

TRANSFORMATION OF ILMENITE  $\text{KSbO}_3$  AND  $\text{NaSbO}_3$  TO CUBIC PHASE  
AND THERMAL STABILITY OF CUBIC PHASE

S. Shimada, K. Kodaira  
Department of Applied Chemistry, Faculty of Engineering  
Hokkaido University, Sapporo, 060 Japan

and

T. Matsushita  
Department of Electrical Engineering, Kumamoto  
Institute of Technology, 860 Japan

(Received September 11, 1986; Communicated by J. B. Goodenough)

ABSTRACT

Two metastable cubic phases of the  $\text{Pn}3$  and  $\text{Im}3$   $\text{KSbO}_3$  were synthesized by heating the ilmenite ( $\text{R}\bar{3}$ ) phase at  $1100^\circ\text{C}$  for 8 days and the  $\text{R}\bar{3}$  phase mixed with  $\text{KF}$  at  $1000^\circ\text{C}$ , respectively. The transformation of the  $\text{R}\bar{3}$  to the  $\text{Im}3$  phase in the presence of  $\text{KF}$  was found to begin at  $770^\circ\text{C}$  and finish at  $780^\circ\text{C}$  by high temperature X-ray diffraction, and the  $\text{Im}3$   $\text{KSbO}_3$  was assumed to be stabilized by  $\text{F}^-$  ions. The amount of  $\text{KF}$  present in the  $\text{Im}3$   $\text{KSbO}_3$  was semi-quantitatively determined to be 7 mol% by X-ray photoelectron spectroscopy. The  $\text{Im}3$   $\text{KSbO}_3$  was found to be stable up to  $1215^\circ\text{C}$ , change to the  $\text{Pn}3$  phase at  $1230^\circ\text{C}$  and finally to the  $\text{R}\bar{3}$  Phase at  $1230^\circ$ - $1250^\circ\text{C}$ . The  $\text{Im}3$   $\text{NaSbO}_3$  was also synthesized by heating the  $\text{R}\bar{3}$   $\text{KSbO}_3$  and  $\text{NaSbO}_3$  in the presence of  $\text{NaF}$  at  $1200^\circ\text{C}$  and at  $1300^\circ$ - $1340^\circ\text{C}$ , respectively.

MATERIALS INDEX: potassium antimony oxide, sodium antimony oxide

### Introduction

Although compounds of  $\text{MeSbO}_3$  having monovalent ions ( $\text{Me}=\text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Tl}, \text{Ag}$ ) have been synthesized(1),  $\text{CuSbO}_3$  containing monovalent copper ions has not been known yet. In course of attempts to synthesize  $\text{CuSbO}_3$  using  $\text{CuSb}_2\text{O}_6$  it was found that two kinds of new copper antimony oxide,  $\text{Cu}_4\text{SbO}_{4.5}$ (2) and  $\text{Cu}_9\text{Sb}_4\text{O}_{19}$ (3,4) are formed: the former is produced by decomposition of  $\text{CuSb}_2\text{O}_6$  at  $1050^\circ\text{C}$  in  $\text{N}_2$  and the latter by high pressure reaction of  $\text{CuSb}_2\text{O}_6$  and  $\text{CuO}$  at  $1000^\circ\text{C}$ - $1100^\circ\text{C}$  and 10 Kbar. Then, the flux method was tried to obtain single crystals of these new oxides from the system of  $\text{KF}/(\text{CuSb}_2\text{O}_6 + \text{CuO})$  at  $1000^\circ\text{C}$ , resulting in formation of a cubic phase of  $\text{KSbO}_3$ . Since the stable phase of  $\text{KSbO}_3$  has the ilmenite structure( $\text{R}\bar{3}$ ), the resulting metastable cubic phase is assumed to be due to reaction of  $\text{K}^+$  ions and  $\text{CuSb}_2\text{O}_6$  in the presence of  $\text{F}^-$  ions. This assumption encouraged us to carry out the subsequent heat treatment of the  $\text{R}\bar{3}$   $\text{KSbO}_3$  in the presence of  $\text{KF}$ , leading to formation of a body-centered cubic phase( $\text{Im}\bar{3}$ ).

