Phase Equilibria and Crystal Growth in the Alkali Antimonate Systems

\[ \text{Sb}_2\text{O}_4 - \text{NaSbO}_3, \text{Sb}_2\text{O}_4 - \text{KSB}_3\text{O}_5, \text{and Sb}_2\text{O}_4 - \text{NaSbO}_3 - \text{NaF}^* \]

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Phase equilibrium diagrams have been constructed from experimental data for the systems \( \text{Sb}_2\text{O}_4 - \text{NaSbO}_3, \text{Sb}_2\text{O}_4 - \text{KSB}_3\text{O}_5, \) and \( \text{Sb}_2\text{O}_4 - \text{NaSbO}_3 - \text{NaF}^* \). The system \( \text{Sb}_2\text{O}_4 - \text{NaSbO}_3 \) contains only an intermediate pyrochlore type solid solution with a maximum melting point of 1490 °C at a Na:Sn atom ratio of 3:5. The \( \text{Sb}_2\text{O}_4 - \text{KSB}_3\text{O}_5 \) system contains in addition to the pyrochlore phase a compound \( 3\text{K}_2\text{O} \cdot 5\text{Sb}_3\text{O}_5 \) which melts congruently at about 1450 °C and two polymorphs of \( \text{K}_2\text{O} \cdot 2\text{Sn}_3\text{O}_5 \). The low temperature form of \( \text{K}_2\text{O} \cdot 2\text{Sn}_3\text{O}_5 \) was found to be monoclinic \( \text{P}_{2}/c \) with \( a=7.178, b=13.378, c=11.985~\text{Å}, \beta=124^\circ 10' \). The melting point of \( \text{Sb}_2\text{O}_4 \) was found to be 1350 ± 5 °C and \( \text{NaSbO}_3 \) and \( \text{KSB}_3\text{O}_5 \) both melt congruently at 1555 ± 5 °C and 1410 ± 5 °C respectively. The previously reported cubic form of \( \text{KSB}_3\text{O}_5 \) was found to be a K⁺ deficient phase stabilized by reaction with atmospheric moisture. A similar cubic phase which appears to be a good Na⁺ ion conductor can be synthesized in the ternary system \( \text{NaSbO}_3 - \text{Sn}_2\text{O}_4 - \text{NaF} \).

Key words: Alkali antimonates; crystal growth; ionic conductors; potassium antimonate; sodium antimonate; sodium antimony oxysulfuride.

1. Introduction

The search for potential candidates for ionic conductors together with the lack of detailed phase equilibrium data has served as an impetus to investigate the alkali antimonate systems.

In the system Na₂O-Sb₂O₃-O₂ the compound NaSbO₃ was reported to occur by Schrewelius [1] and to be hexagonal with an ilmenite structure, \( a=5.316, c=15.95~\text{Å} \). A pyrochlore solid solution was found to occur by Steward and Knop [2]. No melting data was previously reported.

In the system K₂O-Sb₂O₃-O₂ the compound KSB₃O₅ with an ilmenite structure has been previously reported by Spiegelberg [3]. A body centered cubic solid solution phase originally reported as KSB₃O₅ [3] has been found to occur metastably in the system. The \( \text{K}_2\text{O} \cdot 5\text{Sb}_3\text{O}_5 \) compound was originally reported by Aurivillius [4] and this phase, orthorhombic with \( a=24.274, b=7.157, c=7.334~\text{Å} \), space group \( \text{Pbam} \) and the new compound \( \text{K}_2\text{O} \cdot 2\text{Sn}_3\text{O}_5 \), monoclinic with \( a=19.473, b=7.452, c=7.198~\text{Å}, \beta=94^\circ 34' \), space group \( \text{C}2/'\text{m} \) were reported by H.Y.-P Hong [5].

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 [6] \( a=5.436, b=11.76 \) and \( c=4.81~\text{Å} \) and \( \beta-\text{Sb}_2\text{O}_4 \) which is monoclinic [7] \( a=11.905, b=4.834, c=5.383~\text{Å}, \beta=101^\circ 22' \). In the following discussion all ratios (1:3, 3:5, etc.) refer to the alkali/metal atom ratio rather than to the particular starting material that may have been used.

2. Specimen Preparation and Test Methods

In order to minimize the effect of foreign anion contamination in \( \text{Sn}_2\text{O}_4 \), high purity antimony metal was ground and oxidized on Pt setters in air at elevated temperatures. It was found that the formation of a thin antimony oxide coating at 450 °C prevented further surface reaction of antimony with the platinum. Once this coating was formed the temperature could be raised to 500 °C for relatively rapid oxidation without reaction with the platinum setter. Spectrographic analysis of \( \text{Sb}_2\text{O}_4 \) indicated that platinum contamination was only 2 ppm. The only other metals found in quantities greater than the detectable limit were traces of Zr and Tb.

Mixtures of \( \text{Sn}_2\text{O}_4 \) with sodium or potassium carbonate were prepared by weighing to the nearest ±0.1 mg in sufficient quantities to yield a 1 g batch. No corrections were made for percentage purity except loss on ignition. Each batch was hand mixed under acetone with a mortar and pestle. The mixtures were placed on setters fabricated from platinum foil and calcined in air at 500 °C for 60 hs. Following this preliminary calcine the mixtures
received a second calcine at 700 °C for 60 hs. In the K₂O–Sb₂O₅ system the specimens received a third calcining at higher temperatures in a small platinum tube for 1 h. To minimize volatility at higher temperatures, sealed platinum tubes approximately 2 cm long were employed for all succeeding experiments unless otherwise stated. About one-third of the volume was occupied by the specimen and the remainder of the tube was flattened prior to sealing. At elevated temperatures the expansion of the flattened portion of the tube provided the necessary additional volume for expansion of the vapors without rupture. The actual pressure inside the tube is unknown. At elevated temperatures, thermocouple contamination sometimes resulted. To minimize this contamination problem the thermocouples were changed occasionally.

