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LETTER TO THE EDITOR

Synthesis and Characterization of Perovskite-Type $BaTl_{0.5}Sb_{0.5}O_3$ and $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$

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$BaTl_{0.5}Sb_{0.5}O_3$ has been synthesized for the first time and has a perovskite-related structure. Neutron diffraction studies show that this compound is isostructural to $BaPbO_3$. Solid solutions of the type $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ are also prepared for x values up to 0.5; electrical measurements showed that all the compounds are semiconducting.

Introduction

Metallic $BaPbO_3$ may be converted to a superconductor by substitution of either Bi (*1*) or Sb (*2*) for Pb. The former substitution resulted in superconductors with transition temperatures as high as 13 K, while the latter exhibited much lower transition temperatures (~3 K). Dilution of the s^1 cation Bi^{IV} or Sb^{IV} by the s^0 cation Pb^{IV} has been accomplished in the $BaBi_{1-x}Pb_xO_3$ and $BaPb_{1-x}Sb_xO_3$ systems, respectively. This dilution of an s^1 by an s^0 cation disrupts the charge density wave (CDW) which leads to delocalization, and the resulting metallic phase becomes superconducting. It is likely that the electron–electron attractive interaction which leads to the CDW is essentially the same as the electron–electron interaction which leads to superconductivity (*3*). The objective of this study was to synthesize new complex perovskite-type compounds with Sb (5 *s* cation) and Tl (6 *s* cation) at the B-site.

Experimental

Compounds were synthesized by heating stoichiometric quantities of BaO_2, Sb_2O_3, and Tl_2O_3 at 850–900°C for 12 hr in sealed gold tubes. Our attempts to synthesize these compounds in air at the above temperatures always resulted in formation of the perovskite phase with other impurity phases, possibly due to the volatilization of Tl at high temperatures. X-ray diffraction data were

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recorded using a SCINTAG diffractometer with Cu*Kα* radiation. Unit cell parameters were refined by least squares.

Neutron diffraction data on $BaTl_{0.5}Sb_{0.5}O_3$ were collected at the McMaster Nuclear Reactor at 295 K using 1.3915 Å neutrons from a (200) copper monochromator. The sample was contained in a thin-walled vanadium can. A description of the diffractometer including the position-sensitive detector and of the data handling procedures has been given elsewhere (*4*). No corrections for extinction or absorption were applied.

Results and Discussion

Characterization of $BaTl_{0.5}Sb_{0.5}O_3$

The X-ray diffraction pattern for $BaTl_{0.5}Sb_{0.5}O_3$ could be readily identified as indicating a perovskite-related phase. The powder diffraction pattern contained very few reflections, which could be indexed on the basis of a pseudo-cubic cell with a unit cell parameter of ~4.19 Å. Neutron diffraction refinement of $BaTl_{0.5}Sb_{0.5}O_3$ was undertaken in order to accurately determine the crystal structure and stoichiometry. The structure refinement was carried out in space group *Imma* (No. 74) in anticipation that $BaTl_{0.5}Sb_{0.5}O_3$ would be isostructural with $BaPbO_3$ (*5*). The mean effective ionic radius of Tl^{3+} and Sb^{5+} (sixfold coordination) is 0.74 Å while that of Pb^{4+} is 0.78 Å (*6*). Inspection of the powder neutron diffraction pattern provided no evidence for an ordering between Tl^{3+} and Sb^{5+} which would result in doubling of unit cell axis lengths. Such changes would be seen easily, as the scattering lengths of Tl (8.785 fm) and Sb (5.641 fm) differ significantly as do the ideal Sb–O and Tl–O bond distances (sum of ionic radii). In the refinement a mean scattering length of 7.21 fm was used for the $Tl_{0.5}Sb_{0.5}$ site, 5.25 fm for Ba, and 5.81 fm for oxygen (*7*).

TABLE I

FINAL ATOM POSITIONS, CELL PARAMETERS, AND *R*-FACTORS FOR $BaTl_{0.5}Sb_{0.5}O_3$

Atom	x	y	z	$B(Å^2)$
Ba(4e)	0	0	−0.0028(17)	0.50(5)
$Tl_{0.5}Sb_{0.5}$(4b)	0	0	$\frac{1}{2}$	0.14(4)
O1(4e)	0	$\frac{1}{4}$	0.4682(25)	0.61(30)
O2	$\frac{1}{4}$	0.0142(18)	$\frac{1}{4}$	1.18(18)

Note. Space group *Imma* (No. 74). Cell parameters (Å): a = 5.9136(33), b = 8.3969(40), and c = 5.9304(21). R_{wp} = 8.52, R_p = 6.47, R_N = 6.2, R_E = 2.55.

Table I specifies the refined atomic positions, isotropic temperature factors, occupancy factors, and agreement indices for the sample studied. The model used in the refinement assumed full occupancy of all sites. Attempts to refine site occupancy factors did not result in significantly improved agreement indices. The quality of the fit is illustrated in Fig. 1. Table II lists selected bond distances and angles for $BaTl_{0.5}Sb_{0.5}O_3$.

The results are similar to those of $BaPbO_3$ except that the two Tl,Sb–O distances differ by a greater amount, 0.011 Å, compared with 0.005 Å for $BaPbO_3$; also, the octahedral distortion is greater as indicated by the more acute bond angles. The average Tl,Sb–O distance, 2.101 Å, agrees reasonably well with the sum of the ionic radii, 2.09 Å, assuming twofold coordination for oxygen.

