

## LETTER TO THE EDITOR

# On the Structure of $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$ : An Ordered Perovskite

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The structure of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  has been investigated by powder X-ray diffraction. The profile refinement shows that the structure is of the  $(\text{NH}_4)_3\text{FeF}_6$ -type, having a high degree of ordering between Tl and Sb, with the space group  $Fm\bar{3}m$  and lattice parameter  $a = 8.3809(1)$  Å. The oxygen atoms are shifted away from the Tl toward the Sb, creating an alternative arrangement of larger  $\text{TlO}_6$  and smaller  $\text{SbO}_6$  octahedra with the Tl–O and Sb–O bond distances being 2.21 and 1.98 Å, respectively. ©

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### 1. INTRODUCTION

In the Ba–Tl–Sb–O system a new perovskite,  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$ , has been reported (1). However, structure determination has shown that it is isostructural to  $\text{BaPbO}_3$  with random distribution of Tl and Sb on octahedral sites. As for many perovskites of the general formula  $A(B, B')\text{O}_3$ , an ordered arrangement of  $B$  and  $B'$  cations is most probable when large differences exist in either their charges or their ionic radii (2). Doubt is also cast on the structure of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  by a recent paper describing the structure of the ordered perovskite  $\text{BaBi}_{0.5}\text{Sb}_{0.5}\text{O}_3$  (3). Following the refinement procedure in Ref. (1), the space group  $Imma$  has been chosen since the neutron powder diffraction pattern showed no evidence for an ordering between Tl and Sb which have large difference in the neutron scattering lengths (8.79 and 5.64 fm, respectively). Nevertheless, care should be taken as well because of the high value of the neutron radiation scattering length of oxygen (5.81 fm). Any small shifts of oxygen atoms from their ideal positions may significantly change the intensity of superreflections, producing even nonobservable intensity in some particular cases.

On the other hand, X-ray diffraction is not sensitive to oxygen when there exist heavy metals. The ordering phenomena can be better observed if the difference in scattering power of  $B$  and  $B'$  cations is larger enough. There are currently a lot of interests in the perovskites containing the post transition metals. In particular, some of them exhibit

high temperature superconductivity (4–6). As detailed structural knowledge such as order–disorder is important to understand their different electronic behaviors as well as to evaluate their potential candidates for high- $T_c$  superconductivity, we have carried out a structural study of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  using powder X-ray diffraction. The results are reported in this letter.

### 2. EXPERIMENTAL

$\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  was prepared according to Ref. (1). A thoroughly ground stoichiometric mixture of  $\text{BaO}_2$ ,  $\text{Tl}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$  powders was sealed in a gold tube which was then sealed in an evacuated quartz tube. The mixture was slowly heated to 900°C, kept at that temperature for 24 hr, and finally cooled to room temperature over about 15 hr.

The X-ray diffraction data were collected on a Philips PW 1050 diffractometer, using  $\text{CuK}\alpha$  radiation, in the  $2\theta$  range between 10° and 110° in steps of 0.02° with a counting time of 10 s. The structure has been analyzed by Rietveld's method (7) using the GSAS program package (8). A Chebyshev polynomial with six terms has been used to fit the background. The profiles have been fitted using a Gaussian and a Lorentzian term.

### 3. STRUCTURAL STUDY

The X-ray diffraction pattern of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  is shown in Fig. 1. It consists of strong peaks characteristic of primitive cubic perovskite plus a few weak lines arising from the superlattice. No evidence for a distortion from the cubic symmetry is observed in the X-ray diffraction data. Only splitting due to  $K\alpha_1$  and  $K\alpha_2$  radiation is resolved in the  $2\theta$  range above about 70°. Thus the hole pattern can be indexed in a F-centered cubic cell with the cell edge  $a \approx 2a_p$ , where  $a_p$  is the cell lattice of the primitive cubic perovskite.

The structure refinements were carried out in the space group  $Fm\bar{3}m$  (No. 225), with the Tl and Sb atoms initially

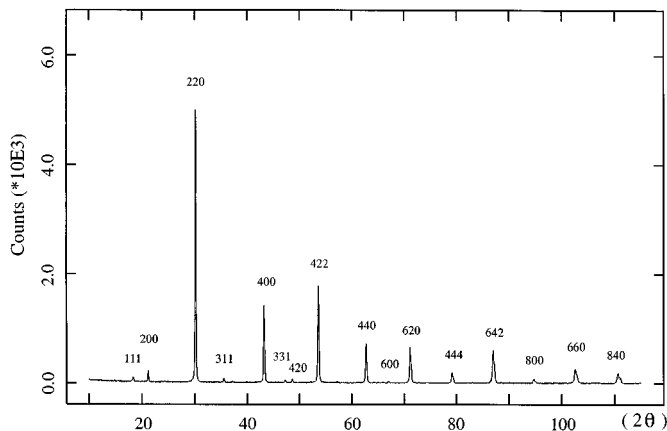


FIG. 1. X-ray diffraction pattern of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$ . The pattern is indexed with F-centered double cubic cell.