An electrically heated vertical tube furnace was used for quenching. The temperature was controlled to about ±2 °C. Temperatures were measured with a Pt versus Pt 10 percent Rh thermocouple which was calibrated several times during the course of the work. Due to the marked volatility of the antimonates and the reactivity of the alkaline materials at elevated temperatures, thermocouple contamination sometimes resulted. To minimize this contamination problem the thermocouples were changed frequently. The overall accuracy of the reported temperature is estimated to be about ±5 °C.

The first sign of glazing of the specimen surface established the solidus values. The few liquidus values that are reported were established by the formation of a concave meniscus. No attempt was made to obtain liquidus values in the Sb₂O₅-rich portion of these systems because of the high vapor pressure.

Equilibrium is generally considered to have been obtained when x-ray diffraction patterns of specimens successively heated for longer times and/or at higher temperatures show no change. X-ray powder diffraction patterns were made using a high angle recording Geiger counter diffractometer and nickel-filtered copper radiation with a scan rate of 1/4° 2θ/min and a chart speed of 1/4 in/min. The unit cell dimensions reported can be considered accurate to about ±5 in the last decimal place listed.

3. The System Sb₂O₅–NaSb₂O₅

The system between the compositional limits of NaSb₂O₅ and Sb₂O₅ has been examined in detail. The phase equilibrium diagram, figure 1, has been constructed from the data given in table 1. When Sb₂O₅ is reacted at low temperature (500–1000 °C) with alkali carbonate it generally loses CO₂ and gains oxygen from the atmosphere to satisfy the equilibrium conditions of the phases formed, which may involve oxidation of the antimony ions. It is therefore understood that the phase diagrams determined in the antimonate systems reported here may not be strictly binary.

The compound NaSb₂O₅ (ilmenite-type) was found in this work to melt at about 1555 ± 5 °C. An intermediate pyrochlore solid solution exists from about 37.5 mol percent Na₂O:62.5 mol percent Sb₂O₅ to 24 mol percent Na₂O:76 mol percent Sb₂O₅ at 1350 °C. The 1:3 composition probably does not really correspond structurally to [NaSb₅⁺4−]Sb₅osomes− although the 3:5 composition may be written as [Na₁₋₅Sb₂₀₋₅]Sb₂₀₅−₅—see section 6.1. The 3Na₂O:5Sb₂O₅ composition apparently melts congruently at 1490 ± 5 °C. The solidus curve falls from this temperature to about 1340 ± 5 °C at 24 mol percent Na₂O:76 mol percent Sb₂O₅. A two phase region exists between the pyrochlore solid solution and Sb₂O₅. An unknown phase was found to occur in the system which could be made approximately single phase by calcining the composition 15 mol percent Na₂O:85 mol percent Sb₂O₅ at 750 °C and reheating in a sealed Pt tube to 1000 °C for 64 h in the presence of PtO₂. This phase has an as yet unindexed x-ray diffraction pattern with the four strongest lines occurring at d values equal to 2.283, 2.798, 3.453, 8.23 A.

In the Sb₂O₅ rich portion of the system from 10 percent Na₂O (or K₂O):90 percent Sb₂O₅ to 100 percent Sb₂O₅, experimental interpretation at or near the liquidus is exceedingly difficult since the conventional picture of solid and liquid is not evident. At the composition 15 mol percent Na₂O (or K₂O):85 mol percent Sb₂O₅, quenched liquid plus solid is evident. From this data the solidus can be delineated. However at or near Sb₂O₅, the solid appears to transform to vapor with no indication of the liquid phase. The most likely interpretation of the data is shown in the circular insert in figure 1, indicating that solid Sb₂O₅ + solid pyrochlore, melts to solid pyrochlore and liquid. Within experimental error, the sublimation and eutectic points appear to be at the same temperature and the field Sb₂O₅ + Liq (labeled S + L) is not seen.

3.1. NaSb₂O₅

The compound NaSb₂O₅ was first reported by Schreweilus [1] to be hexagonal, a=5.316 and c=15.95 A with an ilmenite structure. This compound was found in the present work to melt congruently at about 1555 ± 5°C. No other stable polymorphs were encountered.

3.2. Pyrochlore Solid Solution

One intermediate phase, a cubic pyrochlore solid solution was characterized in the system. The compositional range varies from approximately Na₈Sb₄O₁₇ to 3Na₂O:5Sb₂O₅ with unit cell dimensions varying from 10.289 to 10.286 A respectively. Since the pyrochlore is a tunnel structure and this pyrochlore is the only sodium containing pyrochlore reported that can be formulated by direct synthesis it was worthy of further study as a possible ionic
For ionic conductivity measurements, pellets of Na$_2$O:2Sb$_2$O$_4$ (1.9 cm 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 single phase material with a density of 96 percent theoretical (see sec. 6.1). The ionic conductivity of these pellets was measured at NASA Lewis Research Center [8] and they were found to be essentially insulators.

