\text{NaNO}_3$  and exchanged at  $450^\circ\text{C}$  for 64-68 hours. At the completion of the exchange period, the excess  $\text{NaNO}_3$  was removed by leaching in methyl alcohol, the pellets were dried at  $200^\circ\text{C}$  for 0.5 hours and then placed in a fused quartz tube, evacuated and sealed.

During the exchange period, the pellets appeared to suffer no physical degradation and x-ray powder diffraction of a sample obtained from the center of a test pellet showed that complete exchange to the  $\text{Na}^+$  phase had occurred.

Six pellets of the "2:3"  $\text{K}^+$  phase and three pellets of the exchanged "2:3"  $\text{Na}^+$  phase have been submitted for evaluation.

#### 2.7.2 $4\text{Rb}_2\text{O}:11\text{Nb}_2\text{O}_5$ (11-layer phase)

Pellets of the 4:11 composition were prepared by using 1 weight percent stearic acid as a binder, pressed in steel dies at 10,000 psi and sintered at  $1200^\circ\text{C}$  in air for 56 hours. The pellets were sound and showed little tendency to spall or disintegrate during exchange in molten  $\text{KNO}_3$  (see Table 10).

#### 2.7.3 Large Pellets for Ionic Conductivity Measurements

As mentioned several times, the problems of hydration and compositional changes resulting from volatility or change in oxygen content in the alkali niobates, tantalates and antimonates necessitate the use of rather extreme measures to produce sound pellets. The complete encapsulation of the starting composition at the earliest stage possible in the fabrication process appears to be successful in some cases. In such cases, the specimen remains encapsulated until ready for evaluation.

Two compositions were prepared for large dense specimens to be sent to LeRC,  $41\text{K}_2\text{O}:59\text{Nb}_2\text{O}_5$  and  $\text{NaSbO}_{3-x}\text{F}_x$ . The  $\text{NaSbO}_{3-x}\text{F}_x$  was prepared by holding  $7\text{Sb}_2\text{O}_4:93\text{KF}$  at  $\sim 1000^\circ\text{C}$  for less than 10 minutes and then

separating the fines from the coarser grains by washing, settling, and centrifuging the insoluble product. The fines were then ion exchanged two times with  $\text{NaNO}_3$  at  $450^\circ\text{C}$  - 2 hrs. The exchanged phase ( $\text{NaSbO}_{3-x}\text{F}_x$ ) gave an x-ray pattern which was single phase cubic. The powders were pressed into 3/4" diameter pellets which were repressed isostatically at 20,000 psi. These pellets were placed in platinum envelopes, sealed on three sides and were again isostatically pressed to remove most of the air from the container. The envelopes were sealed and sent to a commercial company for isostatic hot pressing at  $1100^\circ\text{C}$  and 5,000 psi. The  $4\text{K}_2\text{O}:59\text{Nb}_2\text{O}_5$  specimen was submitted to LeRC, unopened, in the platinum envelope. Duplicate specimens were used to determine physical integrity and phase composition of the pellets. The  $\text{NaSbO}_{3-x}\text{F}_x$  specimen was not single phase after hot pressing, apparently as a result of decomposition under pressure. Three phases were evident: a cubic phase, the pyrochlore solid solution and NaF. It was felt that the exchanged product had a composition too close to a phase boundary with resultant instability under pressure. For this reason, it was decided to directly react the constituents to form the desired sodium containing phase directly and then hot press the product. A composition of  $68\text{NaSbO}_3:4\text{Sb}_2\text{O}_4:28\text{NaF}$  was chosen.

Attempts to fabricate a large, dense specimen of the composition  $60\text{NaSbO}_3:4\text{Sb}_2\text{O}_4:28\text{NaF}$  were largely unsuccessful. Direct reaction of the components at  $750^\circ\text{C}$  for 60 hours and  $1000^\circ\text{C}$  for 1 hour in open containers, with periodic grindings, resulted in a product containing  $\text{NaSbO}_3$  (ilmenite) and a trace of NaF. Calcining temperatures as high as  $1265^\circ\text{C}$  were required to form a single phase material of the desired cubic structure. A trace of NaF was always present as a second phase. The use of such high calcining temperatures results in a coarse-grained product which could not easily be ground fine enough to produce a sinterable powder. Attempts to hot press the specimens in platinum envelopes,

using the same technique described above for the 41:59 and  $\text{KSbO}_{3-x}\text{F}_x$  specimens, at a temperature of 1250°C for 10 minutes were unsuccessful. It is recommended that if these experiments are repeated, only the lower temperature calcines (at 750° and 1000°C) should be used, and the final desired phase in the pellet be produced by appropriate choice of time and temperature of hot pressing.

## 2.8 Crystal Growth and Synthesis

Many of the phases discovered during the phase equilibria studies of the alkali tantalate, niobate and antimonate systems have not been previously reported in the literature. One of the objectives of the crystal growth portion of the study has been to synthesize and grow small single crystals for x-ray diffraction studies to provide structural information on these materials and assist in the interpretation of x-ray diffraction powder patterns. The second, and equally important objective, has been to grow single crystals of the potentially useful  $\text{K}^+$  and  $\text{Rb}^+$  phases for use in studies of ion exchange behavior for the purpose of obtaining  $\text{Na}^+$  phases. These studies are described in Section 2.9 of this report.

In general the choice of technique was dictated by the characteristics of the desired phase, i.e. congruent or incongruent melting, volatility of one or more components of the phase, range of coexistence with liquid, and desired final size of crystal. Both fluxed melt and Czochralski techniques were utilized, and in some cases, the flux evaporation technique was used for the preparation of small crystals.

### 2.8.1 Crystal Growth by Pulling from the Melt

#### 2.8.1.1 Hexagonal Tungsten Bronze in the $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5-\text{WO}_3$ System

Selective phase equilibria experiments with mixtures of  $\text{KTaO}_3$  (KT) and  $\text{WO}_3$  in the neighborhood of  $\text{KT}:2\text{WO}_3$  ( $\text{K}_2\text{O}:\text{Ta}_2\text{O}_5:4\text{WO}_3$ ) during the previous contract confirmed the existence of a hexagonal tungsten bronze (HTB)

structure. Single phase compositions were easily prepared between the pyrochlore composition,  $K_2O:Ta_2O_5:WO_3$ , and a composition  $KTaO_3:3WO_3$  where a second, unidentified phase appeared. At the same time, exploratory crystal growth runs at lower  $Ta_2O_5$  contents were encouraging and gave some promise of adaptation to the accelerated crucible rotation technique (ACRT) for single crystal growth of this bronze structure. However, considerably more work is required to determine the liquidus surface and primary field extent before such experiments would be definitive.

A 50 gram batch of  $26.6K_2O:3.3Ta_2O_5:70.1WO_3$ , prepared from  $KT$ ,  $K_2WO_4$  and  $WO_3$  was premelted by induction heating in a platinum crucible. The crucible was then covered and transferred to a growth furnace. Following a 10 hour soak at  $1200^\circ C$ , the temperature was lowered at  $2.5^\circ C\ hr^{-1}$  to  $500^\circ C$  and the crucible removed from the furnace. Results were essentially the same as obtained in previously reported work with a cooling rate of approximately  $30^\circ\ hr^{-1}$ . Crystals were in general small, the largest ranging from about  $6\times6\times0.2\ mm$  to  $3\times3\times0.1\ mm$ . The yield, based on visual estimate, was small.

Because of the small total yield and extensive nucleation and growth of small platelets, an attempt was made to pull crystals of the HTB from the fluxed melt. A 250 gram charge of composition  $27K_2O:5Ta_2O_5:68WO_3$  was placed in a platinum crucible in a growth furnace which was baffled to provide an essentially isothermal chamber except directly above the center of the melt where the platinum pull rod was inserted. The charge was held at  $1225^\circ$  for three hours prior to attempting growth. Although no evidence of solid was present on the surface of the melt, extensive freezing of polycrystalline material occurred when the pull rod was inserted. The temperature was raised in increments and the polycrystalline mass redissolved. All attempts to achieve growth were unsuccessful at temperatures up to  $1250^\circ$ .

In the final attempt, at 1265°C, crystallization on the pull rod was slow enough to allow a 16 hour pull. X-ray diffraction examination of the results indicated that the crystals obtained were the desired phase. However, physically, the crystals were in the form of small plates, bound together by the frozen melt. It appears that a considerable effort would be required to establish suitable conditions for the growth of larger single crystals of this HTB. This would probably require a minimum of 1-2 man years.

#### 2.8.1.2 The System $\text{KNbO}_3\text{-Nb}_2\text{O}_5$

Single crystals of  $\text{K}_4\text{Nb}_6\text{O}_{17}$  have rather easily been grown both at other laboratories [15] and at NBS. However, the material hydrates readily in laboratory air, with subsequent degradation of the crystalline perfection, which is not regained by drying. In order to provide LeRC with a large single crystal which had never been hydrated, a crystal was grown from a melt of the same composition, removed from the puller while still at a temperature of 300-400°C and immediately placed in a fused silica ampoule, evacuated to  $p \leq 2 \times 10^{-5}$  <sup>4/</sup> torr and sealed for transmittal. Later conversations with LeRC indicated that the behavior of this crystal was indeed different, and as described in the section on pellet preparation, never hydrated pellets were also supplied for evaluation.

#### 2.8.1.3 The System $\text{Rb}_2\text{O-Nb}_2\text{O}_5$

A 100 gram batch of  $29\text{Rb}_2\text{O}:71\text{Nb}_2\text{O}_5$  was calcined at 400° for 60 hours and used for crystal pulling experiments. Five single and/or polycrystalline boules of the 4:11 (Rb:Nb) (11-layer) hexagonal phase were pulled from the melt by the top seeded solution method. The crystals were obtained using both seeded and unseeded pull rods. These crystals were used as "purified" material for the growth of single crystal 11L for use as a stable end member of the system and for chemical analysis.

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<sup>4/</sup> The use of torr follows the current common practice of workers in the field. Note that 1 torr =  $1.32 \times 10^{-3}$  atm =  $1.34 \times 10^2$  N/m<sup>2</sup>.



The crystals appear to be susceptible to thermal shock and therefore must be cooled relatively slowly. Self-seeded crystals show a marked preference for growth perpendicular to the c-axis. At least one excellent cleavage (basal-plane) is evident.

Crystals of the hexagonal tungsten bronze (HTB) phase in this system ( $21.75\text{Rb}_2\text{O}:78.25\text{Nb}_2\text{O}_5$ ) were grown by pulling from a melt of the same composition (experiments performed by C. Jones while on an American University Research Participation Program). Large, clear water-white crystals were easily obtained but all fractured into rather large blocks upon cooling. All attempts to prevent cracking were unsuccessful and the cause remains unknown, but may be related to a symmetry change to orthorhombic on cooling.

Crystals of the Gatehouse tungsten bronze (GTB) ( $11.5\text{Rb}_2\text{O}:88.5\text{Nb}_2\text{O}_5$ ) phase were grown from a melt of composition  $16\text{Rb}_2\text{O}:84\text{Nb}_2\text{O}_5$  (experiments performed at NBS by D. Klein while on an American University Research Participation Program). Small single crystal boules were successfully grown, but again fractures developed as soon as the boules were removed from the melt at the completion of the run in spite of all attempts at slow cooling of the boule.

## 2.8.2 Flux Growth

### 2.8.2.1 The System $\text{Rb}_2\text{O}-\text{Nb}_2\text{O}_5-\text{MoO}_3$

Nine different compositions in this system were prepared (2 gm batches) and heated by induction to temperatures in the  $900^\circ\text{--}1100^\circ\text{C}$  range in small platinum crucibles. Recrystallization and/or volatility of the  $\text{MoO}_3$  resulted in the formation of small crystals. Crystals (2mm+) of the 11 layer hexagonal (4:11) phase were obtained from compositions of  $30\text{Rb}_2\text{O}:5\text{Nb}_2\text{O}_5:65\text{MoO}_3$  and  $30\text{Rb}_2\text{O}:10\text{Nb}_2\text{O}_5:60\text{MoO}_3$ . A  $27.5\text{Rb}_2\text{O}:10\text{Nb}_2\text{O}_5:62.5\text{MoO}_3$  composition yielded small crystals of the GTB

phase ( $\sim 11.5$  mole %  $\text{Rb}_2\text{O}$ ) and  $\text{H-Nb}_2\text{O}_5$  and  $28\text{Rb}_2\text{O}:5\text{Nb}_2\text{O}_5:67\text{MoO}_3$  yielded small single crystals of the HTB ( $\sim 11.75$  mole %  $\text{Rb}_2\text{O}$ ). No crystals of the unidentified phase occurring at about 15 mole %  $\text{Rb}_2\text{O}$  in the binary system were obtained with any  $\text{MoO}_3$  flux composition. This is further reason to believe this phase may not be an equilibrium compound in the binary system.

#### 2.8.2.2 The System $\text{Rb}_2\text{O}-\text{Ta}_2\text{O}_5-\text{MoO}_3$

Six different compositions were prepared in the ternary system for flux evaporation crystal growth. Single crystals of the 9 layer phase (1:3) were grown using compositions of  $30\text{Rb}_2\text{O}:10\text{Ta}_2\text{O}_5:60\text{MoO}_3$  and  $35\text{Rb}_2\text{O}:5\text{Ta}_2\text{O}_5:60\text{MoO}_3$ . Crystals of the other phases in the binary system  $\text{Rb}_2\text{O}-\text{Ta}_2\text{O}_5$  could not be obtained using this method, probably because their primary fields do not extend to such high  $\text{MoO}_3$  contents, or to the relatively low temperatures involved.

#### 2.8.2.3 The System $\text{Rb}_2\text{O}-\text{Ta}_2\text{O}_5-\text{RbF}$

In view of the success obtained by the flux synthesis route in the  $\text{KSbO}_3-\text{KF}$  system [13] similar attempts were made using  $\text{RbF}$  and  $\text{Ta}_2\text{O}_5$ . A  $95\text{RbF}:5\text{Ta}_2\text{O}_5$  composition was completely liquid at about  $925^\circ\text{C}$  and on cooling yielded acicular crystals of an unknown phase. A  $75\text{RbF}:25\text{Ta}_2\text{O}_5$  composition was heated to about  $1150^\circ\text{C}$  for 30 seconds and quickly cooled. After leaching with water, a sizeable yield of clear, well-formed, octahedral crystals of the  $\text{RbTa}_2\text{O}_5\text{F}$  pyrochlore phase was obtained.

#### 2.8.2.4 The Systems $\text{ASbO}_3-\text{Sb}_2\text{O}_4-\text{AF}$ ( $\text{A} = \text{Na}, \text{K}, \text{Rb}$ )

The techniques for synthesis and growth of small crystals of  $\text{KSbO}_{3-x}\text{F}_x$  by reaction between  $\text{KF}$  and  $\text{Sb}_2\text{O}_5$  at temperatures in the  $1000^\circ\text{C}$  range, developed during this contract, have been described [13].

Attempts were made to melt the flux-synthesized  $\text{KSbO}_{3-x}\text{F}_x$  in air with the thought it might be possible to pull crystals directly from

a melt of that particular composition. The material decomposed as the melting point was reached, indicating that pulling in air would not be feasible. A large batch of ~50 grams was prepared with a composition of  $70\text{KF}:30\text{Sb}_2\text{O}_4$  and heated in an effort to obtain a melt (single phase liquid) suitable for crystal pulling. At all temperatures below which there was excessive volatilization a solid phase remained. It seems obvious now that we have to go much higher in KF concentration to obtain a composition which may be suitable for crystal growth.

Quenching experiments indicated that mostly ilmenite was formed at temperatures up to ~1200°C in the system  $\text{NaF}-\text{NaSbO}_3$ . We decided to attempt a direct synthesis of the sodium cubic phase in the same manner as for the  $\text{KSbO}_{3-x}\text{F}_x$  but at a higher temperature. A 3 gram batch of  $\text{NaF}-\text{Sb}_2\text{O}_4$  (molar ratio 93:7) was heated in a platinum crucible to 1250°C and the NaF allowed to evaporate for 35 minutes. After leaching the residue in water we obtained essentially single phase  $\text{NaSbO}_{3-x}\text{F}_x$ .