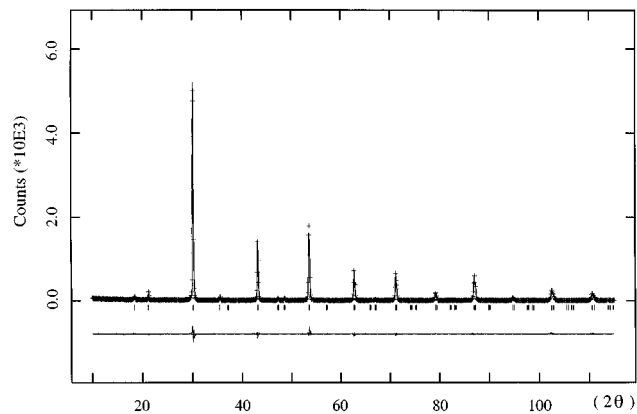


FIG. 2. Observed (+) and calculated (-) profiles of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$ . Tick marks indicate the positions of allowed reflections. A difference curve ( $I_{\text{obs.}} - I_{\text{cal.}}$ ) is shown at the bottom.

distributed in the positions 0,0,0 and 0.5,0.5,0.5, respectively, and the O atoms in  $x,0,0$  ( $x = 0.25$ ). On convergence the O atoms are shifted from  $x = 0.25$  to  $x = 0.268$ , which is consistent with the ordered structural model. However, an inspection of calculated profiles shows a systematic higher value for the superreflections, indicating partial disorder between Tl and Sb. The subsequent refinement of the occupation factor results in about 10% Tl in the Sb position and vice versa. With this model the agreement between the observed and the calculated intensities improved significantly.

The refined cell parameter is  $a = 8.3809(1) \text{ \AA}$ . The final agreement factors are  $R_p = 12.08\%$  and  $R_{wp} = 18.62\%$  with reduced  $\chi^2$  of 1.580. The refined structural and thermal parameters are given in Table 1. A plot of the observed and calculated profiles is shown in Fig. 2 and some selected metal–oxygen distances are listed in Table 2.

TABLE 1  
Refined Atomic Positions and Thermal Parameters of  
 $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$

Atoms	Site	$x$	$y$	$z$	$B (\text{\AA}^2)$	$n$
Ba	8c	0.25	0.25	0.25	0.82(3)	100
Tl(1)	4a	0	0	0	0.69(5)	90.4(8)
Tl(2) <sup>a</sup>	4b	0.5	0.5	0.5	0.66(5)	9.6(8)
Sb(1)	4b	0.5	0.5	0.5	0.66(5)	90.4(8)
Sb(2) <sup>a</sup>	4a	0	0	0	0.69(5)	9.6(8)
O	24e	0.264(1)	0	0	1.9(2)	100

$R_p = 12.08\%$ ,  $R_{wp} = 18.71$ ,  $\chi^2 = 1.580$

<sup>a</sup> About 10% Tl and Sb are disordered as indicated by Tl(2) and Sb(2).

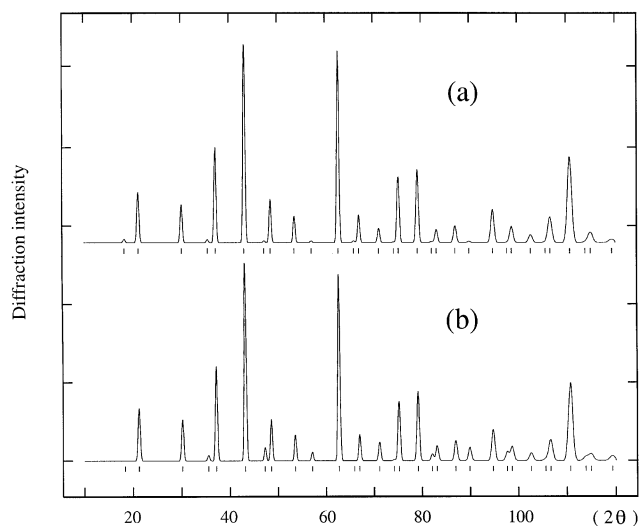
#### 4. DISCUSSION

The structure of  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$  is of simple face-centered cubic  $(\text{NH}_4)_3\text{FeF}_6$ -type, consisting of regular  $\text{TlO}_6$  and  $\text{SbO}_6$  octahedra in a 1:1 ordering scheme on alternate (111) planes. As compared to the ideal perovskite structure, the oxygen atoms are displaced along the pseudocubic  $[100]_p$  axis, corresponding to a shift of about 0.23  $\text{\AA}$  away from Tl toward Sb. The ordering between Tl and Sb is not complete. This may be due to a kinetic effect.