The distribution of the various ions (i.e., Na$^+$, Sb$^{3+}$, Sb$^{5+}$, O$^{-2}$) in the Na$_2$O:2Sb$_2$O$_4$ specimen is currently being determined at NBS from single crystal structure analysis. Until the results of this analysis are forthcoming it may be assumed that the "lone pair" electrons associated with Sb$^{3+}$ will not allow the passage of Na$^+$ through the channels.
| Composition | Heat Treatment$^8$ | Results | Physical Observation | X-ray Diffraction Analysis$^9$ |
|-------------|-------------------|---------|----------------------|-------------------------------|
| Na$_2$O mol % | Sb$_2$O$_3$ mol % | Temp °C | Time hr | |
| 50 | 50 | 1213 | 3 | not melted | Na$_2$SbO$_4$ |
| | | 1264 | 1 | " | " |
| | | 1435 | 1 | " | " |
| | | 1684 | 1 | " | " |
| | | 1502 | 0.8 | " | " |
| | | 1542 | 0.8 | " | " |
| | | 1669 | 0.8 | melted | Na$_2$SbO$_4$ + unknown |
| | | 1426 | 0.8 | " | " |
| 45 | 55 | 1000 | 48 | not melted | Na$_2$SbO$_4$ + pyrochlore ss |
| | | 1100 | 48 | " | " |
| | | 1473 | 25 | partially melted | " |
| | | 1488 | 10 | " | " |
| | | 1495 | 0.8 | " | " |
| 40 | 60 | 1102 | 20 | not melted | pyrochlore ss + Na$_2$SbO$_4$ |
| | | 1305 | 19 | " | " |
| | | 1430 | 0.8 | " | " |
| | | 1470 | 0.8 | " | " |
| | | 1488 | 0.8 | " | " |
| | | 1495 | 0.3 | " | " |
| 37.5 | 62.5 (3:5) | 1100 | 48 | not melted | Pyrochlore ss |
| | | 1192 | 1 | " | " |
| | | 1306 | 19 | " | " |
| | | 1326 | 20 | " | " |
| | | 1351 | 1 | " | " |
| | | 1373 | 2 | not melted (reheat of 1100-4) | pyrochlore ss |
| | | 1391 | 2 | not melted | " |
| | | 1392 | 1.6 | " | pyrochlore ss |
| | | 1412 | 1.6 | " | " |
| | | 1447 | 1.6 | " | " |
| | | 1454 | 3.3 | " | " |
| | | 1458 | 0.8 | " | " |
| | | 1464 | 0.8 | " | " |
| | | 1476 | 0.8 | " | " |
| | | 1487 | 0.8 | " | " |
| | | 1490 | 0.8 | " | " |
| 33.33 | 66.67 (1:2) | 1000 | 8 | not melted | Pyrochlore ss |
| | | 1005 | 8 | " | " |
| | | 1005+b | 1.68 | " | pyrochlore ss |
| | | 1005+b | 91 | " | " |
| | | 1287 | 2 | " | " |
| | | 1292 | 1.5 | " | " |
| | | 1306 | 24 | " | " |
| | | 1307 | 19 | " | " |
| | | 1316 | 0.5 | " | pyrochlore ss |
| | | 1317 | 3.5 | " | " |
| | | 1334 | 0.75 | " | " |
| | | 1360 | 24 | " | " |
| | | 1376 | 0.5 | " | " |
| | | 1378 | 0.5 | " | " |
| | | 1411 | 19 | " | " |
| | | 1418 | 0.2 | " | partially melted |
| | | 1437 | 24 | " | " |
| | | 1475 | 0.2 | " | " |
| 25 | 75 (1:3) | 750 | 60 | not melted | pyrochlore ss + unknown$^e$ |
| | | 800 | 60 | " | " |
| | | 800 | 60 | " | " |
| | | 800 | 336 | " | " |
| | | 1098 | 16 | " | " |
| | | 1192 | 1 | " | pyrochlore ss |
| | | 1200 | 24 | " | " |
| | | 1220 | 2 | " | " |
| | | 1277 | 2 | " | " |
| | | 1306 | 24 | " | " |
| | | 1307 | 0.8 | " | " |
| | | 1317 | 16$^d$ | " | pyrochlore ss |
| | | 1325 | 1 | " | " |
| | | 1339 | 0.8 | " | " |
| | | 1345 | 0.25 | " | " |
| | | 1346 | 0.8 | " | " |
| | | 1358 | 0.8 | " | " |
| | | 1377 | 0.2 | " | partially melted |
| | | 1427 | 0.2 | " | " |
| 23 | 77 | 1220 | 24 | not melted | pyrochlore ss + Na$_2$SbO$_4$ |
| | | 1266 | 4 | " | " |
| | | 1267 | 19 | " | " |
| | | 1299 | 0.8 | " | " |
| | | 1304 | 0.8 | " | " |
| | | 1313 | 0.8 | " | " |
| | | 1322 | 0.8 | " | " |
| | | 1332 | 0.8 | " | " |
| | | 1338 | 0.8 | " | " |

Table 1. Experimental data for compositions in the system sodium antimonate-antimony tetroxide.
### Table 1. Experimental data for compositions in the system sodium antimonate-antimony tetroxide—Continued

| Composition | Heat Treatment<sup>8</sup> | Physical Observation | X-ray Diffraction Analysis<sup>8</sup> |
|-------------|-----------------------------|----------------------|----------------------------------------|
|             | Temp Time  |             |                                        |
| Na₂O az₂      | °C hr     | Physical Observation | X-ray Diffraction Analysis |
| 20           | 80 672    | not melted | pyrochlore az₂<sup>3</sup> |
| 1107         | 1099      |             |                                        |
| 1200         | 24        | not melted | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1220         | 2.5       | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1234         | 2.5       | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1277         | 16        | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1301         | .5        | not melted |                                        |
| 1305         | 19        | "         | NaNb₆<sup>4</sup> |
| 1306         | 24        | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1334         | .08       | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1335         | .08       | "         |                                        |
| 1339         | .2        | "         |                                        |
| 1340         | .08       | "         |                                        |
| 1365         | .2        | partially melted |                                        |
| 1362         | .5        | "         |                                        |
| 15           | 85        | 800 74    | not melted | unknown + pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 800          | 60        | "         | "         | a + pyrochlore az₂ + unknown<sup>5</sup> |
| 1000         | 64        | "         | "         | unknown + tr a-Sb₂O₄<sup>2</sup> + Fried 240<sup>6</sup> |
| 1000         | 64        | "         | "         | unknown + tr a-Sb₂O₄<sup>2</sup> + Fried 240<sup>6</sup> |
| 1007         | 48        | not melted | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> + unknown<sup>5</sup> |
| 1107         | 144       | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1200         | 24        | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1200         | 60        | "         | pyrochlore az₂ + a-Sb₂S₄<sup>4</sup> |
| 1337         | .2        | "         |                                        |
| 1340         | .2        | "         |                                        |
| 1348         | .2        | partially melted |                                        |
| 1362         | .5        | "         |                                        |
| 10           | 90        | 800 74    | not melted | a-Sb₂O₄ + unknown<sup>5</sup> |
| 1007         | 48        | "         | "         | a-Sb₂O₄ + a-Sb₂S₄ + pyrochlore az₂<sup>4</sup> |
| 1107         | 144       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1234         | 2         | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1281         | .33       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1290         | .33       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1300         | .33       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1311         | .2        | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1319         | .33       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1334         | .33       | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1337         | .2        | "         | "         | a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1351         | 1         | partially melted | a + pyrochlore az₂ + quenched liquid<sup>4</sup> |
| 5            | 95        | 1007 48   | not melted | β-Sb₂O₄ + a-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |
| 1107         | 144       | "         | "         | β-Sb₂O₄ + pyrochlore az₂<sup>4</sup> + trace β-Sb₂O₄<sup>4</sup> |
| 1234         | 3.5       | "         | "         | β-Sb₂O₄ + pyrochlore az₂<sup>4</sup> |

<sup>3</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°F/min. For higher heat treatments, specimens were heated in sealed Pt tubes and quenched from temperatures indicated.