It turned out, however, that Brower et al. had already obtained the  $\text{Im}\bar{3}$  phase of  $\text{KSbO}_3$  by heat treatment of the  $\text{R}\bar{3}$  phase in the media of  $\text{KF}$  or by flux evaporation in the system of  $\text{KF}/\text{Sb}_2\text{O}_3$ (5). They have noted that  $\text{F}^-$  ions should stabilize the  $\text{Im}\bar{3}$  phase. Goodenough et al. have independently prepared single crystals of the  $\text{Im}\bar{3}$   $\text{KSbO}_3$   $1/6\text{KF}$  and could explained its stabilization process by  $\text{F}^-$  ions which can be assigned in the  $\text{Im}\bar{3}$  structure by X-ray analysis(6). However, these reports were mainly concerned with synthesis of the  $\text{Im}\bar{3}$   $\text{KSbO}_3$  by flux evaporation method(5,6) and that of  $\text{Im}\bar{3}$   $\text{NaSbO}_3$  by ion exchange of  $\text{Im}\bar{3}$   $\text{KSbO}_3$  with  $\text{NaNO}_3$ (6), or with the ionic conductivity measurements of the  $\text{Im}\bar{3}$   $\text{NaSbO}_3$  or  $\text{KSbO}_3$ (7). Our present work is to investigate transformation of the  $\text{R}\bar{3}$   $\text{KSbO}_3$  or  $\text{NaSbO}_3$  to the  $\text{Im}\bar{3}$  phase in the presence of  $\text{KF}$  or  $\text{NaF}$  and practical synthesis of a cubic phase of  $\text{KSbO}_3$  and  $\text{NaSbO}_3$ , and to examine the thermal stability of the  $\text{Im}\bar{3}$   $\text{KSbO}_3$  in air.

### Experimental

The starting materials were  $\text{KHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Sb}_2\text{O}_3$ . A 2:1 mixture of  $\text{KHCO}_3$  and  $\text{Sb}_2\text{O}_3$  was heated at  $1000^\circ\text{C}$ , to obtain the  $\text{R}\bar{3}$   $\text{KSbO}_3$ . The  $\text{R}\bar{3}$   $\text{NaSbO}_3$  was obtained in a similar way. Heat treatment of the  $\text{R}\bar{3}$   $\text{KSbO}_3$  mixed with a 5-fold mol  $\text{KF}$ ,  $\text{KCl}$  or  $\text{KBr}$  was carried out at  $1000^\circ\text{C}$  for 20 hr. Powders of the  $\text{Im}\bar{3}$  phase produced with  $\text{KF}$  were washed with a hot distilled water until no precipitate of  $\text{BaF}_2$  was observed on adding a  $\text{BaCl}_2$  solution to a filtrate. The semi-quantitative determination of fluorine in the  $\text{Im}\bar{3}$  phase were performed by X-ray photoelectron spectroscopy(XPS). The transformation of the  $\text{R}\bar{3}$   $\text{KSbO}_3$  to the  $\text{Im}\bar{3}$  phase in the presence of  $\text{KF}$  was followed by high temperature X-ray diffraction using a heating rate of  $0.2^\circ\text{C}/\text{min}$ . This transformation was also done by X-ray diffraction(XRD) of the samples quenched after heating a mixture of  $\text{R}\bar{3}$ - $\text{KSbO}_3/\text{KF}$  at a rate of  $5^\circ\text{C}/\text{min}$ . The thermal stability of the  $\text{Im}\bar{3}$   $\text{KSbO}_3$  was examined

by heating to 1300°C in air at a rate of 5°C/min. Heat treatment of the R $\bar{3}$  NaSbO<sub>3</sub> in the media of NaF was carried out at 1290°-1360°C. The reaction of the R $\bar{3}$  KSbO<sub>3</sub> with NaF was also performed at 785°-1200°C for 2 hr, to produce the Im3 NaSbO<sub>3</sub>. For all heating experiments, a Pt crucible with a tightly covered lid was used to prevent the sample evaporating or reacting with a crucible.