The largest crystals were of the order of 1 mm. Some flat hexagonal plates of ilmenite are formed at the lip of the crucible, probably during volatilization of the sodium antimony fluor-oxide, however these can easily be separated mechanically from the cubic phase.

X-ray diffraction patterns (single crystal and powder) of selected washed crystals show only a truly cubic body centered phase ( $a=9.334\text{\AA}$ ). It must be postulated that the composition formed by this technique is slightly different from that made essentially single phase at  $4\text{NaSbO}_3:\text{NaF}$  in a sealed tube.

Exploratory flux evaporation heatings were made in the  $\text{KSbO}_3-\text{Sb}_2\text{O}_4-\text{KF}$  and  $\text{RbSbO}_3-\text{Sb}_2\text{O}_4-\text{RbF}$  systems as a preliminary step in the determination of suitable starting compositions for flux crystal growth of the desired  $\text{ASbO}_{3-x}\text{F}_x$  phases. The results are summarized

in Table 11. None of the reported compositions would appear to be suitable for top-seeded solution growth both from the standpoint of the excessive volatility of the alkali fluoride at the temperatures involved and the presence of a solid phase. The presence of a solid phase at such high concentrations of flux (alkali fluoride) indicates that either a gradient transfer technique in sealed crucibles must be adopted or the suitability of other flux systems investigated.

An attempt was made to synthesize " $\text{RbSbO}_3$ " in the cubic polymorph by direct flux synthesis from the composition  $95\text{RbF}:5\text{Sb}_2\text{O}_3$  heated for one hour at about  $900\text{--}1000^\circ\text{C}$  in an open Pt crucible. Well developed pseudo-octahedral crystals were formed and easily isolated although their exact composition is unknown. However single crystal x-ray diffraction patterns indicated that these crystals were probably triclinic, although the observed unit cell was C-centered.

## 2.9 Ion Exchange

One of the the best screening tests for ionic conductivity of a solid phase is to determine whether or not the alkali ion in the structure can be exchanged with an alkali ion of a different species. This may be tested by heating in a large excess of a molten salt (or solution) containing the second ion. A large number of experiments of this type were performed on many different compounds found in this and the previous year's [1] study. The results of these tests are found in Table 10(a).

Most of the exchange experiments have been performed on powdered materials. In those cases where single crystals could be grown either by flux techniques or melt techniques (see Section 2.8), attempts were also made to ion exchange the single crystals.

In general, the results of ion exchange experiments on single crystals were disappointing in that either disruption of the single crystal

occurred or exchange proceeded at extremely low rates. Thus it appears that a study of technique development for ion exchange of single crystals would be appropriate if these are to be useful in device applications. Consideration should be given to the use of an electric field or other technique in order to obtain a greater driving force for exchange.

Ion exchange experiments were conducted in the  $\text{Rb}_2\text{O-Nb}_2\text{O}_5$  system with particular emphasis on the 11-layer compound occurring at or about  $4\text{Rb}_2\text{O}:11\text{Nb}_2\text{O}_5$  (26.67 mole %  $\text{Rb}_2\text{O}$ ). Ion exchange experiments were conducted on both single crystal fragments obtained from crystals grown from the melt and low temperature calcines of 4:11 powders. The single crystals underwent  $\text{K}^+$  exchange in molten  $\text{KNO}_3$  but disintegrated during  $\text{Na}^+$  exchange in  $\text{NaNO}_3$  during various temperature and time combinations. Pellets of the 11-L phase were pressed both uniaxially and isostatically with and without polyvinyl alcohol binder. Pellets were fired and x-ray patterns made before any attempt was made to induce ion exchange. Generally the  $\text{K}^+$  exchange occurred without too much degradation of the specimen but the pellets disintegrated to a fine powder during  $\text{Na}^+$  exchange. Results of these exchange experiments are also presented in Table 10.(b). The unit cell dimensions for complete ion exchange were developed from ion exchange in molten salts from very small single crystal fragments.

### 3.0 RELATION OF STRUCTURAL MECHANISMS OF NON-STOICHIOMETRY TO IONIC CONDUCTIVITY

It is probably generally accepted that a phase which exhibits unusual ionic conductivity must necessarily be structurally non-stoichiometric. Unfortunately the opposite is not necessarily true. Nevertheless a crystallographic understanding of non-stoichiometric phases is an obvious necessity to the tailoring of new fast-ion conductors. For this reason it is worthwhile to discuss the nature of the non-stoichiometry which has been observed in this study for those phases which seem to be of interest.

### 3.1 Hexagonal Tungsten Bronze-type Phases (HTB)

It has already been mentioned in the previous summary report [1] that the hexagonal tungsten bronze-type phase (HTB) found in binary alkali niobate and tantalate systems has alkali ions in non-stoichiometric positions and excess  $\text{Nb}^{+5}$  or  $\text{Ta}^{+5}$  ions. These excess pentavalent ions may well block the alkali ion conductivity as these hexagonal bronzes cannot be ion exchanged. There are two mechanisms that have proved effective in altering the ion exchange characteristics of the hexagonal tungsten bronze-type structures. One is to change the total alkali:other cation valence ratio by substituting  $\text{W}^{+6}$  for  $\text{Ta}^{+5}$ , for instance in the system  $\text{KTaO}_3\text{-WO}_3$ . In this case the HTB phase occurs at about the 1:2 ratio and the  $\text{K}^+$  ion can be replaced with  $\text{Na}^+$  by heating in a large excess of  $\text{NaNO}_3$ . Unfortunately the Na-tantalum-tungstate is not stable above about  $450^\circ\text{C}$  and therefore cannot be formed into low porosity ceramics by conventional techniques. The single crystals of HTB grown with the potassium tungstate flux (Section 2.8.2.1) need some greater driving force than temperature ( $<450^\circ$ ) to obtain complete exchange with  $\text{Na}^+$  ions. The alternate to replacing  $\text{Ta}^{+5}$  ions with  $\text{W}^{+6}$  ions is to change the structure enough to allow ion exchange (See Section 3.3).

### 3.2 Pyrochlore Phases

In the  $\text{KTaO}_3\text{-WO}_3$  system a pyrochlore phase also occurs at about the 1:1 ratio or  $\text{K}_{1.0}[\text{TaW}]_6\text{O}_{24}$ . Unfortunately the pyrochlore in this system transforms to a tetragonal tungsten bronze (TTB) at high temperatures. Although it can be ion exchanged with  $\text{Na}^+$ , this pyrochlore phase also is not stable above about  $450^\circ\text{C}$ . The only stable  $\text{Na}^+$  containing pyrochlore is the one in the  $\text{Sb}_2\text{O}_4\text{-NaSbO}_4$  system and apparently this one is not a good ionic conductor.

The distribution of  $\text{Na}^+$ ,  $\text{Sb}^{+3}$ ,  $\text{Sb}^{+5}$  and  $\text{O}^{-2}$  ions in a pyrochlore single crystal is currently under evaluation by the Crystallography Section at NBS. However, certain assumptions can be made which may enable us to postulate the approximate distribution. The formula for the compositions observed to result in a pyrochlore structure might be postulated to be  $[\text{NaSb}^{+3}] \text{Sb}_2\text{O}_7$  for the Na/Sb ratio of 1:3,  $[\text{Na}_{1/3} \text{Sb}_{2/3}^{+3}] \text{Sb}_2\text{O}_{6.67}$  for 1:2, and  $[\text{Na}_{1/2} \text{Sb}_{1/2}^{+3}] \text{Sb}_2\text{O}_{6.5}$  for 3:5. However, these compositions do not illustrate the structural nature of pyrochlore nor account for the observation that the "lone pair" electrons associated with  $\text{Sb}^{+3}$  will not allow  $\text{O}^{-2}$  ions to completely coordinate the antimony and result in apparent vacancies.

The structural formula of pyrochlore should be written as  $[\text{A}_2\text{X}] [\text{B}_2\text{X}_6]$  to emphasize the fact that the octahedral network of  $\text{B}_2\text{X}_6$  is required to be complete if the structure is to be stable. The  $\text{A}_2\text{X}$  ions fill the intersecting channels in this  $\text{B}_2\text{X}_6$  framework. In our material the  $\text{B}_2\text{X}_6$  framework must be represented as  $[\text{Sb}_2^{+5}\text{O}_6]^{-2}$  and must be stoichiometric. All remaining  $\text{Na}^+$  and  $\text{O}^{-2}$  ions, as well as  $\text{Sb}^{+3}$ , must be in the  $[\text{A}_2\text{X}]^{+2}$  portion of the formula. All  $\text{Sb}^{+5}$  must be in  $\text{B}_2\text{X}_6$  and only  $\text{Sb}^{+3}$  in  $\text{A}_2\text{X}$ . Furthermore the maximum number of the sum of  $\text{Na}^{+1}$ ,  $\text{Sb}^{+3}$  excess  $\text{O}^{-2}$  (beyond  $\text{O}_6^{-2}$ ) and "lone pair" electrons cannot exceed three. One can then write the general formula as  $[\text{A}_2\text{O}]^{+2} [\text{Sb}_2\text{O}_6]^{-2}$  with  $[\text{A}_2\text{O}]^{+2}$  equal to

$$\text{Na}_{2/k}^{+1} + \text{Na}_x^{+1} + \text{Sb}_{kx}^{+3} + \text{O}_y^{-2} + \boxed{\text{L.P.}}_{kx} \leq 3$$

where k equals the ratio Sb/Na. Using the ionic valences and the sum of the ions equal to three, maximum densities can be calculated and compared with the observed to test the structural hypothesis. The maximum density for the Na/Sb ratio of 1:3 represented by the formula

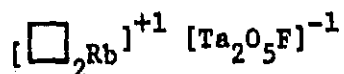
$[\text{Na}_{0.917}^{+1} \text{Sb}_{0.75}^{+3} \text{O}_{0.583}^{-2} \boxed{\phantom{0.75}}_{0.75}]^{+2} [\text{Sb}_2^{+5}\text{O}_6]^{-2}$  is calculated to be 5.469 units.

For the Na/Sb ratio of 3:5 with the formula

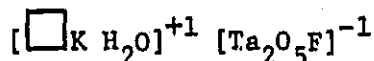
$[\text{Na}_{1.5}^{+1}\text{Sb}_{0.5}\text{O}_{0.5}^{-2}\square_{0.5}]^{+2} [\text{Sb}_2\text{O}_6]^{-2}$  the density is calculated as 5.406.

For the intermediate composition with the Na/Sb ratio of 1:2 and a formula of  $[\text{Na}_{1.294}^{+1}\text{Sb}_{0.588}^{+3}\text{O}_{0.529}^{-2}\square_{0.588}]^{+2} [\text{Sb}_2\text{O}_6]^{-2}$  the maximum density is found to be 5.481. The density found for our isostatically hot pressed specimens is 96.0% of the maximum theoretical density. It should be remembered however that the true theoretical density of any given Sb/Na ratio will decrease with decrease in temperature. Thus the densities obtained on our hot pressed specimens are, in all probability, greater than 96% of theoretical in view of the expected increased oxidation of the Sb at the relatively low temperatures involved.

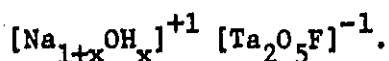
As stated above, the pyrochlore structural formula should be written as  $[\text{A}_2\text{X}] [\text{B}_2\text{X}_6]$ . The  $\text{RbTa}_2\text{O}_5$  is apparently equivalent to the formula



as shown by Hong's structural study [16] of single crystals prepared by the flux synthesis method described by NBS [17]. The  $\text{Rb}^+$  ion is apparently too large for the A sites and it is this preference for the larger anion site that makes this compound stable. During ion exchange in  $\text{KNO}_3$  the  $\text{K}^+$  ion apparently enters the A site and, upon exposure to atmospheric moisture, an  $\text{H}_2\text{O}$  molecule occupies the site formerly containing  $\text{Rb}^+$ . The formula is then

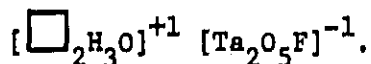


During sodium exchange it is apparently possible to obtain a non-stoichiometric amount of Na in this lattice. The formula for this phase can probably be written as





The product obtained by acid leaching of this pyrochlore is apparently



Although infra-red analysis of the  $\text{Na}^+$  exchange product does not indicate  $(\text{OH})^-$  [18] it would probably be worthwhile to examine this product with NMR for hydrogen resonance, a much more sensitive method than infra-red adsorption.

### 3.3 Hexagonal Tungsten Bronze - Pyrochlore Series

The  $[\text{B}_2\text{X}_6]$  framework of the pyrochlore structure can be described as being made up of alternating layers of the hexagonal tungsten bronze structure separated by layers of isolated octahedra sharing only two corners with the adjacent HTB layers. If this structure is modified by increasing the sequence number of either of these types of layers from ABAB to AABAAB or AAABAAAB etc., a sequence of hexagonal phases would be formed having the same a axis as the HTB structure and with varying but integral multiplicities of the c axis dimension. Such phases are actually encountered in the  $\text{K}_2\text{O-Ta}_2\text{O}_5$  [1,2]  $\text{Rb}_2\text{O-Nb}_2\text{O}_5$  and  $\text{Rb}_2\text{O-Ta}_2\text{O}_5$  systems and have been estimated by us to represent 9-layer, 16-layer and 11-layer sequences. All of the phases can be ion exchanged for  $\text{Na}^+$  unlike the HTB in the same systems. The reason for this appears to be that a rotation or translation of a portion of the layer sequence allows the isolated vertical channels found in the HTB structure to be changed to intersecting channels as in the cubic pyrochlore structure. The exact crystallographic nature of these compounds is currently under investigation by Dr. B. T. Gatehouse at Monash University, Melbourne, Australia. Unfortunately, however, the  $\text{Na}^+$  ion exchanged products are again not stable above about  $450^\circ\text{C}$ .

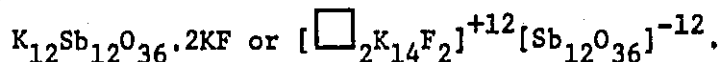
As is the case with the pyrochlore compounds the  $\text{K}_2\text{O}$  containing phases have unit cell dimensions very similar to or even larger than the corresponding  $\text{Rb}_2\text{O}$  containing phases. For instance the c-axis for

the 11-layer phase in the  $K_2O-Ta_2O_5$  system is 43.512A while that in the  $Rb_2O-Nb_2O_5$  system is 43.18A and in the  $Rb_2O-Ta_2O_5$  43.19A. This may be due to a real difference in total alkali content. It may also be due to hydration of the  $K_2O$  phases. No high temperature x-ray data is available to check this hypothesis but small single crystals of the 2:5  $K_2O:Ta_2O_5$  phase have been noted to crack, spall and jump on exposure to air.

### 3.4 Body Centered Cubic Antimonates

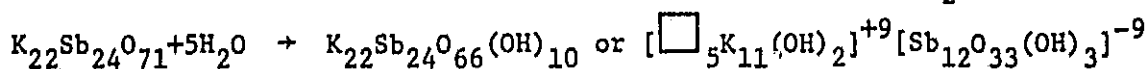
A successful method of synthesizing cubic potassium antimonate by heating in molten KF was published by the present authors during this contractual period [13]. The major reason for the success in obtaining completely single phase fluorine stabilized cubic potassium antimonate is that the potassium ilmenite is  $H_2O$  soluble and may be easily separated from the cubic material.