<sup>4</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>5</sup> Specimen heated with PtO₂ at 68,900 psi in sealed Pt tube.

<sup>6</sup> Specimen heated in sealed Pt tube at 5,000 psi.

<sup>7</sup> Specimen previously heated at 1292°C for 1.5 hours.

<sup>8</sup> Specimen heated in sealed Pt tube at presence of water. The unknown phase formed is probably a hydrate.

<sup>x</sup> Specimen heated in sealed Pt tube in PtO₂.

<sup>9</sup> Specimen heated in presence of 5:95 Na₂O:Sb₂O₄ which served as a buffer.

<sup>10</sup> In spite of extensive x-ray study it has not been determined which of the polymorphic forms of Sb₂S₄<sup>4</sup> is the stable form.

<sup>11</sup> Sb₂S₄<sup>4</sup> probably soaked into Pt container and the composition changed to pyrochlore az₂.

<sup>12</sup> Platinum tube leaked.

<sup>13</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 PtO₂ and can be eliminated by additional calcining of 1200°C for several hours. Once eliminated this phase does not appear to reform at lower temperatures in laboratory time.

<sup>14</sup> Specimen contained non-equilibrium material derived from a liquid when quenched from above the liquidus and examined at room temperature.
3.3. Polymorphism of Sb\textsubscript{2}O\textsubscript{4}

Two stable polymorphs of Sb\textsubscript{2}O\textsubscript{4} have been reported in the literature. They are $\alpha$-Sb\textsubscript{2}O\textsubscript{4}, which is orthorhombic [6], $a=5.436$, $b=11.76$, $c=4.810$ Å and $\beta$-Sb\textsubscript{2}O\textsubscript{4}, which is monoclinic [7], $a=11.905$, $b=4.834$, $c=5.383$ Å and $\beta=101^{\circ}22'$. From table 2a it can readily be seen that specimens quenched from a temperature-composition region represented on the phase diagram, figure 1, as Sb\textsubscript{2}O\textsubscript{4}+ pyrochlore may contain either $\alpha$-Sb\textsubscript{2}O\textsubscript{4} and/or $\beta$-Sb\textsubscript{2}O\textsubscript{4} when quenched from high temperatures and ambient pressures and examined at room temperature. From this seemingly inconsistent data it would appear that $\alpha$-Sb\textsubscript{2}O\textsubscript{4} and $\beta$-Sb\textsubscript{2}O\textsubscript{4} have a polytypic relationship.

Composition Heat Treatment Results

| Starting Material | Heat Treatment | Environment | Physical Observation | Crystallographic Analysis |
|-------------------|---------------|-------------|----------------------|---------------------------|
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 1223, 0.5 | sealed Pt tube | not melted | $\alpha + \beta$
| $\beta$-Sb\textsubscript{2}O\textsubscript{4} | 1223, 0.5 | unsealed Pt tube | not melted | $\beta + \alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 1303, 19 | sealed Pt tube | not melted | $\beta + \alpha$
| $\beta$-Sb\textsubscript{2}O\textsubscript{4} | 1330, 0.25 | sealed Pt tube | not melted | $\beta + \alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 1339, 0.08 | sealed Pt tube | not melted | $\beta + \alpha$
| $\beta$-Sb\textsubscript{2}O\textsubscript{4} | 1345, 0.08 | sealed Pt tube | not melted | $\beta + \alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 1350, 0.08 | sealed Pt tube | melted (vapor soaked into Pt) | $\beta$
| $\beta$-Sb\textsubscript{2}O\textsubscript{4} | 1350, 0.08 | sealed Pt tube | melted | $\beta$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 1200, - | high temperature | $\alpha$ (starting material remained $\alpha$ up to 1200°C) | $\alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 750, 24 | open tray | $\alpha$ | $\alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 800, - | open tray | $\alpha$ | $\alpha$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 900, - | open tray | $\alpha + \beta$ | $\alpha + \beta$
| $\alpha$-Sb\textsubscript{2}O\textsubscript{4} | 950, - | open tray | $\alpha + \beta$ | $\alpha + \beta$

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\textsubscript{2}O\textsubscript{4} polymorph and $\beta$ to the $\beta$-Sb\textsubscript{2}O\textsubscript{4} polymorph.

Material placed on platinum slide and heated and examined by x-ray diffraction at various temperatures.

Poorly crystalline as received Sb\textsubscript{2}O\textsubscript{4} 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 2a. Experimental data for polymorphism in antimony tetroxide

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To help resolve this problem a high resolution electron microscope study should be done.

From the data in table 2b it appears that the $\beta$ form is the equilibrium high pressure form of Sb\textsubscript{2}O\textsubscript{4}. Insufficient data have been collected to establish if an equilibrium boundary curve exists between $\alpha$-Sb\textsubscript{2}O\textsubscript{4} and $\beta$-Sb\textsubscript{2}O\textsubscript{4} at various temperatures and pressures. When specimens are sealed and heated under pressure in the presence of PtO\textsubscript{2} in either Pt or Au tubes single phase $\beta$-Sb\textsubscript{2}O\textsubscript{4} is obtained. However when heated under pressure without the PtO\textsubscript{2}, a two phase specimen results, $\beta$-Sb\textsubscript{2}O\textsubscript{4} and the dense high pressure form of Sb\textsubscript{2}O\textsubscript{3} (valentinite). A similar polytypic relationship probably exists for the two polymorphs of Sb\textsubscript{2}O\textsubscript{3}.
4. The System Sb₂O₃-KSbO₃

This system has been examined between the compositional limits of KSbO₃ and Sb₂O₃. The results are given in the data presented in table 3 from which the phase relationships have been established as shown in figure 2.