### Results and discussion

#### Synthesis of the primitive and body-centered cubic phase of KSbO<sub>3</sub>

Table 1 shows the phases obtained by heating the R $\bar{3}$  KSbO<sub>3</sub> alone and in the presence of KF, KCl, or KBr at 1000°-1100°C.

TABLE 1

Heat treatment of R $\bar{3}$ -KSbO<sub>3</sub> without and with KCl, KBr, KF

Starting material	Temp. (°C)	Time	Resulting phases
R $\bar{3}$ -KSbO <sub>3</sub>	1000	8 days	R $\bar{3}$ -phase
R $\bar{3}$ -KSbO <sub>3</sub>	1100	8 days	Pn3-phase
R $\bar{3}$ -KSbO <sub>3</sub> +KCl	1000	20 hrs	R $\bar{3}$ -phase + minor unknown peaks
R $\bar{3}$ -KSbO <sub>3</sub> +KBr	1000	20 hrs	R $\bar{3}$ -phase
R $\bar{3}$ -KSbO <sub>3</sub> +KF	1000	20 hrs	Im3-KSbO <sub>3</sub>

Heating the R $\bar{3}$  phase alone at 1000°C for 8 days gives no change, but at 1100°C gives the primitive cubic phase (Pn3) which showed a 9.1% weight loss. The Pn3 phase was first reported by Spiegelberg (8) who obtained this phase by prolonged heating of the R $\bar{3}$  phase at 1000°C. Brower et al. assumed his synthesis to result from stabilization by impurities resulted from the porcelain crucibles and practically synthesized this phase at 1000°C by adding SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, or other small cations (5). Since our experiments used a Pt crucible, the formation of the Pn3 phase is not considered to be due to contamination of impurities from the crucibles, but rather due to evaporation of KSbO<sub>3</sub> component corresponding to 9.1 wt% loss. It is also seen that while KCl or KBr has no effect on formation of the Im3 phase, the presence of KF changes the R $\bar{3}$  to the Im3 phase. The lattice parameter of the Im3 phase thus produced was determined to be a = 9.58<sub>1</sub> Å, using (310) reflection.

#### Transformation of the R $\bar{3}$ KSbO<sub>3</sub> to the Im3 phase in the presence of KF

Figures 1 and 2 show X-ray diffraction patterns of the samples of the  $R\bar{3}$   $\text{KSbO}_3$  with KF in a heating state and of products quenched after heating the same samples, respectively.

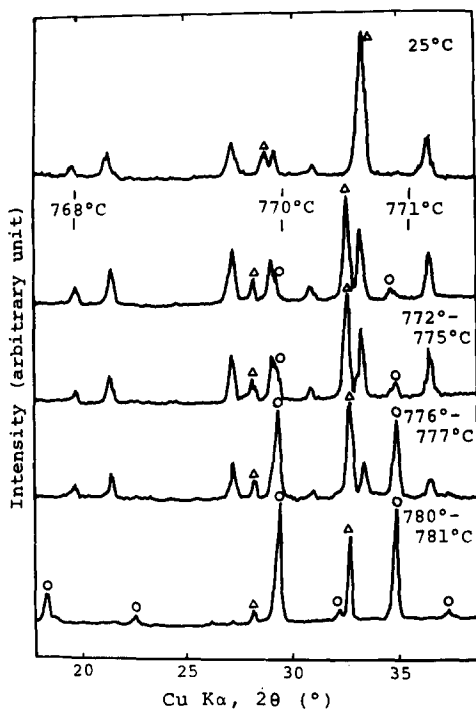


Fig. 1

High temperature X-ray diffraction patterns of the reaction of  $R\bar{3}$ - $\text{KSbO}_3$  with KF.