An examination of the structural model of the octahedral framework of the body centered cubic antimonate phase suggests that this structure must always have some anion (X) occupancy in the 000,  $1/2\ 1/2\ 1/2$  position. The structural formula thus appears to be  $[A_{16}X_2]^{+12}[Sb_{12}O_{36}]^{-12}$  with the alkali ion in position (A) located at (or just off) the juncture of the open cages. However, it seems very likely from both structural reasons (bond lengths, etc.) and valency considerations that either or both of the non-framework positions will be nonstoichiometric. Valency considerations require that at least two out of 16 alkali ions must be missing and the structural formula then be  $[\square_2A_{14}X_2]^{+12}[Sb_{12}O_{36}]^{-12}$ . This formula corresponds to the composition reported by the Lincoln Laboratory report [19] for the single crystal x-ray diffraction analyses of the phase synthesized with KF according to the NBS method [13]:

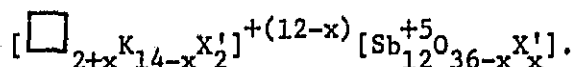


It seems quite likely, however, that this general formula does not completely account for all of the preparations which have been observed to form this structure, whether body centered or primitive. The observation that a primitive phase can be formed, in air, by reaction with atmospheric moisture at a 48:52 ratio suggests that this phase may well have considerably less than 14 alkali ions per unit cell. The formula must be compensated, in this case, by a substitution of a monovalent anion (OH, F) in the octahedral framework. The general formula then becomes  $[\square_{2+x}A_{14-x}X_2]^{+(12-x)}[Sb_{12}O_{36-x}X_x]^{-(12-x)}$ .

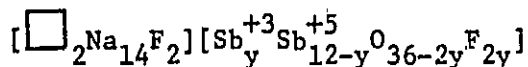
The composition found at 48:52 in the potassium antimonate system can be written (assuming a ratio of 11:12 K/Sb or 47.826%  $K_2O$ ):



which also can be described as  $6KSbO_3:3Sb_2O_5:5KOH$  (see Figure 8). The general formula describing the  $K^+$  containing compositions is then

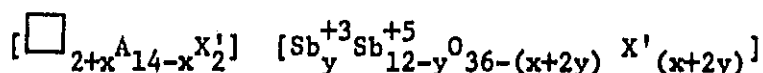


The above formula contains only pentavalent antimony and apparently does not completely explain the compositions which form a 'stable' body centered cubic phase in the system  $NaSbO_3:Sb_2O_{4+x}:NaF$ . The only formula which does not involve the loss or gain of  $O^{-2}$  (or  $F^-$ ) when the  $Sb_2O_4$  is added in a sealed tube corresponds to:

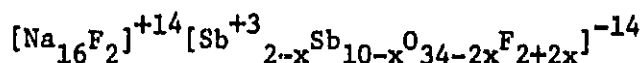


which is represented by the join 6:1 -- 3:7 on Figures 5 and 6. There is really no place in the framework structure for  $Sb^{+3}$  and it is difficult to believe that octahedrally coordinated antimony can be  $Sb^{+3}$ . The lone pair electrons can be attached to the sodium ions instead of the antimony or just in the vacancies. However, for convenience, the

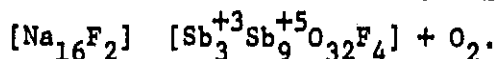
formulas can be written involving  $\text{Sb}^{+3}$ . The new formula would then have two variables:



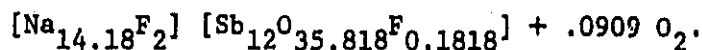
represented by the plane in the quaternary system  $\text{NaSbO}_3:\text{Sb}_2\text{O}_3:\text{NaF}$  bounded by the 6:1 -- 3:4 and 6:1 -- 3:7 joins of Figures 5 and 6. However the single phase region in this system actually appears to contain more NaF than described by this general formula. Apparently some  $\text{O}^{-2}$  is evolved in the sealed Pt tubes, the amount depending on uncontrolled variables such as the amount of free volume in the tube and on changes from the original composition during treatment. The absolute maximum amount of NaF which can be accommodated structurally by the body centered cubic phase can be described by the formula



which represents a line in the system shown by the join 3:1 -- 3:8 in Figure 6 and involves the evolution of one molecule of gas ( $\text{O}_2$ ) per formula unit. The results of our investigations so far suggest that the body centered phase approaches this formula as a limit. The composition of the cubic phase in equilibrium with excess  $\text{Sb}_2\text{O}_4$  and molten NaF actually appears to touch this line at approximately  $10\text{NaSbO}_3:\text{Sb}_2\text{O}_4:6\text{NaF}$  or



The single phase distorted cubic material on the binary join  $\text{NaSbO}_3:\text{NaF}$  appears to have a composition between 6:1 and 5:1 or approximately  $11\text{NaSbO}_3:2\text{NaF}$  or



The compositions in the quaternary system thus probably lie on a join between these two end members.

A large number of experiments were performed in an attempt to synthesize ceramic products of single phase body centered cubic sodium antimonate "stabilized" with  $F^+$ . Although we have not yet succeeded in preparing such a ceramic all indications point to a short time heat treatment with specific specimen preparation techniques. These almost unique conditions indicate that the body centered cubic phase is not really stable under the conditions at which it is formed. Thus either its true stability field may lie at some higher or lower partial pressure of  $O_2$  (or OH) or it may always be metastable under any conditions.

### 3.5 The Phase $2K_2O:3Nb_2O_5$

In the previous contract summary report [1] it was reported that the compound occurring at about  $2K_2O:3Nb_2O_5$  had the unit cell dimensions  $a=7.822$ ,  $b=33.019$ ,  $c=6.481A$  when not hydrated. Only the b axis expanded upon exposure to moisture as previously mentioned by Nassau [15]. From these unit cell dimensions several postulations can be made. The a direction corresponds to  $2 \times 3.911$  or two O-Nb-O distances and probably represents two Nb-octahedra sharing oxygen at their corners. The c direction corresponds to  $2 \times 3.2405$  or two times the O-O distance corresponding to edge sharing of the Nb-octahedra. The b direction is  $\sim 10$  times the value for edge sharing. It may be assumed that the structure is made up of layers or slabs perpendicular to b, composed of octahedra edge-shared in the c direction and corner shared in the a direction. These slabs must be separated by layers of  $K^+$  ions and the  $K^+$  ions should then be rather mobile. That this is actually the case is demonstrated by our reported ion exchange with  $Na^+$  where the b axis changes to  $30.78A$  and the conductivity measurements made by LeRC [20]. The actual crystal structure of this phase is currently under investigation by Dr. N.C. Stephenson of the New South Wales Institute of Technology, Sydney, Australia.

Although no ionic-conductivity or even ion exchange studies have been performed on the compound  $K_2O:3Nb_2O_5$  it is sufficiently similar to the 2:3 phase to warrant some additional study.

#### 4.0 SUMMARY OF RESULTS

1. Single crystals of hexagonal tungsten bronze (HTB) were synthesized in the system  $KTaO_3-WO_3-K_2WO_4$  by the flux technique. No crystals large enough to measure conductivity by the presently utilized techniques were successfully obtained.
2. The phase equilibria up to and including the liquidus of portions of the systems  $Rb_2O-Nb_2O_5$  and  $Rb_2O-Ta_2O_5$  have been studied and phase diagrams have been constructed most consistent with the experimental data. Single crystals were grown of most of the compounds in the niobate system and the phases were investigated for ion exchange properties. Single crystal and polycrystalline specimens were submitted to the sponsor for evaluation.
3. The phase equilibria up to and including the liquidus of the systems  $Sb_2O_4-NaSbO_3$  and  $Sb_2O_4-KSbO_3$  have been studied and a phase diagram has been constructed most consistent with the experimental data. Polycrystalline ceramic specimens of the pyrochlore phase were prepared and submitted to the sponsor for evaluation.
4. The stabilization of cubic antimonates by addition of  $F^+$  was studied in an attempt to provide a low porosity  $Na^+$  ion ceramic specimen for evaluation. Although small single crystals were easily synthesized by the alkali fluoride flux technique, no crystals larger than  $\sim 1-2$  mm were obtained.
5. Many other alkali-oxide rare earth oxide and  $Bi_2O_3$  systems were examined but no new interesting phases identified.
6. The phase occurring at about  $2K_2O:3Nb_2O_5$  was found to have interesting ion exchange and ionic conductivity properties.

## 5.0 FUTURE WORK

1. Develop techniques to grow large crystals from a flux. Such techniques have only been reported for a very few phases and generally involve an inordinate amount of man hours to produce results.
2. Develop techniques to ion exchange large crystals, perhaps by utilizing an electronic current with a hot alkali salt or solution.
3. Investigate and develop improved fabrication techniques to produce dense, sound pellets of the  $68\text{NaSbO}_3:4\text{Sb}_2\text{O}_4:28\text{NaF}$  composition in a size suitable for definitive ionic conductivity measurements and examine the effect of varying composition on conductivity.
4. Obtain crystallographic structure analyses on  $2\text{K}_2\text{O}:3\text{Nb}_2\text{O}_5$  and on  $4\text{Rb}_2\text{O}:11\text{Nb}_2\text{O}_5$  (now being conducted by N.C. Stephenson and B. Gatehouse).

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## Figure Captions

Figure 1. Phase equilibrium diagram for the system  $\text{Nb}_2\text{O}_5\text{-4Rb}_2\text{O:11Nb}_2\text{O}_5$ .

- - liquidus values from reference [21]
- - completely melted
- ◐ - partially melted
- x - no melting

Figure 2. Phase equilibrium diagram for the system  $\text{Ta}_2\text{O}_5\text{-4Rb}_2\text{O:11Ta}_2\text{O}_5$ .

- ◐ - partially melted
- - no melting

Figure 3. Phase equilibrium diagram for the system  $\text{Sb}_2\text{O}_4\text{-NaSbO}_3$ .  
Not necessarily a true binary system. (L = liquid, S = solid, V = vapor)

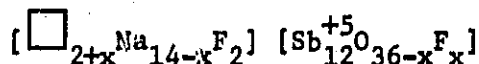
- - melting
- x - no melting

Figure 4. Phase equilibrium diagram for the system  $\text{Sb}_2\text{O}_4\text{-KSbO}_4$ .  
Not necessarily a true binary system.

- - melting
- x - no melting
- ss - solid solution
- 1:2 -  $\text{K}_2\text{O:2Sb}_2\text{O}_5$
- 3:5 -  $\text{3K}_2\text{O:5Sb}_2\text{O}_5$
- $\text{P2}_1/\text{c}$  - low temperature form of  $\text{K}_2\text{O:2Sb}_2\text{O}_5$

Figure 5. Phase relations in the quaternary system  $\text{NaSbO}_3\text{-Sb}_2\text{O}_3\text{-Sb}_2\text{O}_5\text{-NaF}$ .

The join 6:1--3:4 represents the formula



The join 6:1--3:7 represents the formula

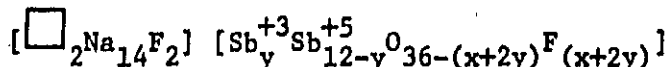
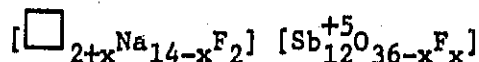
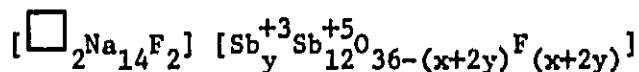


Figure 6. Phase relations in the ternary system  $\text{NaSbO}_3\text{-Sb}_2\text{O}_4\text{-NaF}$

The join 6:1--3:4 represents the formula



The join 6:1--3:1 represents the formula



The join 3:1 --3:8 represents the formula

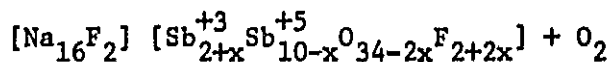
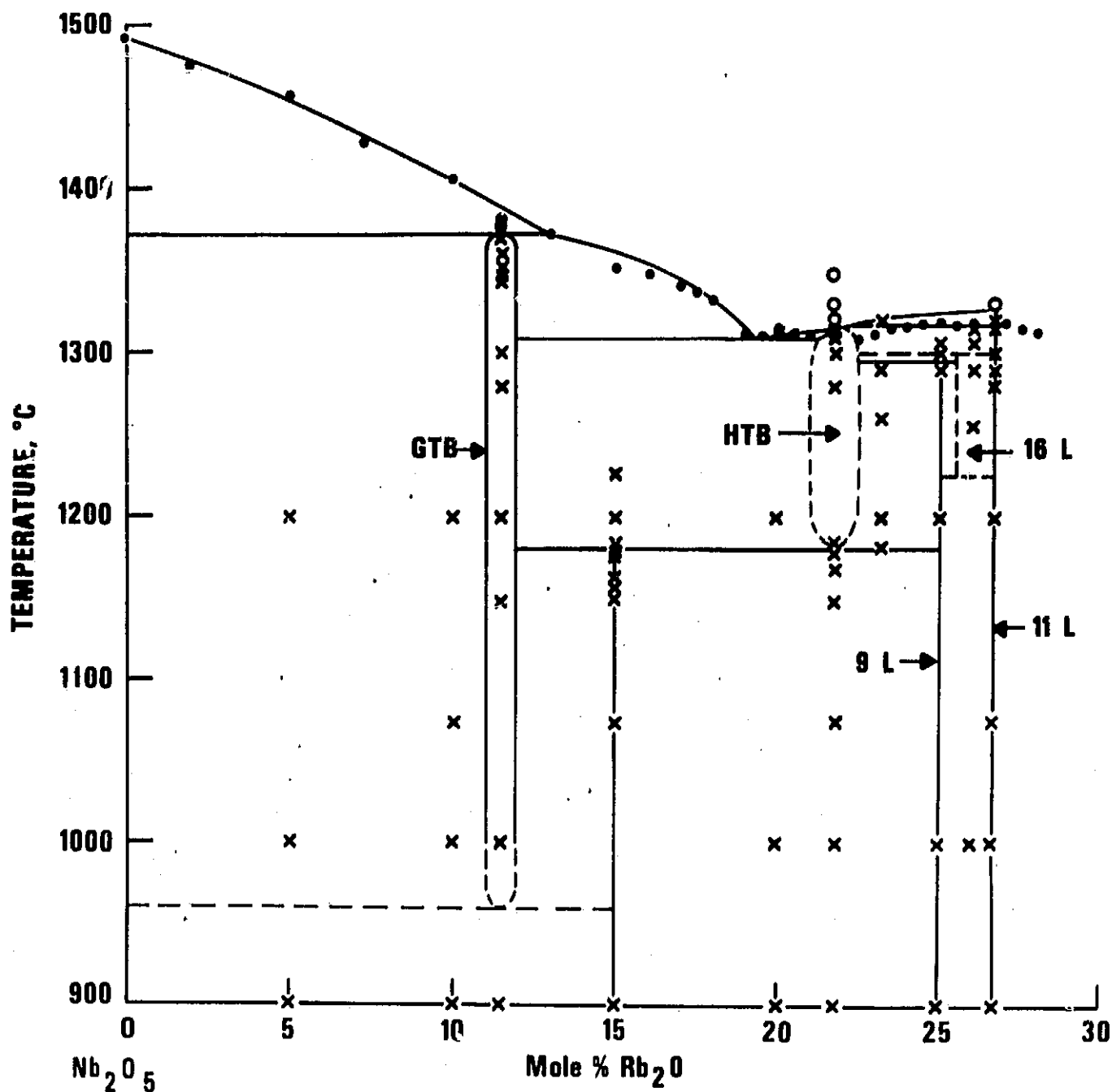
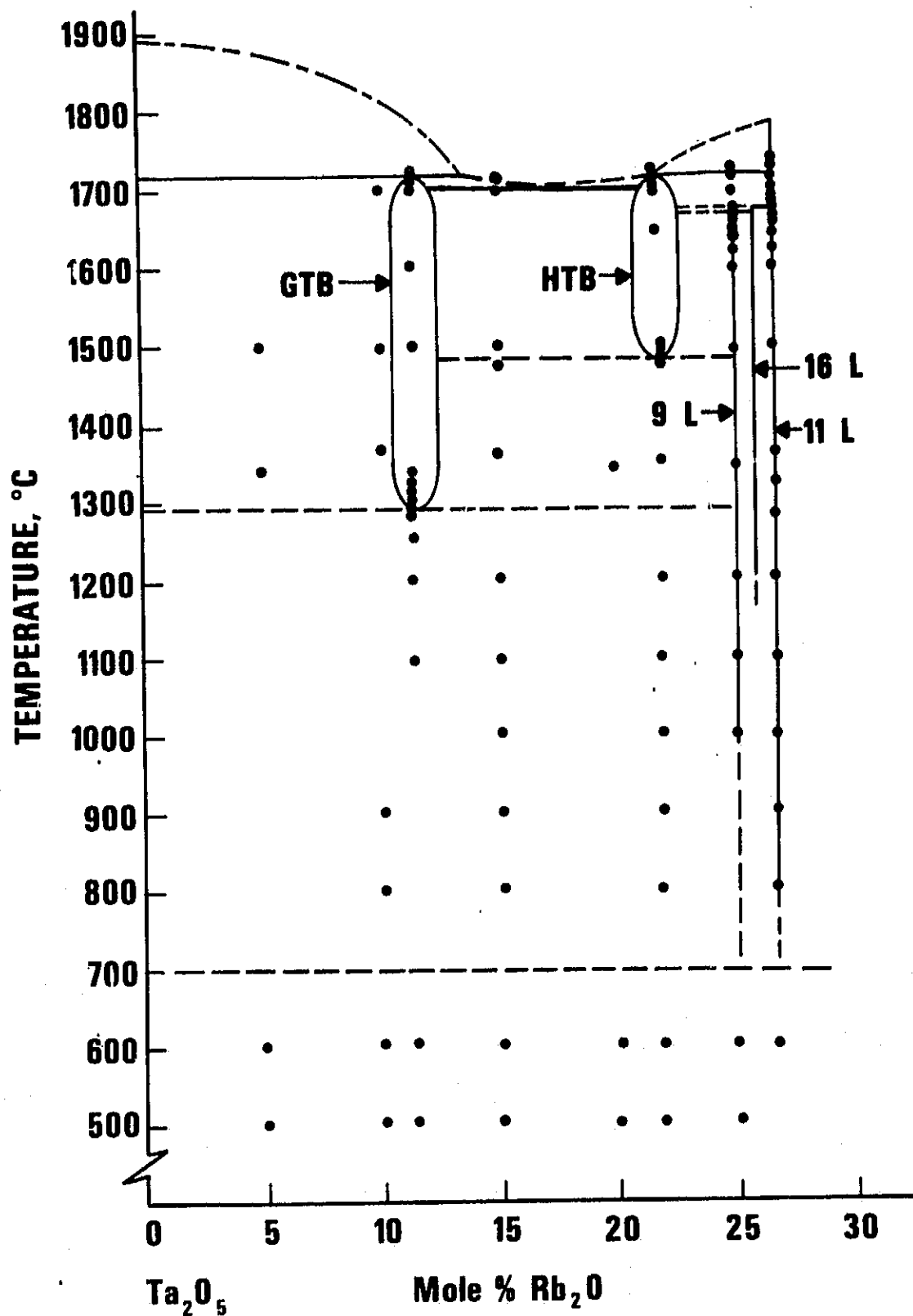