4.1. Compounds in the System

The compound KSbO₃ with an ilmenite structure \( a=5.361, \ c=18.213 \), was previously reported [3] and was found in this work to melt congruently at about 1420±5 °C. A body centered cubic solid solution phase originally reported as KSbO₃ [3] has been found to occur metastably at about 47.5 percent K₂O. The 3K₂O:5Sb₂O₃ compound was found to melt congruently at about 1450 °C. The K₂O:2Sb₂O₃ compound was found to have a phase transition at about 1000 °C and to dissociate to pyrochlore plus 3K₂O:5Sb₂O₃ at about 1150 °C. The low temperature form of K₂O:2Sb₂O₃ labeled \( P_{2\text{h}}/c \), represents a monoclinic phase with \( a=7.178, \ b=13.378, \ c=11.985 \) A and \( \beta=124°10' \). Single crystals of this phase were grown by flux evaporation from the composition 50K₂O:5Sb₂O₃:45MoO₃. 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 K₂O:2Sb₂O₃. The pyrochlore solid solution exists at 1150°C from about 15 mol percent K₂O:85 mol percent Sb₂O₃ to greater than 30 mol percent K₂O:70 mol percent Sb₂O₃. The melting characteristics of these phases have been partially determined as shown in table 3 and figure 2.

4.2 Hydroxyl Ion Stabilization of Cubic Potassium Antimonate

The compound KSbO₃ was reported previously as being cubic at ambient conditions after treatment at high temperatures and pressures [9].

In the current work, occasional small amounts of a cubic phase were seen in the x-ray powder diffraction pattern of KSbO₃ ilmenite heated at ambient pressure. For these reasons, specimens of 1:1 and 3:5 mol ratios K₂O:Sb₂O₃ were equilibrated in air at 750°C for 60 h to oxidize and form the phases KSbO₃ and K₃Sb₅O₁₄ and then reheated for 1 h at 1200°C to drive off all excess moisture. X-ray diffraction patterns of these specimens showed single phase ilmenite and the 3K₂O:5Sb₂O₃ compound. Portions of these 1200°C calcines were then weighed and mixed in acetone in the appropriate ratios to yield compositions of 46, 47, 47.5, 48 and 49 mol percent K₂O. Each of these specimens was dried at 240°C for 1 h and heated in open Pt tubes at 1200°C for 1 h. Only the x-ray pattern of the 46 percent specimen showed a small amount of 3K₂O:5Sb₂O₃, the others contained only the cubic phase. A new specimen of

| Composition Starting Material | Heat Treatment | Pressure | Results b/ | X-ray Diffraction Analysis |
|-------------------------------|---------------|----------|------------|--------------------------|
| \( \alpha\)-Sb₂O₄ \( a/ \) | \( \alpha\)-Sb₂O₄ prepared by the oxidation of Sb at 530°C on Pt tray. This material was reheated at 800°C - 60 hr . | 88,000 | \( \beta \) + Sb₂O₃ \( b/ \) | 88,000 | \( \beta \) |
| \( \beta\)-Sb₂O₄ | \( \beta\)-Sb₂O₄ | 104,000 | \( \beta \) + trace Sb₂O₃ | 104,000 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 80,000 | \( \beta \) + Sb₂O₃ | 80,000 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 88,000 | \( \beta \) + Sb₂O₃ | 88,000 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 47,500 | \( \beta \) + Sb₂O₃ | 47,500 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 54,760 | \( \beta \) + Sb₂O₃ | 54,760 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 66,500 | \( \beta \) + Sb₂O₃ | 66,500 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 93,000 | \( \beta \) + Sb₂O₃ | 93,000 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 105,000 | \( \beta \) + Sb₂O₃ | 105,000 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 82,500 | \( \beta \) + Sb₂O₃ | 82,500 | \( \beta \) |
| K₂O:2Sb₂O₃ | K₂O:2Sb₂O₃ | 104,000 | \( \beta \) + Sb₂O₃ | 104,000 | \( \beta \) |

\( a/ \) 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.

\( b/ \) High pressure form of Sb₂O₃ (valentinite).

Table 2b. Experimental high pressure data for polymorphism in antimony-tetroxide
| Composition | Heat Treatment<sup>a</sup> | Physical Observation | X-ray Diffraction Analysis<sup>b</sup> |
|-------------|----------------------------|----------------------|----------------------------------------|
| K<sub>2</sub>O | Sb<sub>2</sub>O | Temp | Time | |
| Mol % | Mol % | °C | hr | |
| 5 | 95 | 950 | 60 | not melted |
| | | 1168 | 48 | |
| 10 | 90 | 950 | 60 | not melted |
| | | 1168 | 48 | |
| 15 | 85 | 853 | 24 | not melted |
| | | 950 | 60 | |
| | | 966 | 4 | |
| | | 1168 | 48 | |
| | | 1200 | 19 | |
| 20 | 80 | 950 | 60 | not melted |
| | | 1168 | 48 | |
| 25 | 75 | 950 | 60 | not melted |
| | | 1179 | 48 | |
| | | 1361 | .08 | |
| | | 1375 | .08 | partially melted |
| | | 1385 | .08 | |
| | | 1403 | .08 | completely melted |
| 30 | 70 | 950 | 60 | not melted |
| | | 1178 | 48 | |
| | | 1366 | .08 | |
| | | 1380 | .08 | partially melted |
| | | 1382 | .08 | |
| | | 1399 | .08 | completely melted |
| 33.33 | 66.67 | 950 | 60 | not melted |
| | | 950 | 64 | |
| | | 998 | 70 | |
| | | 1050 | 168 | |
| | | 1050<sup>e</sup> | 168 | |
| | | 1102 | 1 | |
| | | 1106<sup>e</sup> | 64 | |
| | | 1106<sup>e</sup> | 64 | |
| | | 1160<sup>e</sup> | 1 | |
| | | 1179<sup>e</sup> | 48 | |
| | | 1214<sup>e</sup> | 1 | |
| | | 1214<sup>e</sup> | 2 | |
| 35 | 65 | 950 | 60 | not melted |
| | | 1178 | 48 | |
| | | 1380 | .08 | partially melted |
| | | 1397 | .08 | |
| | | 1409 | .08 | completely melted |
| 37.5 | 62.5 | 950 | 60 | not melted |
| | | 1174 | 88 | |
| | | 1195 | 19 | |
| | | 1208<sup>e</sup> | 1 | |
| | | 950<sup>e</sup> | 64 | |
| | | 1310 | 45 | |
| | | 1352 | .08 | |
| | | 1379 | .08 | |
| | | 1399 | .08 | completely melted |
| | | 1416<sup>e</sup> | .08 | |
| 40 | 60 | 950 | 60 | not melted |
| | | 1174 | 88 | |
| | | 1208<sup>e</sup> | 1 | |
| | | 1254<sup>e</sup> | 20 | |
| | | 1362<sup>e</sup> | .5 | |
| | | 1375<sup>e</sup> | .08 | |