Heating rate: 0.2°C/min

○:  $\text{Im}3$ - $\text{KSbO}_3$

△: KF

unmarked peaks:  $R\bar{3}$ - $\text{KSbO}_3$

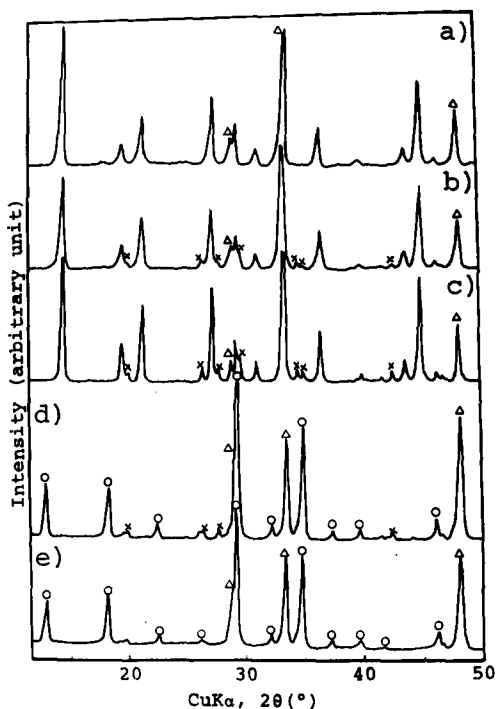


Fig. 2

X-ray diffraction patterns of the sample quenched after the reaction of  $R\bar{3}$ - $\text{KSbO}_3$  with KF.

a) 750°C, b) 760°C,

c) 770°C, d) 780°C,

e) 790°C,

Heating rate: 5°C/min

○:  $\text{Im}3$ - $\text{KSbO}_3$

△: KF

×: unknown peaks

unmarked peaks:  $R\bar{3}$ - $\text{KSbO}_3$

It is seen from Figure 1 that the  $R\bar{3}$  phase is maintained up to 770°C, decreasing with increasing temperatures to 779°C and disappearing at 780°C. Formation of the  $\text{Im}3$  phase is seen to be already evident at 770°C, as both diffraction lines of (310) ( $d=3.038$  Å) and (321) ( $d=2.571$  Å) are observed. These two lines are increasing to 780°C at which temperature the single phase of

the Im3 KSbO<sub>3</sub> is obtained. These results virtually agree with those for the quenched samples (Figure 2). Thus, the transformation of the R3 to the Im3 phase in the presence of KF is found to begin at 770°C and finish at 780°C. Some unknown lines are observed in the quenched samples, as shown in Figure 2, appearing at 760°C and disappearing at 790°C, but are not seen in a heating state. Thus, it is likely that amorphous intermediate is formed in a heating state and crystallizes when the sample is quenched. With respect to KF, the diffraction lines shift to lower angles with increasing temperatures due to the thermal expansion (Figure 1). Thus, it is speculated that expanding KF reacts with KSbO<sub>3</sub> at surfaces to form amorphous intermediate from about 760°C through which F<sup>-</sup> ions migrate into the R3 KSbO<sub>3</sub> that eventually changes to the Im3 structure. Figure 3 shows the K<sub>2p</sub> and F<sub>1s</sub> X-ray photoelectron spectra in KF and those in the Im3 KSbO<sub>3</sub> produced at 1000°C: F<sup>-</sup> ions are seen to be apparently present in the Im3 KSbO<sub>3</sub>. The semi-quantitative analysis of F<sup>-</sup> ions in KSbO<sub>3</sub> was determined to be about 7 mol% by comparing the spectra area ratio of the F<sub>1s</sub> to the K<sub>2p</sub> for KF with that for KSbO<sub>3</sub>. The relative difference in the binding energy between the K<sub>2p</sub> and F<sub>1s</sub> level for pure KF and that for KSbO<sub>3</sub> are almost the same, suggesting that the KF in KSbO<sub>3</sub> exist in an energy level similar to a pure KF. Thus, it seems that the F<sup>-</sup> ions are not substituted for oxygen ions in KSbO<sub>3</sub>, but exist at the tunnel intersections and stabilize the Im3 phase, as have been explained by Goodenough(7).