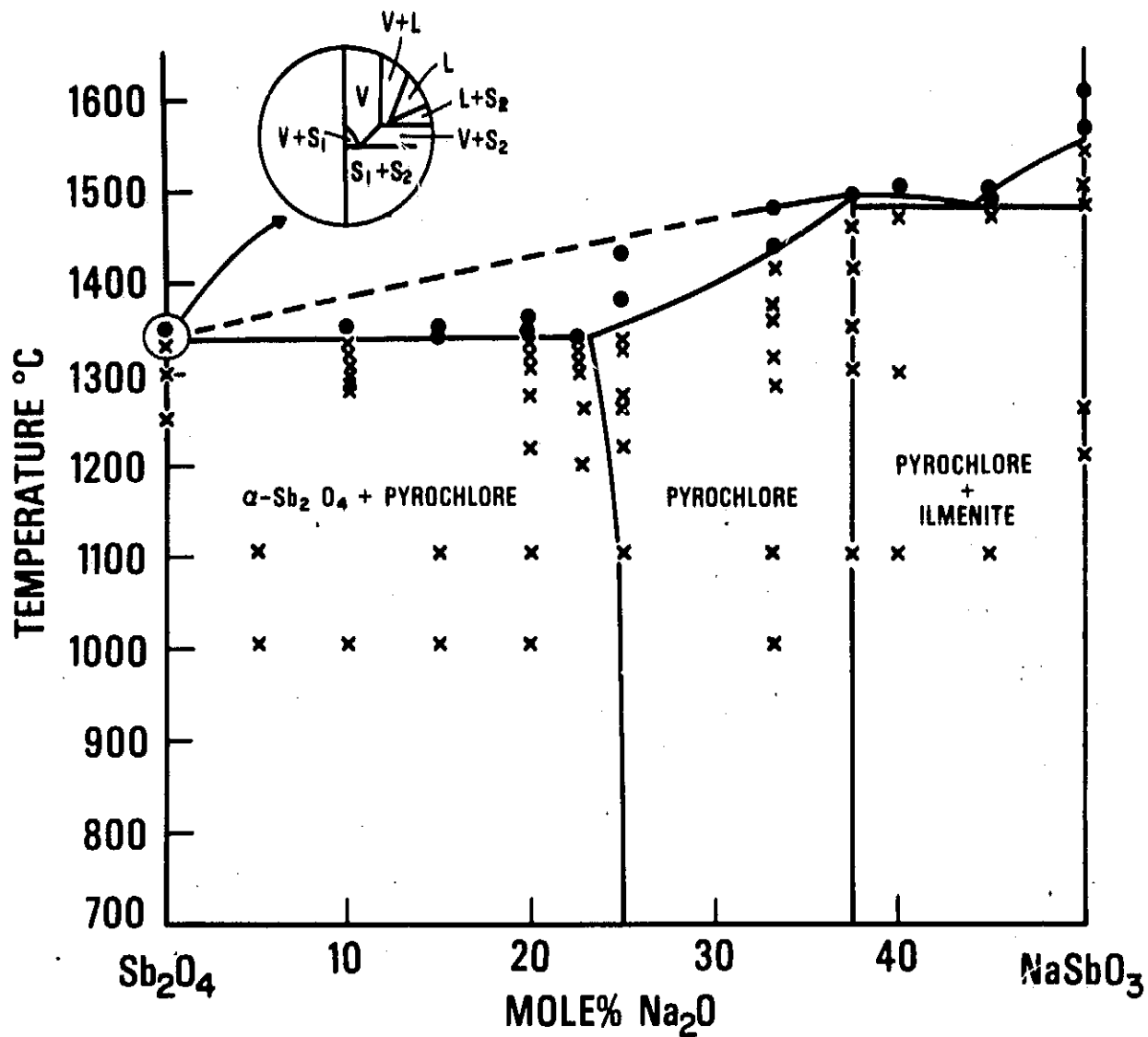
Figure 7. Phase equilibrium diagram for the system  $\text{Nb}_2\text{O}_5\text{-KNbO}_3$

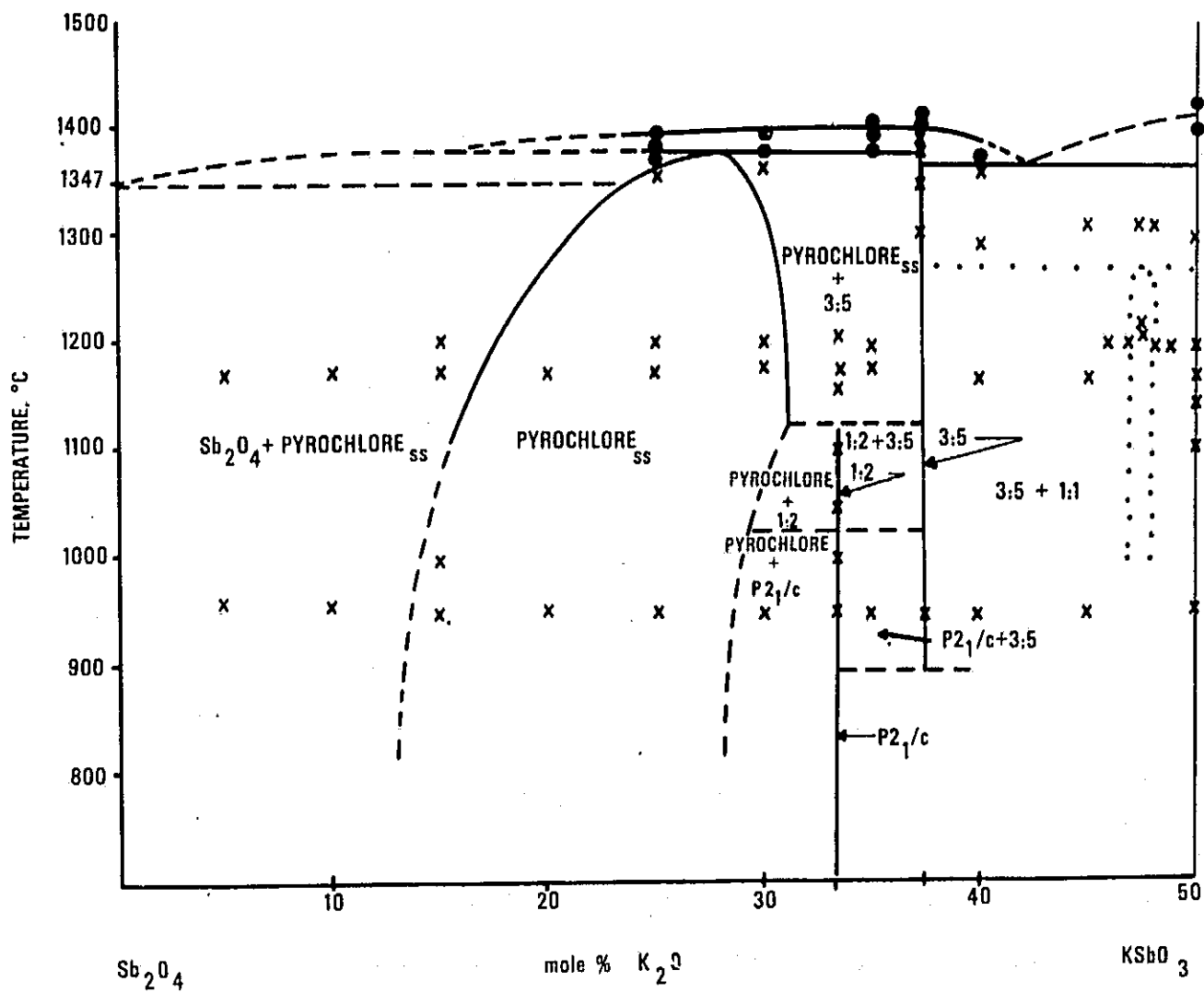
- x - liquidus values from reference [22]
- o - completely melted
- ◐ - partially melted
- - no melting

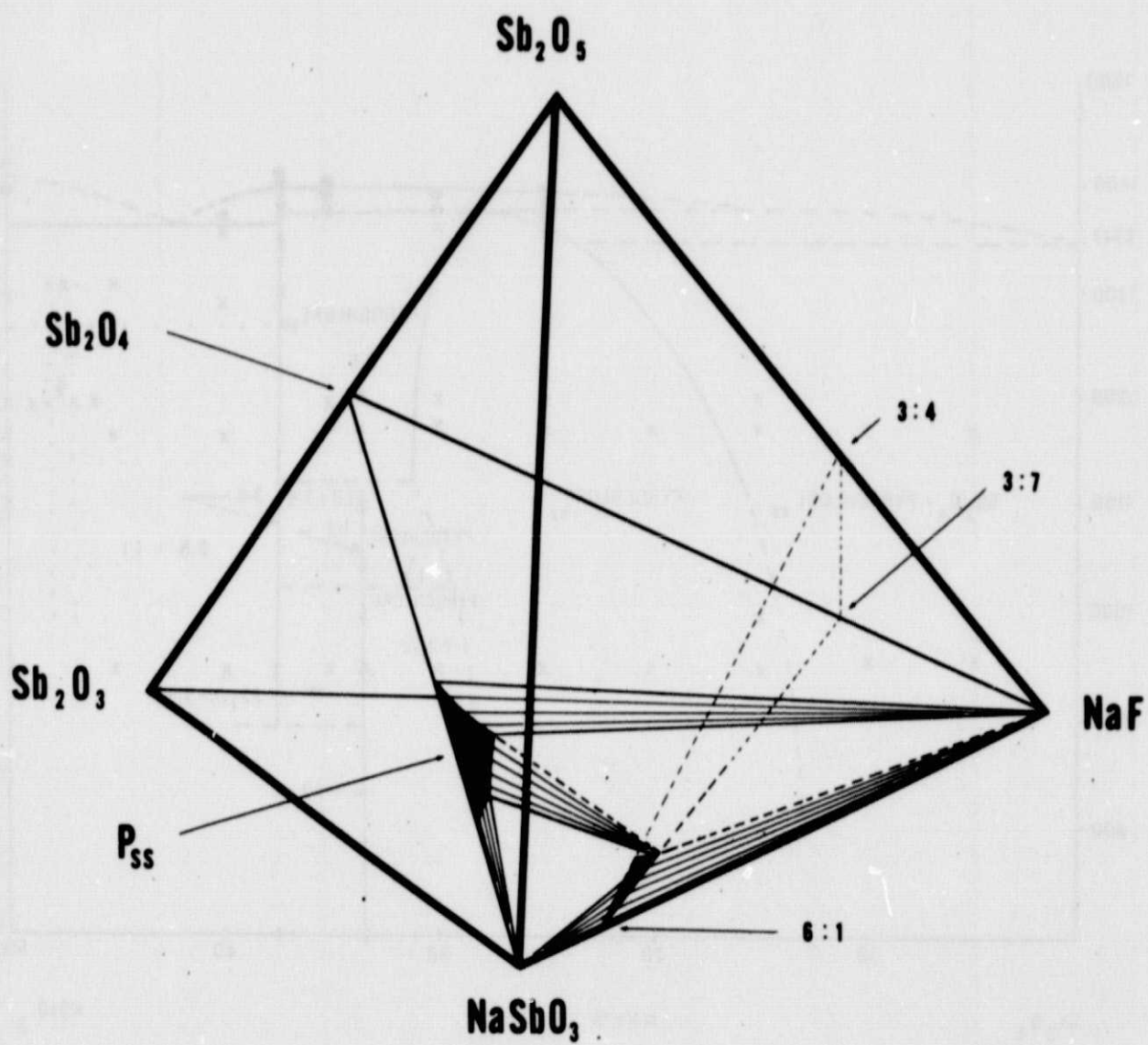
Figure 8. Representation of the ternary system  $\text{KSbO}_3\text{-Sb}_2\text{O}_5\text{-KOH}$  illustrating the hydration of the 11:12 mixture to form the single phase cubic compound when heated in air.