Table 3. Experimental data for compositions in the system potassium antimonate antimony tetroxide
| Composition | Heat Treatment<sup>a/</sup> | Results<sup>b/</sup> |
|-------------|-----------------------------|----------------------|
|             |                             |                      |
|             |                             | **Physical Observation** | **X-ray Diffraction Analysis** |
| K₂O | Sb₂O₅ | Temp °C | Time hr |                        |                                    |
| H₂O | Molar % |          |         |                        |                                    |
| 45 | 55 | 950 | 60 | not melted | 1:1 + cubic + P₂₁/c |
|    |     | 1174 | 88 | " " | cubic + 3:5 |
|    |     | 1208 | 1 | " " | 3:5 + cubic |
|    |     | 1311<sup>g/</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>h/</sup> | 45 | " " | 1:1 |
| 48 | 52 | 1198 | 3 | not melted | cubic |
|    |     | 1200<sup>i/</sup> | 1 | " " | cubic + 3:5 ilmenite |
|    |     | 1200<sup>i/</sup> | 1.5 | " " | 1:1 |
|    |     | 1308<sup>i/</sup> | .5 | " " | cubic + ilmenite + pyrochlore |
|    |     | 1103<sup>c/</sup> | 1 | " " | ilmenite + pyrochlore |
|    |     | 1103<sup>c/</sup> | 3 | " " | " |
| 49 | 51 | 1200 | 1 | not melted | cubic |
| 50 | 50 | 750 | 70 | not melted | " " |
|    |     | 800 | 24 | " " | " |
|    |     | 921 | 1 | " " | " |
|    |     | 946 | 21 | " " | " |
|    |     | 950 | 60 | " " | " |
|    |     | 1103 | 1 | " " | " |
|    |     | 1104 | 22 | " " | " |
|    |     | 1150 | 1 | " " | " |
|    |     | 1174 | 88 | " " | " |
|    |     | 1194 | 1 | " " | " |
|    |     | 1202 | 1 | " " | " |
|    |     | 1214 | 1 | " " | " |
|    |     | 1298 | .5 | " " | " |
|    |     | 1363 | .5 | " " | " |
|    |     | 1403 | .08 | " " | " |
|    |     | 1421 | .08 | " " | " |
|    |     | 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.

<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 P₂₁/c a=7.178, b=13.378, c=11.985, β=124°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 3. Experimental data for compositions in the system potassium antimonate antimony tetroxide—Continued
A paper entitled "Flux Synthesis of Cubic Antimonates" was published by the present authors during the course of this work [10]. 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 K₃SbO₃ 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 "K₃SbO₄."
5. The Systems of NaSbO₃ With Additions

5.1. The System NaSbO₃-NaF

To determine if NaF additions will stabilize the body-centered cubic phase, similar to the KF-phase [10], NaF was added to NaSbO₃ in the ratio of 3NaSbO₃:NaF, 4NaSbO₃:NaF, 5NaSbO₃:NaF and 6NaSbO₃:NaF. After heating at 750 °C and 1000 °C in sealed Pt tubes, the x-ray patterns showed only ilmenite and NaF, however after heating at ~1150 °C all the compositions contained some body centered cubic-type phase. The compositions 3NaSbO₃:NaF and 4NaSbO₃: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 4NaSbO₃: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 °C. At 190 °C the material appeared to start to go cubic and by 220 °C a good quality cubic x-ray diffraction pattern was obtained (a = 9.353 Å). 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 Na⁺ ion exchange.

5.2. The Ternary System NaSbO₃: Sb₂O₅:NaF

X-ray diffraction patterns (single crystal and powder) of selected NaF-flux synthesized [11] washed crystals show only a truly cubic body centered phase (a = 9.334 Å). It must be postulated that the composition formed by this technique is slightly different from that made essentially single phase at 4NaSbO₃: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 4 were prepared and show the reported phases when quenched from 1250 °C. Equilibrium was not obtained in overnight heat treatments at 1200 °C. At 1350 °C the body centered cubic phase started to decompose. The composition 65NaSbO₃:4Sb₂O₅:28NaF (mol %) was chosen as the best composition for further studies on ceramic procedures [11]. The phases found in the specimens heated at ~1250 °C are summarized in “equilibrium” diagrams for the quaternary system NaSbO₃-Sb₂O₅-Sb₂O₃-NaF (fig. 3) and the ternary plane of this system NaSbO₃-Sb₂O₅-NaF (fig. 4).

Figure 3. Phase relations in the quaternary system NaSbO₃-Sb₂O₅-Sb₂O₃-NaF.