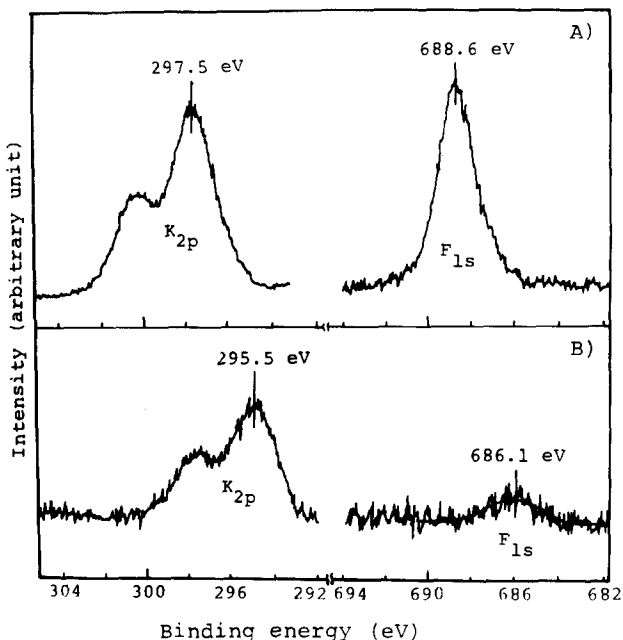


Fig. 3

K<sub>2p</sub> and F<sub>1s</sub> XPS spectra.  
A) KF, B) Im3-KSbO<sub>3</sub>

#### Thermal stability of the Im3 phase-KSbO<sub>3</sub> and synthesis of the Im3 NaSbO<sub>3</sub>

Table 2 shows the phases obtained after heating the Im3 KSbO<sub>3</sub> to 1300°C. It is seen that the Im3 KSbO<sub>3</sub> is stable up to

1215°C and changes to the Pn3 phase at 1230°C. This change must be attributed to evaporation of KF from the Im3 K<sub>2</sub>SbO<sub>3</sub>, since a 1-4 % weight loss was observed at 1215°-1250°C, comparable to that (2 wt%) calculated from the composition K<sub>2</sub>SbO<sub>3</sub> 0.07KF. It appears that a thermal stability of Im3 K<sub>2</sub>SbO<sub>3</sub> is higher than that of R $\bar{3}$  K<sub>2</sub>SbO<sub>3</sub> which evaporates to 9.1 wt% at 1100°C. Then, the Pn3 phase begins to transform to the R $\bar{3}$  phase roughly from 1260°C and completely changes to the R $\bar{3}$  phase at 1300°C.

TABLE 2

Heat treatment of Im3-K<sub>2</sub>SbO<sub>3</sub>

Temp. (°C)	Resulting phases
1150	Im3-phase
1200	Im3-phase
1215	Im3-phase + unknown peaks
1230	Pn3-phase + R $\bar{3}$ -phase (trace)
1240	Pn3-phase + R $\bar{3}$ -phase (trace)
1250	Pn3-phase
1260	Pn3-phase R $\bar{3}$ -phase
1300	R $\bar{3}$ -phase

The samples were heated to a fixed temperature at rate of 5°C/min.

The synthesis of the Im3 NaSbO<sub>3</sub> by heating the R $\bar{3}$  NaSbO<sub>3</sub> with NaF was attempted in a way similar to the case of the Im3 K<sub>2</sub>SbO<sub>3</sub> (Table 3). It is seen that the Im3 phase begins to form at 1300°C and increases at 1320°-1340°C, but the R $\bar{3}$  phase still remains. The Im3 phase thus formed is reversed to the R $\bar{3}$  from 1350°C. Although the single phase of the Im3 NaSbO<sub>3</sub> cannot be obtained by this method, the formation of this phase should be also due to stabilization by the F<sup>-</sup> ions. The lattice parameter of the Im3 phase of NaSbO<sub>3</sub> formed at 1340°C was determined to be a<sub>0</sub>=9.33<sub>9</sub> Å.