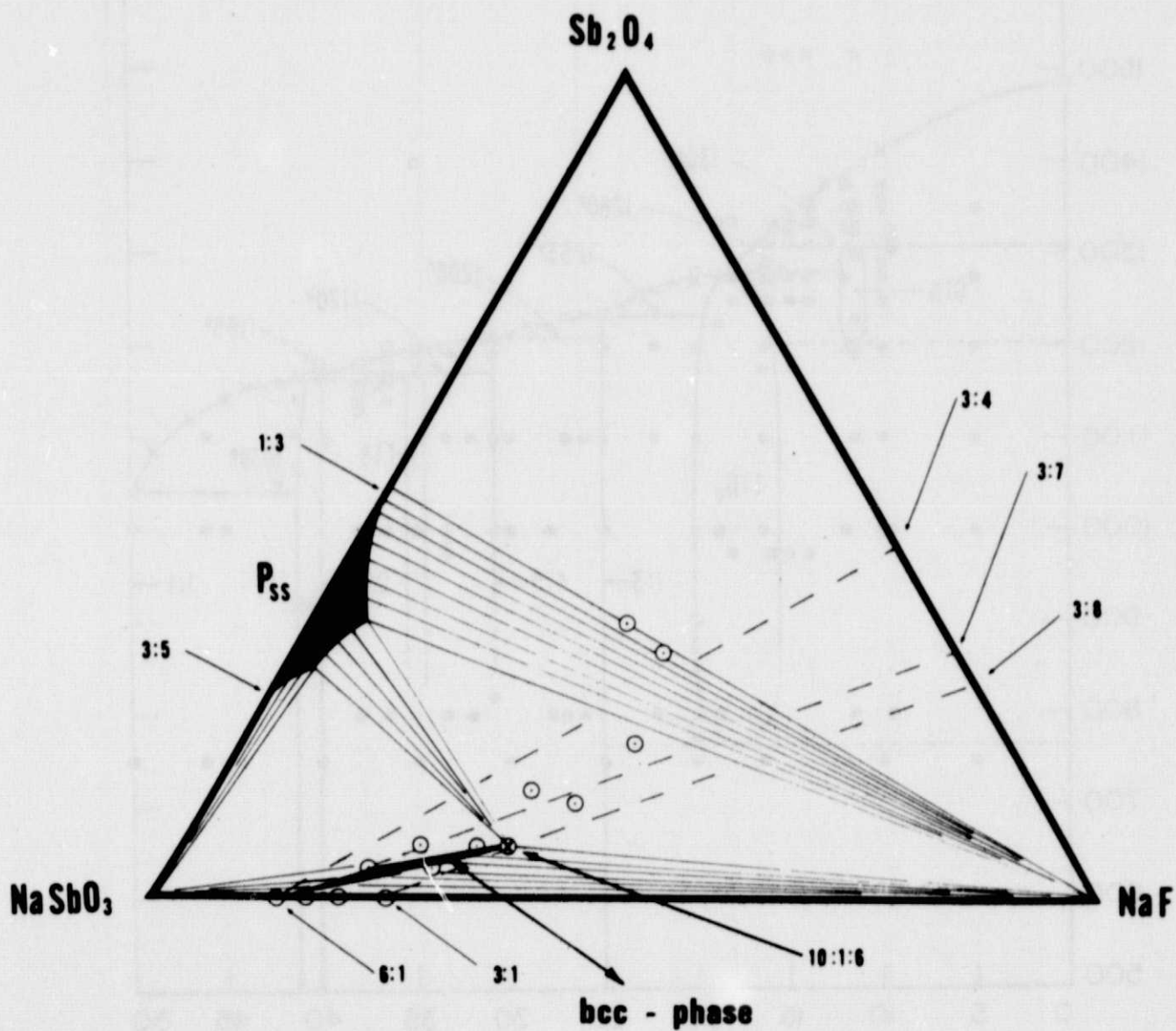


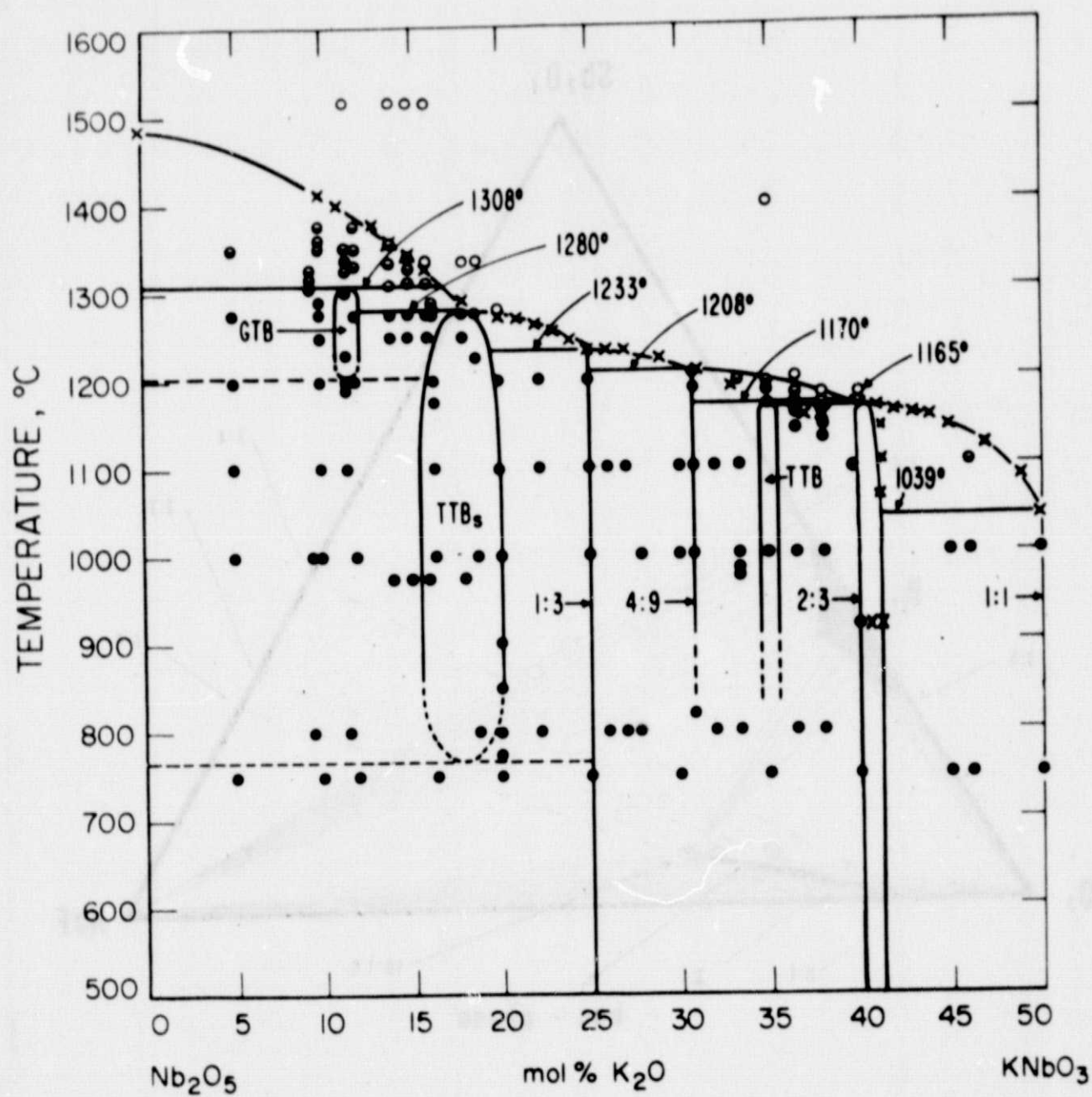












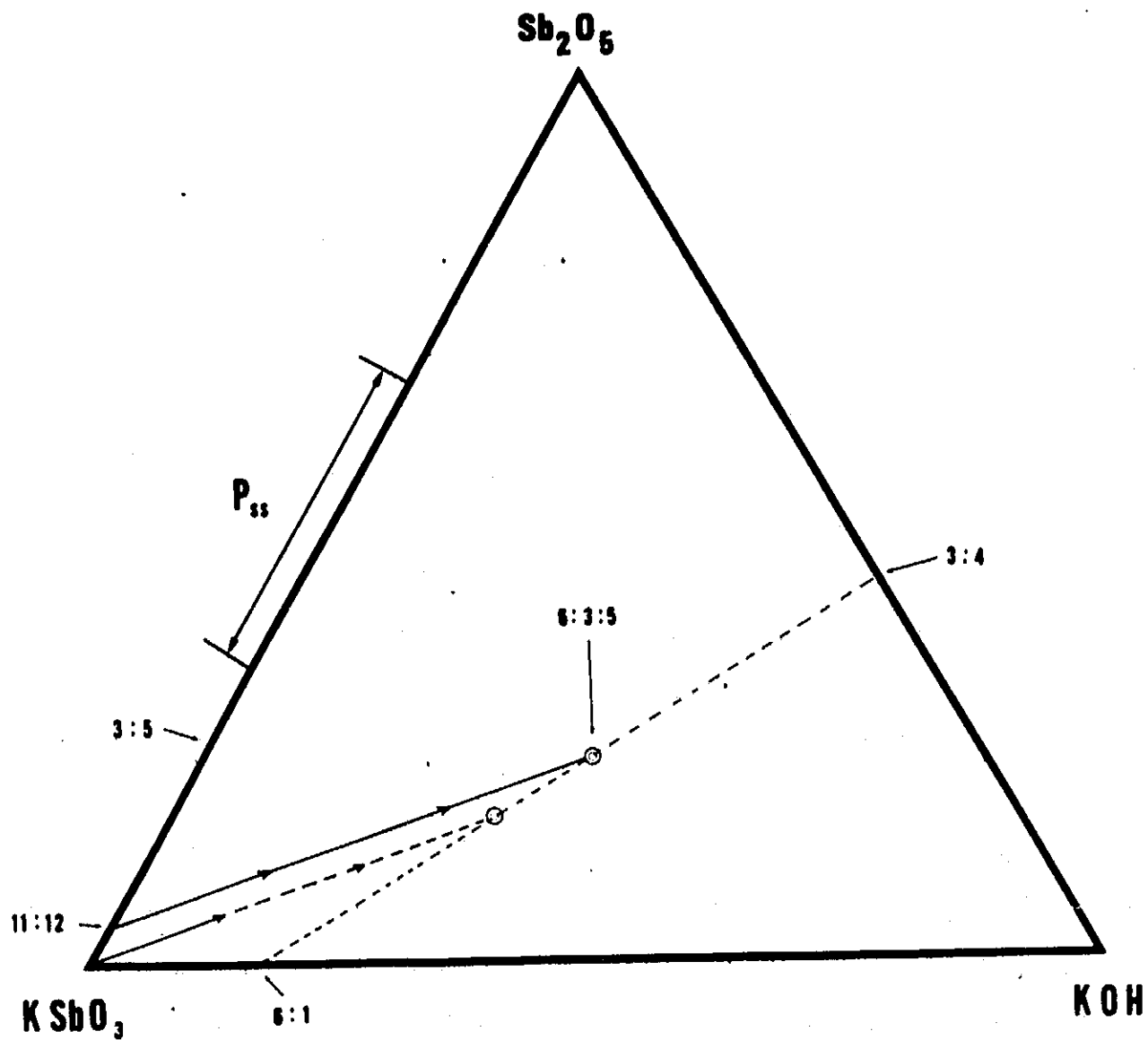


Table 1, Experimental Data for the System  $\text{Nb}_2\text{O}_5$ - $4\text{Nb}_2\text{O}_5$ - $11\text{Nb}_2\text{O}_5$ .

Composition	Previous Heat Treatment Temp, °C	Time hr	Final Heat Treatment Temp, °C	Time hr	Results of Physical Observation	Results of X-ray Diffraction Analysis
$3\text{Nb}_2\text{O}_5:93\text{Nb}_2\text{O}_5$	300	120	300	120 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	300	120	600	90 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 3:17
	600	90				
			800	66		N-Nb <sub>2</sub> O <sub>5</sub> + 3:17
			900	40		N-Nb <sub>2</sub> O <sub>5</sub> + 3:17
			1000	80		N-Nb <sub>2</sub> O <sub>5</sub> + 3:17
			1000	111 <sup>a/</sup>		
			1200	88		N-Nb <sub>2</sub> O <sub>5</sub> + GTS
$10\text{Nb}_2\text{O}_5:90\text{Nb}_2\text{O}_5$	300	120	300	120 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	300	120	600	90 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			800	60		3:17 + N-Nb <sub>2</sub> O <sub>5</sub>
			900	40		3:17 + N-Nb <sub>2</sub> O <sub>5</sub>
			1000	80		3:17 + GTS + N-Nb <sub>2</sub> O <sub>5</sub>
			1000	111 <sup>a/</sup>		GTS + 3:17 + N-Nb <sub>2</sub> O <sub>5</sub>
			1075	60		GTS + N-Nb <sub>2</sub> O <sub>5</sub>
			1200	88		GTS + N-Nb <sub>2</sub> O <sub>5</sub>
$11.5\text{Nb}_2\text{O}_5:88.5\text{Nb}_2\text{O}_5$	300	120	300	120 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	300	120	600	90 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			800	60		3:17 + N-Nb <sub>2</sub> O <sub>5</sub>
			900	40		3:17 + N-Nb <sub>2</sub> O <sub>5</sub>
			1000	80		GTS + 3:17
			1000	111 <sup>a/</sup>		GTS + 3:17
	300	120				
	600	90				
	1000	111				
$15\text{Nb}_2\text{O}_5:85\text{Nb}_2\text{O}_5$			1148	16		GTS
			1200	88		GTS
			1280	40		GTS
			1340	1.5	Not melted	
			1349	23		GTS
			1352	.25	Not melted	
			1355	.33	Not melted	
			1361	1	Not melted	
			1369	.5	Not melted	
			1375	1.5	Partial melted	GTS
$15\text{Nb}_2\text{O}_5:85\text{Nb}_2\text{O}_5$			1380	2	Completed melted	
$20\text{Nb}_2\text{O}_5:80\text{Nb}_2\text{O}_5$	300	120	300	120 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	300	120	600	90 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			750	16.5 <sup>a/</sup>		11-L + N-Nb <sub>2</sub> O <sub>5</sub>
			750	14.5 <sup>a/</sup>		3:17
			800	66		3:17
			900	40		3:17
			1000	80		3:17
			1000	111 <sup>a/</sup>		3:17
			1075	60		3:17
$20\text{Nb}_2\text{O}_5:80\text{Nb}_2\text{O}_5$			1200	88		GTS + NTB
	300	120				
	600	90				
	1000	111				
			1156	36.5		3:17
			1177	24		3:17 + GTS
			1180	23		3:17 + GTS
			1183	64		NTB + GTS
			1226	18		NTB + GTS
			1262	18		
$20\text{Nb}_2\text{O}_5:80\text{Nb}_2\text{O}_5$			1349	23		NTB + GTS
	300	120				
	600	90				
	1000	111				
	1200	16.5				
			1153	84 <sup>a/</sup>		GTS + 3:17
			1153	84 <sup>a/</sup>		GTS + 3:17
$21.75\text{Nb}_2\text{O}_5:78.25\text{Nb}_2\text{O}_5$	300	120	300	120 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	300	120	600	90 <sup>b/</sup>		N-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			800	66		3:17 + 11-L
			900	40		3:17 + 11-L
			1000	80		3:17 + 11-L
			1000	111 <sup>a/</sup>		
			1200	88		9-L + GTS + NTB
$21.75\text{Nb}_2\text{O}_5:78.25\text{Nb}_2\text{O}_5$						
$21.75\text{Nb}_2\text{O}_5:78.25\text{Nb}_2\text{O}_5$						
$21.75\text{Nb}_2\text{O}_5:78.25\text{Nb}_2\text{O}_5$						