The join 6:1—3:4 represents the formula
\[ \square_{2+z}Na_{4-x}F_2 [Sb_{14+z}O_{36-x}F_x]. \]

The join 6:1—3:7 represents the formula
\[ \square_{2}Na_{4}F_2 [Sb_{14+z}O_{36-(z+2)}F_{(z+2)}]. \]

Figure 4. Phase relations in the ternary system NaSbO₃-Sb₂O₅-NaF.

The join 6:1—3:4 represents the formula
\[ [Na_{4+z}F_2] [Sb_{14+z}O_{36-(z+2)}F_{(z+2)}]. \]

The join 3:1—3:8 represents the formula
\[ [Na_{4}F_2] [Sb_{14+z}O_{36-2z}F_{(z+2)}]+O_2. \]
| Composition | Mol % | Temp °C | Time hr | X-ray Analysis                      |
|-------------|-------|---------|---------|-------------------------------------|
| NaSbO$_3$   | 75.08 | 1250    | 19      | single phase distorted cubic        |
| Sb$_2$O$_3$ | 3.15  | 1250    | 19      | body centered cubic + pyrochlore + ilmenite |
| NaF         | 21.77 | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| NaSbO$_3$   | 67.79 | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| Sb$_2$O$_3$ | 6.25  | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| NaF         | 25.96 | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| NaSbO$_3$   | 53.50 | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| Sb$_2$O$_3$ | 12.34 | 1250    | 19      | body centered cubic + pyrochlore + sodium fluoride |
| NaF         | 34.16 | 1250    | 19      | body centered cubic + trace sodium fluoride |
| NaSbO$_3$   | 39.59 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| Sb$_2$O$_3$ | 18.27 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaF         | 42.14 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaSbO$_3$   | 69.05 | 1250    | 19      | body centered cubic + trace sodium fluoride |
| Sb$_2$O$_3$ | 2.90  | 1250    | 19      | body centered cubic + trace sodium fluoride |
| NaF         | 28.05 | 1250    | 19      | body centered cubic + trace sodium fluoride |
| NaSbO$_3$   | 49.28 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| Sb$_2$O$_3$ | 11.37 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaF         | 39.35 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaSbO$_3$   | 31.20 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| Sb$_2$O$_3$ | 28.87 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaF         | 39.93 | 1250    | 19      | pyrochlore + body centered cubic + sodium fluoride |
| NaSbO$_3$   | 84.62 | 1268    | 19      | ilmenite + cubic                  |
| Sb$_2$O$_3$ | --    | 1268    | 19      | ilmenite + cubic                  |
| NaF         | 15.38 | 1268    | 19      | ilmenite + cubic                  |
| NaSbO$_3$   | 74.42 | 1261    | 1       | distorted cubic + ilmenite         |
| Sb$_2$O$_3$ | 2.32  | 1261    | 1       | distorted cubic + ilmenite         |
| NaF         | 23.26 | 1268    | 19      | distorted cubic + NaF              |
| NaSbO$_3$   | 70.00 | 1264    | 1       | cubic + ilmenite                  |
| Sb$_2$O$_3$ | 3.33  | 1264    | 1       | cubic + ilmenite                  |
| NaF         | 26.67 | 1264    | 1       | cubic + ilmenite                  |
| NaSbO$_3$   | 65.96 | 1266    | 1       | cubic + ilmenite                  |
| Sb$_2$O$_3$ | 4.26  | 1266    | 1       | cubic + ilmenite                  |
| NaF         | 29.78 | 1267    | 19      | cubic + NaF                       |
| NaSbO$_3$   | 62.96 | 1266    | 1       | cubic + NaF                       |
| Sb$_2$O$_3$ | 4.94  | 1266    | 1       | cubic + NaF                       |
| NaF         | 32.10 | 1267    | 19      | cubic + NaF                       |
| NaSbO$_3$   | 58.82 | 1267    | 19      | cubic + NaF                       |
| Sb$_2$O$_3$ | 5.89  | 1267    | 19      | cubic + NaF                       |
| NaF         | 35.29 | 1267    | 19      | cubic + NaF                       |
| NaSbO$_3$   | 68.00 | 1000    | 1       | ilmenite + trace NaF              |
| Sb$_2$O$_3$ | 4.00  | 1252    | 16      | cubic + trace ilmenite            |
| NaF         | 26.00 | 1252    | 16      | cubic + trace NaF                 |

$^a/$ Preheated at 750°C for 60 hours open.

Table 4. Experimental data for the ternary system NaSbO$_3$-Sb$_2$O$_3$-NaF.
6. 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 for this study for those phases which seem to be of interest.

6.1. Pyrochlore Phases

In the KTaO₃–WO₃ system a pyrochlore phase occurs at about the 1:1 ratio or K₁₋₁[TaW]O₆ [11, 12]. Unfortunately the pyrochlore in this system transforms to a tetragonal tungsten bronze (TTB) at high temperatures. Although it can be ion exchanged with Na⁺ to produce an ion conducting pyrochlore phase, this phase is not stable above about 450°C [11]. The only stable Na⁺ containing pyrochlore is the one in the Sb₂O₅–Na₂SbO₄ system and apparently this one is not a good ionic conductor.

The distribution of Na⁺, Sb⁺₃, Sb⁺⁵ and 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 [NaSb⁺³]Sb₂O₇ for the Na/Sb ratio of 1:3 and [Na₁.₃Sb₀.₆7O₆ for 1:2, and [Na₁.₅Sb₀.₄5O₆ for 3:5. These compositions do not illustrate the structural nature of pyrochlore nor account for the observation that the "lone pair" electrons associated with Sb⁺³ will not allow O⁻² ions to completely coordinate the antimony and result in apparent vacancies. The structural formula of pyrochlore should be written as [A₂X]₂[B₃X₆] to emphasize the fact that the octahedral network of B₃X₆ is required to be complete if the structure is to be stable. The A₂X ions fill the intersecting channels in this B₃X₆ framework. In our material the B₃X₆ framework must be represented as [Sb⁺³O₆]⁻² and must be stoichiometric. All remaining Na⁺ and O⁻² ions, as well as Sb⁺³, must be in the [A₂X]⁺² portion of the formula. All Sb⁺⁵ must be in B₃X₆ and only Sb⁺³ in A₂X. Furthermore the maximum number of the sum of Na⁺¹, Sb⁺³, excess O⁻² (beyond O⁻⁰) and "lone pair" electrons cannot exceed three. One can then write the general formula as [A₂O]⁺²[Sb₂O₆]⁻² with [A₂O]⁺² equal to

\[ [Na_{k+1} + Na^{+1} + Sb^{+3} + O_{-2}^+ + L.P.]_{1.2} \leq 3 \]

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

\[ [Na_{0.917}Sb^{+3}O_{-0.583}O_{-0.75}Sb^{+2}O_{-0.75}]^{-2} \]

is calculated to be 5.469 g/cm³.