TABLE 3

Heat treatment of R $\bar{3}$ -NaSbO<sub>3</sub> with NaF

Starting material	Temp. (°C)	Resulting phases
R $\bar{3}$ -NaSbO <sub>3</sub> + NaF	1290	R $\bar{3}$ -phase
	1300	R $\bar{3}$ -phase Im3-phase
	1320	R $\bar{3}$ -phase, Im3-phase
	1340	R $\bar{3}$ -phase, Im3-phase
	1350	R $\bar{3}$ -phase + Im3-phase (trace)
	1360	R $\bar{3}$ -phase

The samples were heated to a fixed temperature at a rate of 5°C/min.

When the  $R\bar{3}$  KSbO<sub>3</sub> is heated with NaF or LiF, the Im3 phase of NaSbO<sub>3</sub> or LiSbO<sub>3</sub> is expected to form by stabilization of the Im3 phase by F<sup>-</sup> ions and by ion exchange of K<sup>+</sup> by Na<sup>+</sup> or Li<sup>+</sup>. Table 4 shows the phase obtained by heat treatment of the  $R\bar{3}$  KSbO<sub>3</sub> with LiF and NaF. LiF does not produce the Im3 phase but the Pncn phase of LiSbO<sub>3</sub>. NaF produces the Im3 phase at 950°-1200°C. The F<sup>-</sup> ions should cause the  $R\bar{3}$  phase to change to the Im3 phase in a way similar to the case of the system  $R\bar{3}$ -KSbO<sub>3</sub>/KF. X-ray diffraction showed that the Im3 phase forms a solid solution of (K,Na)SbO<sub>3</sub>. The lattice parameter of a mixed phase obtained at 950°, 1100° and 1200°C was determined to be a<sub>0</sub>=9.474, 9.418 and 9.339 Å, respectively. The composition of a mixed phase can be estimated by the interpolation of these lattice parameters between those of the pure Im3 KSbO<sub>3</sub> (a<sub>0</sub>=9.581 Å) and NaSbO<sub>3</sub> (a<sub>0</sub>=9.339 Å), as listed in Table 4. It is seen that the solid NaF already produces the Im3 phase at 950°C (the melting point of NaF : 998°C). An increase of temperature increases a tendency for Na<sup>+</sup> to exchange K<sup>+</sup> ions, and almost the pure Im3 phase of NaSbO<sub>3</sub> can be obtained at 1200°C.

TABLE 4

Reaction of  $R\bar{3}$ -KSbO<sub>3</sub> with LiF or NaF for 2 hrs

Starting material	Temp. (°C)	Resulting phases
KSbO <sub>3</sub> + LiF	785 - 950	Pncn-LiSbO <sub>3</sub>
KSbO <sub>3</sub> + NaF	950	Im3-K <sub>0.55</sub> Na <sub>0.45</sub> SbO <sub>3</sub>
	1100	Im3-K <sub>0.3</sub> Na <sub>0.7</sub> SbO <sub>3</sub>
	1200	Im3-NaSbO <sub>3</sub>

#### Acknowledgments

Financial support for this work was in part given by the Kurata Research Grant. We are indebted to Dr. H. Konno in our Department for XPS measurements and for helpful discussion.

#### References

1. J.B. Goodenough and J. A. Kafalas, *J. Solid State Chem.*, 6, 493(1973).
2. S. Shimada and K.J.D. Mackenzie, *Thermochimica Acta*, 56, 73(1982).
3. S. Shimada, K. Kodaira and T. Matsushita, *Chem. Lett.*, pp1875 (1983).
4. S. Shimada, K. Kodaira and T. Matsushita, *J. Solid State Chem.*, 59, 237(1985).
5. W.S. Brower, D.B. Minor, H.S. Parker, R.S. Roth and J.L. Waring, *Mat. Res. Bull.*, 9, 1045(1974).
6. H.Y-P. Hong, J.A. Kafalas and J.B. Goodenough, *J. Solid State Chem.*, 9, 345(1974).
7. J.B. Goodenough, H.Y-P. Hong and J.A. Kafalas, *Mat. Res. Bull.*, 11, 203(1976).
8. P. Spiegelberg, *Arkiv. f. Kemi. Min. Och Geol*, 14, 1(1940).