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	500	120				
	600	90				
	1000	111				
			1149	23		9-L + 3:17
			1169	18		9-L + 3:17
			1181	89		9-L + G78
			1184	3.5		HTB + 9-L
			1313	64		HTB + 11-L
			1315	0.5	Not melted	
			1320	0.5	Partially melted	HTB + 11-L
			1320	22	Completely melted	HTB + 11-L
			1328	1.5	Completely melted	
			1347	16.5	Completely melted	
23.19Nb <sub>2</sub> O <sub>5</sub> :176.81Nb <sub>2</sub> O <sub>5</sub>	1000	63 <sup>c/</sup>				
			1200	21 <sup>c/</sup>		9-L + HTB
			1255	18		9-L + HTB
			1290	18.5		9-L + HTB
			1306	22		HTB + 11-L
25Rb <sub>2</sub> O:75Nb <sub>2</sub> O <sub>5</sub>	500	120	500	120 <sup>b/</sup>		Nb <sub>2</sub> O <sub>5</sub> + 2:3
	500	120	600	90 <sup>b/</sup>		Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			800	66		11-L + 3:17
			900	40		
			1000	80		11-L + 9-L
			1000	111 <sup>c/</sup>		
			1200	88		9-L
			1280	1		9-L + HTB
			1300	40		9-L
	500	120				
	600	90				
	1000	111				
			1290	18.5		--
			1300	16.5		11-L + HTB
25.5Rb <sub>2</sub> O:174.5Nb <sub>2</sub> O <sub>5</sub>	500	63	500	63 <sup>b/</sup>		
	500	63	600	24 <sup>b/</sup>		
	600	24				
			1000	69 <sup>c/</sup>		9-L + 11-L
			1249	22		9-L
			1258	67		9-L + 16-L
			1262	16		9-L + 16-L
			1265	17		9-L + 16-L
			1275	117		16-L + 7tr
			1284	41		16-L + 7tr
			1285	18		16-L + 11-L
			1287	67		16-L + 11-L
			1291	21		16-L + 11-L
			1294	16		16-L + 11-L
			1297	22		16-L + 11-L
26.67Rb <sub>2</sub> O:73.33Nb <sub>2</sub> O <sub>5</sub>	500	120	500	120 <sup>b/</sup>		H-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	500	120	600	90 <sup>b/</sup>		H-Nb <sub>2</sub> O <sub>5</sub> + 2:3
	600	90				
			750	60		11-L
			800	66		11-L
			900	40		11-L
			1000	80		11-L
			1000	111 <sup>c/</sup>		11-L
			1075	60		11-L
			1200	88		11-L
			1241	18		11-L
			1280	40		11-L
			1300	40		H-L
	500	120				
	500	90				
	1000	111				
			1290	18.5		11-L
			1306	22		11-L
			1316	0.5	Not melted	
			1316	16	Partially melted	
			1320	0.5	Partially melted	
			1330	1.5	Completely melted	

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- <sup>a/</sup> Except as indicated by a footnote the samples were quenched into water from the temperature indicated.
- <sup>b/</sup> The samples were calcined in open Pt crucibles and pulled from the furnaces at the temperatures indicated. Rb<sub>2</sub>O may have been volatilized during these calcines thereby changing the composition to one greater in mole percent Nb<sub>2</sub>O<sub>5</sub>.
- <sup>c/</sup> The sample was a large sealed Pt tube and pulled from the furnace at the temperature and cooled rapidly on a chill block.
- <sup>d/</sup> The sample was removed from the furnace at the temperature indicated and immediately dunked into a beaker of water.

Table 2. Experimental Data for the System  $Ta_2O_5-4Rb_2O:11Ta_2O_5$ .

Composition	Initial Heat Treatment		Final Heat Treatment		Results of Physical Observation	Results of X-ray Diffraction Analysis
	Temp, °C	Time hr	Temp, °C	Time hr		
5Rb <sub>2</sub> O:93Ta <sub>2</sub> O <sub>5</sub>	500	120	500	120 <sup>b/</sup>		L-Ta <sub>2</sub> O <sub>5</sub>
	500	120	600	110 <sup>b/</sup>		
	600	110				
			1340	120		L-Ta <sub>2</sub> O <sub>5</sub> + GTB
10Rb <sub>2</sub> O:90Ta <sub>2</sub> O <sub>5</sub>			1500	144		H-Ta <sub>2</sub> O <sub>5</sub> + GTB
	500	120	500	120 <sup>b/</sup>		--
	500	120	600	110 <sup>b/</sup>		L-Ta <sub>2</sub> O <sub>5</sub>
	600	90				
11.5Rb <sub>2</sub> O:88.5Ta <sub>2</sub> O <sub>5</sub>			800	80		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			900	60		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			1366	120		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1500	120		GTB + H-Ta <sub>2</sub> O <sub>5</sub> (tr)
			1700	1		GTB
	500	120	500	120 <sup>b/</sup>		--
	500	120	600	110 <sup>b/</sup>		--
	600	110				
			1098	136		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			1255	27		9L + L-Ta <sub>2</sub> O <sub>5</sub>
			1318	16		9L + L-Ta <sub>2</sub> O <sub>5</sub>
			1340	120		GTB
			1500	144		GTB
			1603	24		GTB
	1200	150				
			1296	91		L-Ta <sub>2</sub> O <sub>5</sub> + 9L + GTB (tr)
15Rb <sub>2</sub> O:85Ta <sub>2</sub> O <sub>5</sub>			1297	117		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1307	64		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1317	67		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1327	18		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1330	115		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1332	16		GTB + L-Ta <sub>2</sub> O <sub>5</sub>
			1340	72		GTB
			1704	0.5	not melted	
			1709	0.5	not melted	
			1714	.25	not melted	
			1721	2	partially melted	GTB
			1722	1	completely melted	
	1330	115				
	1340	72	1317	67		GTB
			1277	136		GTB
			1297	117		GTB
20Rb <sub>2</sub> O:80Ta <sub>2</sub> O <sub>5</sub>			1331	115		GTB
	500	120	500	120 <sup>b/</sup>		
	500	120	600	110 <sup>b/</sup>		
	600	110				
			800	80		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			900	60		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			1000	40		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			1098	136		L-Ta <sub>2</sub> O <sub>5</sub> + 9L
			1360	120		GTB + 9L
			1473	65		GTB + 9L
			1500	17.5		GTB + HTB
			1500	18		GTB + HTB
			1500	144		GTB + HTB
			1700	2		GTB + HTB
	1200	150				
			1707	0.5	not melted	
			1711	0.5	not melted	
			1714	0.5	completely melted	
			1715	0.5	completely melted	
5Rb <sub>2</sub> O:95Ta <sub>2</sub> O <sub>5</sub>	500	120	500	120 <sup>b/</sup>		
	500	120	600	110 <sup>b/</sup>		
	600	110				
			1340	120		9L + GTB

$21.75\text{Rb}_2\text{O}:78.25\text{Ta}_2\text{O}_5$		300	120 <sup>b/</sup>			
500	120	600	110 <sup>b/</sup>			
500	120					
600	110					
		800	80			9L + L-Ta <sub>2</sub> O <sub>5</sub>
		900	80			9L + L-Ta <sub>2</sub> O <sub>5</sub>
		1000	40			9L + L-Ta <sub>2</sub> O <sub>5</sub>
		1100	138			9L + L-Ta <sub>2</sub> O <sub>5</sub>
		1380	120			9L + L-Ta <sub>2</sub> O <sub>5</sub>
		1473	63			9L + GTS
		1500	18			9L + GTS
		1643	24			9L + GTS
		1700	2			HTB + 9L (tr)
		1700	1			HTB
		1706	1			HTB
1200	150					
		1474	67			9L + GTS
		1477	23			9L + GTS
		1477	18			9L + GTS
		1479	17			9L + GTS
		1479	18			9L + GTS
		1480	17			9L + GTS
		1482	18			9L + HTB (1)
		1482	43			9L + HTB
		1484	20			9L + HTB
		1486	41			9L + HTB
		1488	16			9L + HTB
		1488	16			9L + HTB
		1498	21			9L + HTB
		1706	1	not melted		
		1716	1	not melted		
		1717	0.5	partially melted	HTB	
		1721	2	partially melted	HTB	
$25\text{Rb}_2\text{O}:75\text{Ta}_2\text{O}_5$		500	120 <sup>b/</sup>			
500	120	600	110 <sup>b/</sup>			L-Ta <sub>2</sub> O <sub>5</sub>
500	120					
600	110					
		1000	40			9L + L-Ta <sub>2</sub> O <sub>5</sub> (tr)
		1100	138			9L
		1344	120			9L
		1498	144			9L + ? (tr)
		1675	18			16L + HTB
		1700	1			16L + HTB
		1700	1			16L + HTB
		1715	1	not melted		
1200	150					
		1600	20			9L
		1621	3			9L
		1624	17			9L
		1641	21			9L
		1659	19			9L
		1663	67			9L + HTB (tr)
		1677	29			9L + HTB + 16L
		1682	18			16L + HTB
		1722	16	partially melted		
		1725	16	partially melted	16L + HTB	
$26.7\text{Rb}_2\text{O}:73.3\text{Ta}_2\text{O}_5$		500	120 <sup>b/</sup>			
500	120	600	110 <sup>b/</sup>			L-Ta <sub>2</sub> O <sub>5</sub> + 2:3
500	120					
600	110					
		800	80			11L + 2:3
		900	60			11L + 2:3
		1000	40			11L + 2:3
		1098	136			11L + 2:3
		1360	120			16L + 11L
		1500	120			16L + 11L
		1596	24			16L + 11L
		1625	16			16L + 11L
		1640	2			16L + 11L
		1647	1			16L + 11L
		1700	1			11L
		1710	1	not melted		
1200	150					
		1283	72			16L + 11L
		1672	1			11L
		1719	1	not melted		
		1725	0.5			11L
		1726	16			11L

<sup>a/</sup> Except as indicated by <sup>b/</sup> the samples were quenched into water from the temperature indicated.

<sup>b/</sup> The samples were heated at the temperatures indicated in open Pt crucibles. Due to the volatility of Rb<sub>2</sub>O the bulk composition may have shifted to one higher in mole percent Ta<sub>2</sub>O<sub>5</sub>.

Table 3. Experimental Data for Compositions in the System Sodium Antimonate-Antimony Tetroxide.

Composition		Heat Treatment <sup>a/</sup>		Physical Observation	Results X-ray Diffraction Analysis <sup>b/</sup>
Na <sub>2</sub> O mole%	Sb <sub>2</sub> O <sub>4</sub> mole%	Temp °C	Time hr		
50	50	1213		not melted	
		1264	3	" "	NaSbO <sub>3</sub>
		1433	1	" "	" "
		1484	1	" "	" "
		1502	.08	" "	" "
		1542	.08	" "	NaSbO <sub>3</sub> + unknown
		1589	.08	melted	" "
		1602	.08	" "	" "
45	55	1000	48	not melted	
		1100	48	" "	NaSbO <sub>3</sub> + pyrochlore ss
		1473	.23	" "	" "
		1488	.08	partially melted	" "
		1493	.08	completely melted	" "
40	60	1102	20	not melted	pyrochlore ss + NaSbO <sub>3</sub>
		1305	19	" "	" "
		1430	.08	" "	" "
		1470	.08	" "	" "
		1488	.08	" "	" "
		1495	.03	completely melted	" "
37.5	62.5 (3:5)	1100	48	not melted	Pyrochlore ss
		1192	1	" "	" "
		1306	19	" "	pyrochlore ss
		1326	20	" "	" "
		1351	1	" "	" "
		1373	2	not melted (reheat of 1100-4)	pyrochlore ss
		1391	2	not melted	" "
		1392	.16	" "	pyrochlore ss
		1412	.16	" "	" "
		1447	.16	" "	" "
		1454	.33	" "	" "
		1458	.08	" "	" "
		1464	.08	" "	" "
		1476	.08	" "	" "
		1487	.08	" "	" "
		1490	.08	melted	" "
33.33	66.67 (1:2)	1000 <sup>c/</sup>	8	not melted	
		1009 <sup>d/</sup>	168	" "	pyrochlore ss
		1100	3	" "	" "
		1103 <sup>e/</sup>	91	" "	" "
		1287	2	" "	" "
		1292	1.5	" "	" "
		1306	24	" "	" "
		1307	19	" "	pyrochlore ss
		1316	.5	" "	" "
		1317	3.5	" "	" "
		1334	.75	" "	pyrochlore ss
		1380	24	" "	" "
		1376	.5	" "	" "
		1378	.5	" "	" "
		1411	19	" "	" "
		1418	.02	" "	" "
		1437	24	partially melted	" "
		1475	.02	completely melted	" "
25	75 (1:3)	750	60	not melted	pyrochlore ss + unknown <sup>f/</sup>
		800	60	" "	pyrochlore ss + unknown <sup>f/</sup>
		800	60	" "	pyrochlore ss + unknown <sup>f/</sup>
		800	336	" "	pyrochlore ss + unknown
		1098	16	" "	pyrochlore ss
		1192	1	" "	" "
		1200	24	" "	" "
		1220	2	" "	" "
		1277	2	" "	" "
		1306	24	" "	" "
		1307	.08	" "	" "
		1317	16 <sup>g/</sup>	" "	pyrochlore ss
		1325	1	" "	" "
		1339	.08	" "	" "
		1345	.25	" "	pyrochlore ss
		1346	.08	" "	" "
		1358	.08	" "	" "
		1377	.02	partially melted	pyrochlore ss + NaSbO <sub>3</sub>
		1427	.02	" "	" "
23	77	1200	24	not melted	pyrochlore ss + B-Sb <sub>2</sub> O <sub>4</sub>
		1266	4	" "	pyrochlore + g + Si <sup>h/</sup>
		1267	19	" "	pyrochlore ss <sup>i/</sup>
		1299	.08	" "	" "
		1304	.08	" "	" "
		1313	.08	" "	" "
		1322	.08	" "	" "
		1332	.08	" "	pyrochlore ss <sup>i/</sup>
		1338	.08	" "	" "



20	80	1099	672	not melted	pyrochlore <sup>k/</sup>
		1107	244		
		1200	24	not melted	pyrochlore ss + a
		1220	2.5	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub>
		1234	2.5	" "	" "
		1277	16	" "	pyrochlore ss + $\beta$ -Sb <sub>2</sub> O <sub>4</sub>
		1301	.5	not melted	---
		1305	19	" "	NaSbO <sub>4</sub> <sup>k/</sup>
		1306	24	" "	pyrochlore ss + $\beta$ -Sb <sub>2</sub> O <sub>4</sub>
		1314	.08	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub>
		1318	.08	" "	" "
		1335	.08	" "	" "
		1339	.2	" "	" "
		1340	.08	" "	" "
		1345	.2	partially melted	" "
		1362	.5	" "	" "
15	85	800	74	not melted	unknown + pyrochlore ss + $\gamma$ -Sb <sub>2</sub> O <sub>4</sub> <sup>k1/</sup>
		800	60	" "	$\alpha$ + pyrochlore ss + unknown <sup>1/</sup>
		1000	64	" "	unknown + tr $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> (dried 240) <sup>k1/</sup>
		1000	64	" "	unknown + tr $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> <sup>k1/</sup>
		1007	48	not melted	pyrochlore + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + unknown <sup>1/</sup>
		1107	144	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub>
		1200	24	" "	" "
		1200	60	" "	" "
		1337	.2	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub>
		1340	.2	" "	" "
		1348	.2	partially melted	" "
10	90	800	74	not melted	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + unknown <sup>1/</sup>
		1007	48	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore <sup>k1/</sup>
		1107	144	" "	" "
		1234	2	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore ss
		1281	.13	" "	" "
		1290	.33	" "	" "
		1300	.33	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore ss
		1311	.2	" "	" "
		1319	.33	" "	" "
		1334	.33	" "	" "
		1337	.2	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore ss
		1351	1	partially melted	$\alpha$ + pyrochlore ss + quenched liquid <sup>m/</sup>
5	95	1007	48	not melted	$\beta$ -Sb <sub>2</sub> O <sub>4</sub> + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore <sup>k1/</sup>
		1107	144	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore ss + trace $\beta$ -Sb <sub>2</sub> O <sub>4</sub> <sup>k1/</sup>
		1234	3.5	" "	" " " " " "

<sup>k1/</sup> All specimens were preheated to 750°C for 60 hours and 1200°C for 19 hours unless otherwise footnoted. Rate of heating and cooling was approximately 3°/min. For higher heat treatments, specimens were heated in sealed Pt tubes and quenched from temperatures indicated.

<sup>k/</sup> The phases identified are given in the order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated.

<sup>k/</sup> Specimen heated with PtO<sub>2</sub> at 68,900 psi in sealed Pt tube.

<sup>k/</sup> Specimen heated in sealed Pt tube at 5,000 psi.

<sup>k/</sup> Specimen previously heated at 1292°C for 1.5 hours.