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

\[ [Na^{+1.5}Sb^{+3}O_{-0.5}O_{-0.35}Sb^{+2}O_{-0.75}]^{-2} \]

the density is calculated as 5.406 g/cm³. For the intermediate composition with the Na/Sb ratio of 1:2 and a formula of [Na₁.₂₉₄Sb₀.₅₈₆O₆.₅₈₂O₂]⁺²[Sb₂O₆]⁻² the maximum density is found to be 5.481 g/cm³. The density found for our isostatically hot pressed specimens is 96.0 percent 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 percent of theoretical in view of the expected increased oxidation of the Sb at the relatively low temperatures involved.

6.2. Body Centered Cubic Antimonates

A successful method of synthesizing cubic potassium antimonate by heating in molten KF was published by the present authors [10]. The major reason for the success in obtaining completely single phase fluorine stabilized cubic potassium antimonate is that the KSbO₃ ilmenite form is H₂O 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 and 1/2 1/2 1/2 positions. The structural formula thus appears to be [A₁₅X]⁺¹²[Sb₁₂O₃₆]⁻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 nonframework positions will be non-stoichiometric. Valency considerations require that at least two out of 16 alkali ions must be missing and the structural formula then becomes

\[ [\Box_{2}A_{15}X_{6}]^{+12}[Sb_{12}O_{36}]^{-12} \]

This formula corresponds to the composition reported by Goodenough, et al. [13] for the single crystal x-ray diffraction analyses of the phase synthesized with KF according to the NBS method [10]:

\[ K_{12}Sb_{13}O_{36}.2KF or \[ \Box_{2}K_{14}F_{2}^{+12}[Sb_{12}O_{36}]^{-12}. \]

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 \([\text{OH}^-, \text{F}^-]\) in the octahedral framework. The general formula then becomes \(\square_{3\frac{1}{2}}A_{14-x}X'_2\)\(^{(12-x)}[\text{SB}_{12}O_{26}(OH)_3]^{-9}\)\(\square_{3\frac{1}{2}}\)\(A_{14-x}X'_2\). The composition found at \(\sim 48:52\) in the potassium antimonate system can be written (assuming a ratio of 11:12 K/Sb or 47.826\% K_2O):

\[
K_{25}\text{Sb}_{25}O_{71} + 5\text{H}_2\text{O} \rightarrow K_{25}\text{Sb}_{25}O_{66}(OH)_{10}
\]

or

\[
[\square_{5}K_{11}(OH)_2]^{+9}[\text{SB}_{12}O_{26}(OH)_3]^{-9}
\]

which also can be described as \(6\text{KSB}_3\text{O}_5\text{Sb}_2\text{O}_5\text{Sb}_5\). The general formula describing the \(K^+\) containing compositions is then

\[
[\square_{2+x}K_{14-x}X'_2]^{(12-x)}[\text{SB}_{12}O_{38-2x}F_{2x}]^{-12-x}
\]

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 \(Na\text{Sb}_3\text{O}_5\text{Sb}_2\text{O}_5\text{Sb}_5\):NaF. The only formula which does not involve the loss or gain of \(O^2-\) (or \(F^-\)) when the \(\text{Sb}_2\text{O}_4\) is added in a sealed tube corresponds to:

\[
[\square_{2}Na_{14}F_{2}] [\text{Sb}^3_{7}\text{Sb}^5_{12-x}O_{38-2y}F_{2y}]
\]

which is represented by the join 6:1—3:7 on figures 3 and 4. There is really no place in the framework structure for \(\text{Sb}^5^+\) and it is difficult to believe that octahedrally coordinated antimony can be \(\text{Sb}^5^+\). However, for convenience, the formulas can be written involving \(\text{Sb}^3^+\). The new formula would then have two variables:

\[
[\square_{2+x}A_{14-x}X'_2][\text{Sb}^3_{7}\text{Sb}^5_{12-x}O_{38-2x}F_{2x}]
\]

represented by the plane in the quaternary system \(Na\text{Sb}_3\text{O}_5\text{Sb}_2\text{O}_5\text{Sb}_5\text{NaF}\) bounded by the 6:1—3:4 and 6:1—3:7 joins of figures 3 and 4. However the single phase region in this system actually appears to contain more NaF than described by this general formula. Apparently some \(O_F\) 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

\[
[\text{Na}_{15}\text{F}_2]^{+14}[\text{Sb}^3_{7}\text{Sb}^5_{12-x}O_{38-2x}F_{2x}]
\]

which represents a line in the system shown by the join 3:1—3:8 in figure 4 and involves the evolution of one mole of gas (\(O_2\)) 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 10NaSbO3:Sb2O3:6NaF or

\[
[\text{Na}_{15}\text{F}_2][\text{Sb}^3_{7}\text{Sb}^5_{12-x}O_{38}F_{2x}] \equiv O_2.
\]

The single phase distorted cubic material on the binary join \(Na\text{Sb}_3\text{O}_5\text{Sb}_2\text{O}_5\text{NaF}\) appears to have a composition between 6:1 and 5:1 or approximately 11NaSbO3:2NaF or

\[
[\text{Na}_{14.14}\text{F}_2][\text{Sb}^3_{7}\text{Sb}^5_{12-x}O_{38.18}F_{0.18}] \equiv 0.0909 O_2.
\]

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

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