Subramanian *et al.* have reported a body-centered unit cell for  $\text{BaTl}_{0.5}\text{Sb}_{0.5}\text{O}_3$ , with cell parameters  $a \approx b \approx \sqrt{2}a_p$ ,  $c \approx 2a_p$  (1). They were unable to detect the doubling of the unit cell resulting from an ordering between Tl and Sb. This is not correct; the underlying cation ordering is clearly revealed by the (111) reflection. For double cubic perovskite of the formula  $A_2BB'O_6$  the intensity of the (111) reflection is proportional to the difference in scattering power of the  $B$  and  $B'$  atoms when all atoms are situated in the ideal positions. A disordered arrangement of  $B$  and  $B'$  should result in zero intensity. Although many perovskites  $A_2BB'O_6$  do not have strictly cubic structures due to the tilts of octahedra and/or small displacements of oxygen atoms from their ideal positions, the intensity of (111) reflection for disordered structure would remain extremely weak and is not practically observable in X-ray diffraction pattern since the X-ray scattering is dominated by the heavy atoms.

TABLE 2  
Selected Interatomic Distances ( $\text{\AA}$ )

Tl–O	2.21(1)	× 6
Sb–O	1.98(1)	× 6
Ba–O	2.9654(4)	× 12



**FIG. 3.** Calculated neutron powder diffraction profiles for  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$ . The calculation were made in the space group  $Fm\bar{3}m$ ,  $\lambda = 1.5418 \text{ \AA}$ , with Ba atoms located at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , Tl at  $(0, 0, 0)$ , Sb at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and O at  $(x, 0, 0)$  ( $x = 0.25$  in (a) and  $x = 0.264$  in (b)) positions, respectively.

Therefore, cation ordering in  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$  is clearly illustrated by the presence of substantial intensity of (111) reflection (Fig. 1).

The mistake made by Subramanian *et al.* may be due to the technique used (1). Although the neutron scattering length of Tl is significantly higher than that of Sb, the intensity of some superreflections due to their ordering could be canceled by a small shift of O atoms away from Tl toward Sb. This is further illustrated by the calculated profiles of  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$  for neutron diffraction shown in Fig. 3. It can be seen that the weak but detectable (111) reflection becomes nonobservable if the oxygen shift is  $\Delta x = 0.014$ . Thus, the failure to observe the cations ordering may well be accidental. It should be pointed out that the ordering phenomenon in  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$  does not seem to depend on the sample's history, since the X-ray diffraction pattern reported by Subramanian *et al.* is essentially the same as ours (1). Furthermore, the refined oxygen positions in Ref. (1) do not correspond to a rigid-octahedron tilt model (e.g., O-(Tl,Sb)-O  $83.1^\circ$ ) as observed for  $\text{BaPbO}_3$  (9–11).

In  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$ , the Ba are coordinated by 12 oxygens with the Ba–O distance of 2.97  $\text{\AA}$ . This value is in rough agreement with the distance calculated from the ionic radii (3.01  $\text{\AA}$ ) (12). The Tl–O and Sb–O distances are 2.21 and 1.98  $\text{\AA}$  respectively agreeing very well with the distances expected for  $\text{Tl}^{3+}$  and  $\text{Sb}^{5+}$  (12).

As for many perovskites containing two different octahedral cations, an ordered arrangement depends, primarily, on the difference in charge and bond lengths between them. In a series of perovskites of the formula  $\text{BaM}_{0.5}^{3+}\text{Nb}_{0.5}^{5+}\text{O}_3$ , Galasso *et al.* have found that the critical percentage difference in ionic radii for cations ordering is between 7 and 17% (13). Using this criterion,  $\text{BaTi}_{0.5}\text{Sb}_{0.5}\text{O}_3$  with the percentage difference of ionic radii of 32% should have an ordered structure as was observed. It is interesting to note that  $\text{BaIn}_{0.5}\text{Bi}_{0.5}\text{O}_3$  is reported to have a primitive cubic cell (14). Evidently, the lack of ordering between  $\text{In}^{3+}$  and  $\text{Bi}^{5+}$  is due to the too small difference in their ionic radii (5%).

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