<sup>k/</sup> Specimen heated in sealed Pt tube in presence of water. The unknown phase formed is probably a hydrate.

<sup>k/</sup> Specimen heated in sealed Pt tube in PtO<sub>2</sub>.

<sup>k/</sup> Specimen heated in presence of 5:95 Na<sub>2</sub>O:Sb<sub>2</sub>O<sub>4</sub> which served as a buffer.

<sup>k/</sup> In spite of extensive x-ray study it has not been determined which of the polymorphic forms of Sb<sub>2</sub>O<sub>4</sub> is the stable form.

<sup>k/</sup> Sb<sub>2</sub>O<sub>4</sub> probably soaked into Pt container and the composition changed to pyrochlore ss.

<sup>k/</sup> Platinum tube leaked.

<sup>k/</sup> Unknown phase, d-spacing of major lines given in text. This phase is probably a hydrated phase which exists in the presence of moisture and/or PtO<sub>2</sub> and can be eliminated by an additional calcining of 1200°C for several hours. Once eliminated this phase does not appear to reform at lower temperatures in laboratory time.

<sup>k/</sup> Specimen contained non-equilibrium material derived from a liquid when quenched from above the liquidus and examined at room temperature.

Table 4a. Experimental Data for Polymorphism in Antimony Tetroxide

Composition Starting Material	Heat Treatment		Environment	Results	
	Temp °C	Time hr		Physical Observation	X-ray Diffraction Analysis <sup>a/</sup>
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1223	.5	sealed Pt tube	not melted	$\alpha$ + tr $\beta$
	"	"	unsealed Pt tube	" "	$\alpha$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	1223	.5	sealed Pt tube	not melted	$\beta$ + tr $\alpha$
	"	"	unsealed Pt tube	volatilized	--
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	1223	2	sealed Pt tube	not melted	$\beta$ + tr $\alpha$
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	"	"	sealed Pt tube	" "	$\alpha$ + Sb <sub>2</sub> O <sub>3</sub>
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1303	19	sealed Pt tube	not melted	$\beta$ + $\alpha$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	"	"	" " "	" "	$\beta$
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1327	.08	sealed Pt tube	not melted	$\alpha$ + $\beta$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	"	"	" " "	" "	$\beta$ + $\alpha$
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1330	.25	sealed Pt tube	not melted	$\beta$ + $\alpha$
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1339	.08	sealed Pt tube	not melted	$\alpha$ + $\beta$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	"	"	" " "	" "	$\beta$ + $\alpha$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	1345	.08	sealed Pt tube	not melted	$\beta$ + $\alpha$
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	1350	.48	sealed Pt tube	melted (vapor soaked into Pt)	--
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	1350	.08	sealed Pt tube	melted ? large tabular vapor grown crystals	--
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> <sup>b/</sup>	1200	-	high temperature x-ray		$\alpha$ (starting material remained $\alpha$ up to 1200°C)
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> <sup>c/</sup>	750	24	open tray		$\alpha$
"	800	"	" "		"
"	900	"	" "		$\alpha$ + $\beta$
"	950	"	" "		" "

<sup>a/</sup> The phases identified are given in the order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated.  $\alpha$  refers to  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> polymorph and  $\beta$  to the  $\beta$ -Sb<sub>2</sub>O<sub>4</sub> polymorph.

<sup>b/</sup> Material placed on platinum slide and heated and examined by x-ray diffraction at various temperatures.

<sup>c/</sup> Poorly crystalline as received Sb<sub>2</sub>O<sub>4</sub> was heated 750°C - 24 hours and the same specimen which was never ground was reheated at 800°C - 24 hours, then 900°C - 64 hours and finally 950°C - 24 hours.

Table 4b. Experimental High Pressure Data for Polymorphism in Antimony-Tetroxide.

Composition Starting Material	Heat Treatment Temp °C	Time hrs	Environment	Pressure psi	Results <sup>b/</sup> X-ray Diffraction Analysis
$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> <sup>a/</sup>	700	24	Sealed Au tube	88,000	$\beta^c/ + \text{Sb}_2\text{O}_3^d/$
"	750	48	" " "	59,680	" " "
"	750	96	" " "	73,200	" " "
"	750	16	" " "	89,400	$\beta + \text{trace Sb}_2\text{O}_3$
"	751	116	" " "	109,000	$\beta + \text{Sb}_2\text{O}_3$
"	760	96	Sealed Au tube with PtO <sub>2</sub>	80,000	$\beta$
"	766	96	Sealed Au tube	88,000	$\beta + \text{Sb}_2\text{O}_3$
"	775	115	" Pt "	47,500	$\alpha + \text{Sb}_2\text{O}_3$
"	775	48	" Au "	54,760	$\beta + \text{Sb}_2\text{O}_3$
"	775	48	" Pt "	66,500	" " "
"	800	24	" Au "	93,000	" " "
"	800	24	Sealed Au tube with PtO <sub>2</sub>	105,000	$\beta$
"	850	16	Sealed Au tube	82,500	$\beta + \text{Sb}_2\text{O}_3$
"	900	72	Sealed Pt tube with PtO <sub>2</sub>	104,000	$\beta$
$\beta$ -Sb <sub>2</sub> O <sub>4</sub>	900	72	" " " " "	104,000	$\beta$

<sup>a/</sup>  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> prepared by the oxidation of Sb at 530°C on Pt tray. This material was reheated at 800°C - 60 hrs.

<sup>b/</sup> The phases identified are given in the order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperatures to which the specimen was heated.

<sup>c/</sup>  $\beta$  form of Sb<sub>2</sub>O<sub>4</sub>.

<sup>d/</sup> High pressure form of Sb<sub>2</sub>O<sub>3</sub> (valentinite).

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Table 5. Experimental Data for Compositions in the System Potassium Antimonate-Antimony Tetroxide.

Composition		Heat Treatment <sup>a/</sup>		Results	
K <sub>2</sub> O Mole%	Sb <sub>2</sub> O <sub>4</sub> Mole%	Temp °C	Time hr	Physical Observation	X-ray Diffraction Analysis <sup>b/</sup>
5	95	950	60	not melted	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub> <sup>c/</sup>
		1168	48	" "	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub> + pyrochlore ss
10	90	950	60	not melted	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub> <sup>c/</sup>
		1168	48	" "	" "
15	85	853	24	not melted	
		950	60	" "	pyrochlore ss
		966	4	" "	
		1168	48	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub>
		1200	19	" "	pyrochlore ss + $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> + $\beta$ -Sb <sub>2</sub> O <sub>4</sub>
20	80	950	60	not melted	pyrochlore ss
		1168	48	" "	" "
25	75	950	60	not melted	P2 <sub>1</sub> /c <sup>d/</sup> + pyrochlore ss
		1179	48	" "	pyrochlore ss
		1361	.08	" "	
		1375	.08	partially melted	pyrochlore ss
		1385	.08	" "	
		1403	.08	completely melted	
30	70	950	60	not melted	P2 <sub>1</sub> /c <sup>d/</sup> + pyrochlore ss
		1178	48	" "	1:2 + pyrochlore ss
		1366	.08	" "	
		1380	.08	partially melted	pyrochlore ss + 3:5
		1382	.08	" "	
		1399	.08	completely melted	
33.33	66.67	950	60	not melted	3:5 + P2 <sub>1</sub> /c <sup>d/</sup>
		950	64	" "	
		998	70	" "	P2 <sub>1</sub> /c <sup>d/</sup>
		1050	168	" "	
		1050 <sup>a/</sup>	168	" "	
		1102	1	" "	1:2 <sup>e/</sup> + 3:5 + pyrochlore ss + P2 <sub>1</sub> /c
		1106	64	" "	1:2 <sup>e/</sup> + 3:5 + pyrochlore
		1106 <sup>f/</sup>	64	" "	1:2 + 3:5
		1160 <sup>f/</sup>	1	" "	3:5 + pyrochlore ss
		1179	48	" "	1:2 + 3:5 + pyrochlore ss
		1214 <sup>g/</sup>	1	" "	3:5 + pyrochlore ss
		1214	2	" "	" "
35	65	950	60	not melted	pyrochlore + 3:5 + pyrochlore ss
		1178	48	" "	1:2 + 3:5
		1380	.08	partially melted	3:5 + pyrochlore
		1397	.08	" "	
		1409	.08	completely melted	
37.5	62.5	950	60	not melted	
		1174	88	" "	
		1195	19	" "	3:5
		1208	1	" "	3:5 + trace cubic
		950 <sup>a/</sup>	64	" "	
		1310	45	" "	3:5 + trace 1:1 <sup>g/</sup>
		1352	.08	" "	
		1379	.08	" "	
		1399	.08	completely melted	
		1416	.08	" "	
40	60	950	60	not melted	
		1174	88	" "	3:5 + cubic
		1208	1	" "	" "
		1295 <sup>a/</sup>	20	" "	3:5 + 1:1
		1362 <sup>a/</sup>	.5	" "	" "
		1375 <sup>a/</sup>	.08	partially melted	

45	55	950	60	not melted	1:1 + cubic + $P2_1/c$
		1174	88	" "	cubic + 3:5
		1208	1	" "	3:5 + cubic
		1311 <sup>a/</sup>	1	" "	3:5 + 1:1
46	54	1200 <sup>h/</sup>	1	not melted	cubic + 3:5
47	53	1194 <sup>h/</sup>	3	not melted	cubic + trace 3:5
		1200	1	" "	cubic
47.5	52.5	1212 <sup>h/</sup>	88	not melted	cubic + 3:5 + 1:1
		1218 <sup>h/</sup>	17	" "	cubic + 1:1 + 3:5
		1310 <sup>a,h/</sup>	45	" "	1:1
48	52	1198	3	not melted	cubic
		1200	1	" "	"
		1200 <sup>i/</sup>	1:5	" "	cubic + 3:5 ilmenite
		1308	.5	" "	1:1
		1103 <sup>c/</sup>	1	" "	cubic + ilmenite + pyrochlore
		1103 <sup>i/</sup>	3	" "	ilmenite + pyrochlore
49	51	1200	1	not melted	cubic
50	50	750	70	not melted	
		800	24	" "	
		921	1	" "	
		946	21	" "	ilmenite
		950	60	" "	"
		1103	1	" "	"
		1104	22	" "	"
		1150	1	" "	"
		1174	88	" "	"
		1194	1	" "	"
		1202	1	" "	"
		1214	1	" "	"
		1298	.5	" "	"
		1363	.5	" "	"
		1403	.08	" "	"
		1421	.08	melted	
		1426	.08	" "	

<sup>a/</sup> All specimens were preheated to 500 and 700°C for 60 hours unless otherwise footnoted. Rate of heating and cooling were approximately 3°/min. Specimens were heated in sealed Pt tubes and quenched from temperatures indicated.

<sup>b/</sup> The phases identified are given in order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated. 1:2 -  $K_2O \cdot 2Sb_2O_5$ ; 3:5 -  $3K_2O \cdot 5Sb_2O_5$  and 1:1 -  $KSbO_3$  - ilmenite structure.

<sup>c/</sup> Non-equilibrium mixture - see Discussion in text.

<sup>d/</sup> The phase was indexed from single crystal x-ray precession data which has shown the compound is monoclinic space group  $P2_1/c$   $a=7.178$ ,  $b=13.378$ ,  $c=11.985$ ,  $\beta=124^\circ 10'$ .

<sup>e/</sup> This specimen was previously heated to 500°, 700° and 1200°C - 19 hours in a sealed Pt tube.

<sup>f/</sup> Specimen heated in open Pt tube.

<sup>g/</sup> Specimen leaked and changed composition.

<sup>h/</sup> Composition prepared from a mixture 1:1 and 3:5 - see text for explanation.

<sup>i/</sup> Specimen calcined and examined by x-ray diffraction while in form of pellet.

Table 6. Experimental Data for the Ternary System  $\text{NaSbO}_3$ - $\text{Sb}_2\text{O}_4$ - $\text{NaF}$ .

Composition	Mole %	Heat Treatment <sup>a/</sup>		X-ray Analysis
		Temp °C	Time hr	
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	75.08 3.15 21.77	1250	19	single phase distorted cubic
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	67.79 6.25 25.96	1250	19	body centered cubic + pyrochlore + ilmenite
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	53.50 12.34 34.16	1250	19	body centered cubic + pyrochlore + sodium fluoride
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	39.59 18.27 42.14	1250	19	body centered cubic + pyrochlore + sodium fluoride
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	69.05 2.90 28.05	1250	19	body centered cubic + trace sodium fluoride
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	49.28 11.37 39.35	1250	19	pyrochlore + body centered cubic + sodium fluoride
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	31.20 28.87 39.93	1250	19	pyrochlore + sodium fluoride
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	84.62 -- 15.38	1268	19	ilmenite + cubic
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	74.42 2.32 23.26	1261 1268	1 19	distorted cubic + ilmenite distorted cubic + NaF
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	70.00 3.33 26.67	1264	1	cubic + ilmenite
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	65.96 4.26 29.78	1266 1267	1 19	cubic + ilmenite cubic + NaF
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	62.96 4.94 32.10	1266 1267	1 19	cubic + NaF cubic + NaF
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	58.82 5.89 35.29	1267	19	cubic + NaF
$\text{NaSbO}_3$ $\text{Sb}_2\text{O}_4$ $\text{NaF}$	68.00 4.00 28.00	1000 1252 1265 1265 1265	1 16 .1 1.5 72	ilmenite + trace NaF cubic + trace ilmenite cubic + NaF cubic + NaF cubic + NaF

<sup>a/</sup> Preheated at 750°C for 60 hours open.

Table 7. Experimental Data for Alkali Bismuth Oxide Systems.

Composition	Temp. °C	Time hr	Results of X-ray Diffraction Analysis
$\text{Na}_2\text{O}:\text{Bi}_2\text{O}_3$	500	96	$\text{Bi}_2\text{O}_3$ + tr unknown
	500	120	$\text{Bi}_2\text{O}_3$
$\text{K}_2\text{O}:\text{Bi}_2\text{O}_3$	500	66	$\text{Bi}_2\text{O}_3$
	500	120	" $\text{Bi}_2\text{O}_3$
$\text{K}_2\text{O}:3\text{Bi}_2\text{O}_3$	500	66	$\text{Bi}_2\text{O}_3$

Table 8. Experimental Data for Alkali-Rare Earth Systems.

Composition	Temp °C	Time hr	Results of X-ray Diffraction Analysis
$\text{Na}_2\text{O}:\text{Nd}_2\text{O}_3$	800	23	$\alpha\text{-Nd}_2\text{O}_3$
$\text{K}_2\text{O}:\text{Nd}_2\text{O}_3$	950	66	$\alpha\text{-Nd}_2\text{O}_3 + ?$
$\text{K}_2\text{O}:3\text{Nd}_2\text{O}_3$	950	66	$\alpha\text{-Nd}_2\text{O}_3 + ?$
$3\text{K}_2\text{O}:\text{Y}_2\text{O}_3$	600	20	$\text{Y}_2\text{O}_3 + \text{K}_2\text{CO}_3$
	700	20	" "
	800	20	" "
	950	66	$\text{Y}_2\text{O}_3$
$\text{K}_2\text{O}:\text{Y}_2\text{O}_3$	500	24	$\text{Y}_2\text{O}_3$
$\text{Na}_2\text{O}:\text{Sm}_2\text{O}_3$	800	23	$\text{Sm}_2\text{O}_3$
	950	1.5	
$\text{Na}_2\text{O}:3\text{Sm}_2\text{O}_3$	800	23	$\text{Sm}_2\text{O}_3$
	950	1.5	
$89.6\text{Na}_2\text{O}:10.4\text{Sm}_2\text{O}_3$	$\sim 1350$	$1\frac{\text{a}}{\text{hr}}$	$\text{Sm}_2\text{O}_3$
$\text{K}_2\text{O}:3\text{Sm}_2\text{O}_3$	800	23	$\text{Sm}_2\text{O}_3$
	950	1.5	
$\text{K}_2\text{O}:\text{Sm}_2\text{O}_3$	800	23	$\text{Sm}_2\text{O}_3$
	950	$1.5\frac{\text{b}}{\text{hr}}$	
	1250	$16.5\frac{\text{b}}{\text{hr}}$	$\text{Sm}_2\text{O}_3 + ?$
	1350	$17.5\frac{\text{b}}{\text{hr}}$	$\text{Sm}_2\text{O}_3$
$\text{K}_2\text{O}:\text{Gd}_2\text{O}_3$	750	90	--
	1000	92	--
	1365	$67\frac{\text{b}}{\text{hr}}$	$\text{B-Gd}_2\text{O}_3 + \text{C-Gd}_2\text{O}_3$
	1370	$16\frac{\text{b}}{\text{hr}}$	

a/ The sample was heated in an open Pt crucible in an induction heater and the temperature recorded via an optical pyrometer.

b/ Quenched from temperature indicated.



Table 9. Further Experimental Data for the System  $\text{Nb}_2\text{O}_5\text{-KNbO}_3$ .

Composition	Temp °C	Time hr	Results of X-ray Diffraction Analysis
40.5 $\text{K}_2\text{O}$ :59.5 $\text{Nb}_2\text{O}_5$	600	40	
	750	84	
	1000	48	2:3 hydrate + TTB
	1000	48 <sup>a/</sup>	2:3 anhydrous + TTB
41 $\text{K}_2\text{O}$ :59 $\text{Nb}_2\text{O}_5$	600	48	
	700	85	
	750	60	
	800	90	
	1000	48 <sup>a/</sup>	2:3 anhydrous
	1000	48	2:3 hydrate
	1000	48 <sup>c/</sup>	2:3 anhydrous
	1000	60 <sup>b/</sup>	" "

<sup>a/</sup> Slide heated @ 220° for 96 hours.

<sup>b/</sup> Slide heated > 125°C.

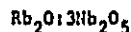
<sup>c/</sup> Slide heated to 110°C.

Table 10a. Summary of Ion Exchange Experiments

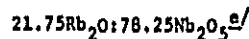
EXCHANGE MEDIUM	TEMP °C	TIME	RESULTS
$7K_2O:13Nb_2O_5$			
$NaNO_3$	340°	2 hr	Decomposed to $KNbO_3$ + $H-Nb_2O_5$
$3NaNO_2:2NaNO_3$	244°	24 hr	Unchanged 7:13 (TTB) + Na-TTB(?)
	244°	72 hr	Unchanged 7:13 + $NaNbO_3$ (tr)
$NaNO_3(aq)^{a/}$	104°	2 hr	No change
$18.75K_2O:81.25Nb_2O_5$			
$NaNO_3$	~500°	2 hr	$NaNbO_3$
	330°	2 hr	$H-Nb_2O_5$ + residual TTB
$11.3K_2O:88.5Nb_2O_5$			
$NaNO_3(aq)^{a/}$	100°	2 hr	Decomposed to $H-Nb_2O_5$ + TTB
$2K_2O:3Nb_2O_5$			
$NaNO_3$	~500°	2 hr	$NaNbO_3$ perovskite
	340°	1 hr	Decomposed to $KNb_3O_8$ + $KNbO_3$
$NaNO_3(aq)^{a/}$	100°	2 hr	Decomposed to $NaNbO_3$
	25°	72 hr	higher hydrate (b=42.2) + TTB <sup>d/</sup>
	25°	4 hr	higher hydrate (b=42.2) + TTB <sup>d/</sup>
$NaOH(aq)^{b/}$	25°	18 hr	higher hydrate + TTB <sup>d/</sup>
$H_2O$ (deionised)	25°	18 hr	No change
$NaI$ (ac) <sup>c/</sup>	25°	18 hr	Unchanged 2:3 + TTB + higher hydrate (acetone) <sup>d/</sup>
$41K_2O:59Nb_2O_5$			
--	As prepared	hydrated	Hydrated "2:3"
--	As prepared	anhydrous	Single phase "2:3"
$NaNO_3$	450	3.5	Complete exchange
	500	1	Complete exchange
	450	4	Pellets hydrated and decapitated while being x-rayed
$KTaWO_6$			
$NaNO_3$	~500°	2 hr	$NaTaO_3$
	315°	2 hr	two phases: $KTaWO_6$ + $NaTaWO_6$
$NaNO_3(aq)^{a/}$	105°	1 hr	$NaTaWO_6$ a=10.375
$RbNO_3(aq)^{a/}$	105°	1 hr	$RbTaWO_6$ (a=10.352) + unknown phase
$H_2O$ (deionised)	100°	1 hr	$KTaWO_6$
$K_{.3}Ta_{.7}O_{.3}O_3$			
$NaNO_3$	~500°	2 hr	$NaTaO_3$ + HTB
	340°	2 hr	No change
$K_2O:2Ta_2O_5$			
$NaNO_3$	~500°	2 hr	No change using either 900° (rhomb) or 1300° (TTB) calcined starting material
$4Rb_2O:11Nb_2O_5^{a/}$			
Single Exchange			
$KNO_3$	400°	3 hr	K exch. 11 L phase a=7.354 c=43.398
	400°	16 hr	K exch. 11 L phase
$KNO_3$	400°	16 hr	K exch. 11 L phase
	450°	36	K exch. 11 L phase
$NaNO_3$	500	1 hr	Partially exch. a=7.4 c=43.6
	450	64 hr	Partially decomposed
	414	17 hr	Partially exch. a=7.458 c=43.19
	400	16 hr	Partially exch. a=7.472 c=43.23

### Double Exchange

$\text{KNO}_3/400^\circ/3 \text{ hr} \rightarrow \text{NaNO}_3/400^\circ/1.5 \text{ hr}$	$a=7.458$	$c=43.398$
$\rightarrow \text{NaNO}_3/400^\circ/16 \text{ hr}$	$a=7.362$	$c=43.869$
$\text{KNO}_3/400^\circ/16 \text{ hr} \rightarrow \text{NaNO}_3/450^\circ/66 \text{ hr}$	$a=7.366$	$c=43.898$
$\text{KNO}_3/400^\circ/16 \text{ hr} \rightarrow \text{NaNO}_3/450^\circ/98 \text{ hr}$	$a=7.332$	$c=43.997$



$\text{KNO}_3$	$450^\circ$	3 hr	K exch. 9 L phase $a=7.56$ $c=36.52$
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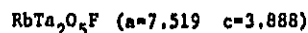


### Single Exchange

$\text{KNO}_3$	$450^\circ$	18 hr	No exchange (?)
	$450^\circ$	99 hr	
$\text{NaNO}_3$	$450^\circ$	99 hr	Partial exchange, increase in 'c' and partial decomposition

### Double Exchange

$\text{KNO}_3/450^\circ/18 \text{ hr} \rightarrow \text{NaNO}_3/450^\circ/23 \text{ hr}$	Partial exchange
--	------------------

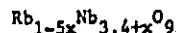


### Single Exchange

$\text{KNO}_3$	$340^\circ$	2.5	Partial exch. (?)
	$340^\circ$	15	$a=7.512$ $c=3.879$
	$450^\circ$	16	" "
$\text{NaNO}_3$ (aq. 20 w Z)	$340^\circ$	3.5	No exchange
$\text{NaNO}_3$			No exchange

### Double Exchange

$\text{KNO}_3/450^\circ/16 \text{ hr} \rightarrow \text{NaNO}_3/340^\circ/2 \text{ hr}$	No exchange
$\text{KNO}_3/450^\circ/16 \text{ hr} \rightarrow \text{NaNO}_3/450^\circ/44.5 \text{ hr}$	Some decomposition + partial exchange $a=7.51$ $c=3.814$



$\text{NaNO}_3$	$\sim 500^\circ$	2 hr	Unchanged HTB + $\text{Na}_2\text{Nb}_4\text{O}_{11}$ (tr) + $\text{NaNbO}_3$ (tr)
	$330^\circ$	2 hr	No change
$3\text{NaNO}_2 : 2\text{NaNO}_3$	$240^\circ$	22 hr	No change
$\text{KNO}_3$	$\sim 500^\circ$	2 hr	$\text{KNbO}_3$ + unchanged HTB

a/ 20 percent by weight of nitrate in deionized water

b/ 20 percent by weight of hydroxide in deionized water

c/ 10 percent by weight salt in acetone

d/ when dried at  $220^\circ\text{C}$  this "higher hydrate" or "acetate" changes to a 2:3 type structure with a and c the same as original but with a very small b axis of 30.78A by comparison with the original  $b=33.019\text{A}$ .

e/ single crystal fragments

Table 10b. Summary of Ion Exchange Experiments with  $4\text{Rb}_2\text{O} \cdot 11\text{Nb}_2\text{O}_5$  Pellets.

Starting Material	Pressing History	Firing History	K <sup>+</sup> Exchange History	Na <sup>+</sup> Exchange History	Remarks
$4\text{Rb}_2\text{O} \cdot 11\text{Nb}_2\text{O}_5$	10000 psi <u>a</u> / 500 °C-90 hr <u>c</u> /	1200 °-7 hr			Pellets cracked during firing a = 7.522 c = 43.180
			KNO <sub>3</sub> -20hr @ 400° partial exchange <u>a</u> /		Pellet fragment disintegrated a = 7.128, c = 43.469
		+15°/hr 1200 °-7 hr	KNO <sub>3</sub> -16 hr @ 400° partial ex- change	NaNO <sub>3</sub> -18 hr @400° partial ex- change	Pellet fragment did not disintegrate K <sup>+</sup> a = 7.575, c = 43.469 Na <sup>+</sup> a = 7.390, c = 43.663
		+5°/minute 1200°-1hr +5°/minute	KNO <sub>3</sub> -1 hr @400° complete exchange		pellet did not disintegrate K <sup>+</sup> a = 7.545, c = 43.332
		+3°/minute 1200-1 hr +3° minute	KNO <sub>3</sub> -19 hr @400° complete exchange		pellet displayed some spalling K <sup>+</sup> a = 7.555 c = 43.428
500-120 hr 600-90 hr <u>d</u> /	10000 psi <u>a</u> /	1100°C- 1 hr	KNO <sub>3</sub> -16 hr @400° complete exchange	NaNO <sub>3</sub> -21 hr @400°	K <sup>+</sup> a = 7.551, c = 43.401 Na <sup>+</sup> cells not calculated due to broadness of lines in diffraction
		1100°C-1.5 hr	KNO <sub>3</sub> 16 hr @400° partial exchange	NaNO <sub>3</sub> -41 hr @400° partial exchange	Na exchanged pellet decomposed K <sup>+</sup> a = 7.547, c = 43.428 Na <sup>+</sup> a = 7.404, c = 43.332
		1100°C-1 hr	KNO <sub>3</sub> -72 hr @400° complete exchange	NaNO <sub>3</sub> -32 hr @300° partial exchange	K <sup>+</sup> a = 7.557, c = 43.442 Na <sup>+</sup> a = 7.484, c = 43.482
	10000 psi <u>a</u> / 20000 psi <u>b</u> /	1100-1hr 1200-1 hr 1100 - 16 hr 1200 -2 hr	KNO <sub>3</sub> -16 hr @400° complete ex- change		Pellet cracked during final 1200 ° firing K <sup>+</sup> a = 7.557 c = 43.442
500-90		+5°/minute 1200-5 hr +5° minute	KNO <sub>3</sub> -2 hr 400°C complete exchange		powder fired in open tube K <sup>+</sup> a = 7.549, c = 43.387
			KNO <sub>3</sub> -18hr <u>d</u> / @400° complete exchange	NaNO <sub>3</sub> -18 hr @400° complete exchange	K <sup>+</sup> a = 7.553 c = 43.387 Na <sup>+</sup> a = 7.375 c = 43.830

a/= hydraulic  
pressure  
b/= isostatic  
pressure  
c/= Without PVA  
binder  
d/= with PVA  
binder  
e/= Complete  
exchange

	a	b
RbNb	= 7.522Å	43.180Å
KNb	= 7.554Å	43.398Å
NaNb	= 7.368Å	43.869Å

Table 11. Alkali Fluoride -  $\text{Sb}_2\text{O}_4$ ; Flux Evaporation

Composition	Temp/Time	Results
98KF:2 $\text{Sb}_2\text{O}_4$	1100°-1200°C 6 hrs	Solid + liquid x-ray shows $\text{KSbO}_{3-x}\text{F}_x$ small crystals formed
88.0KF:7.2 $\text{KSbO}_3$ :4.8 $\text{Sb}_2\text{O}_4$	1100° - 1 hr	Solid + liquid small crystals formed
90KF:2 $\text{Sb}_2\text{O}_4$ :8 $\text{B}_2\text{O}_3$	1100° - 2 hr, slow cool to 1000°	Solid + liquid small crystals formed
95RbF:5 $\text{Sb}_2\text{O}_4$	900° - 1000°C 1 hr	Solid + liquid small crystals formed

Table 12. Summary of X-ray Data.

System	Designation	Composition		Symmetry	Unit Cell Dimensions				Conditions Limiting Possible Reflections	Probable Space Group
		Alkali Oxide	Metal Oxide		a	b	c	$\beta$		
		Mole%	Mole%		Å	Å	Å			
$\text{Nb}_2\text{O}_5\text{-Nb}_2\text{O}_5$	11-L	26.67	73.33	Hexagonal	7.522	-	43.16	-	$hkl:l=2n$	$R3, R3, R32, R3m, R3m$
	16-L	29.5	74.5	Hexagonal	7.514	-	65.12	-	$hkl:l=2n$	$P6_3mc, P6_3c, P6_3mm$
	9-L	25	75	Hexagonal	7.518	-	36.353	-	$hkl:l=2n$	$P6_3mc, P6_3c, P6_3mm$
	HTB	21.75	78.25	Orthorhombic	12.991	7.350	7.786	-	$hkl:h+k=2n$	$Pnca$
	OTB	11.5	88.5	Tetragonal	37.484	-	3.9737	-	$h0l:l=2n$	$P42_12, P42_1m$
$\text{Nb}_2\text{O}_5\text{-Ta}_2\text{O}_5$	11-L	26.67	73.33	Hexagonal	7.504	-	43.19	-	$hkl:l=2n$	$R3, R3, R32, R3m, R3m$
	9-L	-	-	Hexagonal	7.508	-	36.41	-	$hkl:l=2n$	$P6_3mc, P6_3c, P6_3mm$
	HTB	21.75	78.25	Hexagonal	7.531	-	3.907	-	none	$P6_3mm$
	OTB	11.5	88.5	Tetragonal	27.573	-	3.9018	-	$h0l:l=2n$	$P42_12, P42_1m$
$\text{K}_2\text{O-Sb}_2\text{O}_4$	pyrochlore ss	(variable)								
		13	85	Cubic	10.331	-	-	-	$hkl:h+k, k+l=2n$	$Fd3m$
		30	70	Cubic	10.281	-	-	-	$0kl:h+l=4n$	
	1:2	33.33	66.67	Monoclinic	19.473	7.432	7.198	$94^\circ 54.4'$	$hkl:h+k=2n$	$C2/a (11)$
	$P2_1/c$	33.33	66.67	Monoclinic	7.178	13.378	11.985	$124^\circ 10'$	$hkl:h+k=2n$	$P2_1/c$
									$0kl:l=2n$	
$\text{Na}_2\text{O-Sb}_2\text{O}_4$		37.5	62.5	Orthorhombic	26.274	7.157	7.334	-	$hkl:h+k=2n$	
									$0kl:h=2n$	
									$h0l:h=2n$	
									$hkl:h+k=2n$	$Pnca (11)$
$\text{Na}_2\text{O-Sb}_2\text{O}_4$	pyrochlore ss	(variable)								
		25	75	Cubic	10.289	-	-	-	$hkl:h+k, k+l=2n$	$Fd3m$
		37.5	62.5	Cubic	10.286	-	-	-	$0kl:h+l=4n$	