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $BaTl_{0.5}Sb_{0.5}O_3$ AT 295 K

Tl, Sb–O(1)	2.108(1)	O(1)–Tl,Sb–O(2)	83.1(2)
Tl, Sb–O(2)	2.0971(9)	O(1)–Tl,Sb–O(1)	180.0
Ba–O(1)	3.137(20)	O(2)–Tl,Sb–O(2)	89.65(5)
Ba–O(1)	3.793(20)	O(2)–Tl,Sb–O(2)	180.0
Ba–O(2)	3.043(9)	Tl,Sb–O(1)–Tl,Sb	169.7(8)
Ba–O(2)	2.890(9)		
O(1)–O(2)	2.789(6)		
O(1)–O(2)	3.147(6)		
O(2)–O(2)	2.975(2)		
O(2)–O(2)	2.957(2)		

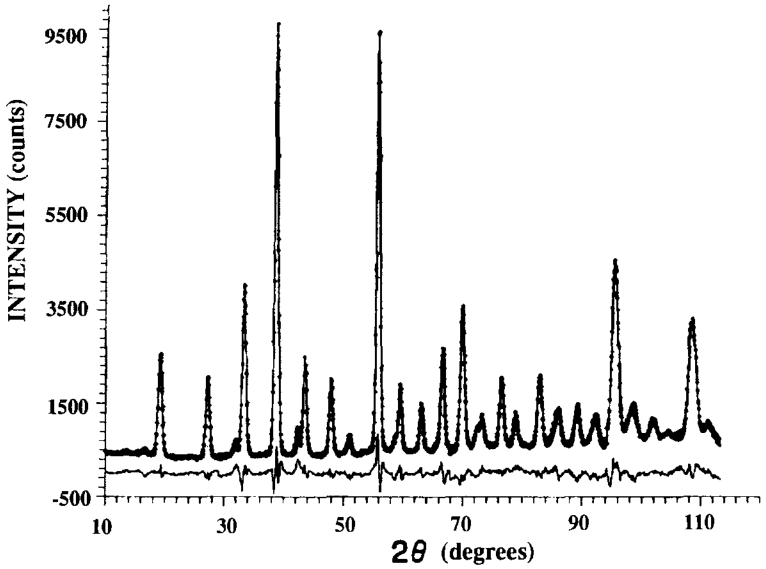

FIG. 1. Neutron diffraction profile fit and difference plot for $BaTl_{0.5}Sb_{0.5}O_3$.

Although $BaBiO_3$ (with Bi^{3+} and Bi^{5+} at the B-site) has a perovskite-type structure, our attempts to synthesize isostructural $BaSb^{IV}O_3$ by reacting BaO, Sb_2O_3, and Sb_2O_5 or BaO_2 and Sb_2O_3 in closed reaction vessels always resulted in the formation of $BaSb_2O_6$ and other impurity phases.

$BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ Solid Solution

Perovskite-related structures were also encountered in $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ phases for x values in the range 0.1 to 0.5. Annealing these samples at 400–500°C on a thermogravimetric balance did not show any weight gain, indicating that the oxygen stoichiometry assigned from the Tl to Sb ratio is reasonably correct. X-ray diffraction patterns revealed a typical distorted perovskite-type structure. In Fig. 2 the powder X-ray diffraction pattern of $BaTl_{0.9}Sb_{0.1}O_{2.6}$ is compared with $BaTl_{0.5}Sb_{0.5}O_3$. Examination of the X-ray powder diffraction pattern for $BaTl_{0.6}Sb_{0.4}O_{2.9}$ ($x = 0.1$) showed the compound to be isostructural with $BaPbO_3$ (Table III). However, X-ray diffraction pat-

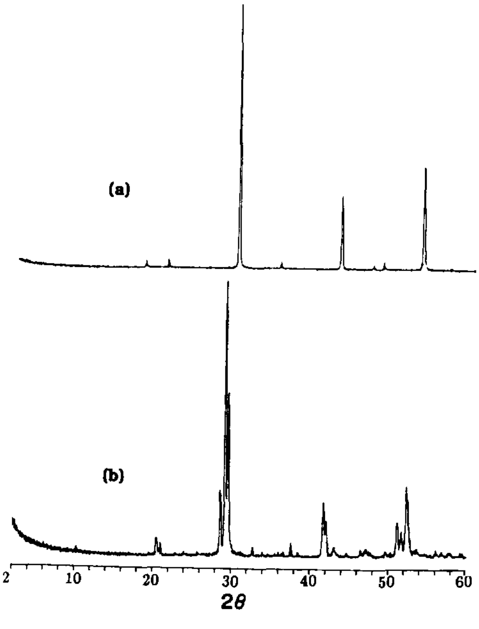

FIG. 2. X-ray diffraction patterns for (a) $BaTl_{0.5}Sb_{0.5}O_3$ and (b) $BaTl_{0.9}Sb_{0.1}O_{2.6}$.

TABLE III

X-RAY DATA FOR $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$

x	a(Å)	b(Å)	c(Å)	Space group
0.0	5.918(2)	8.392(2)	5.929(1)	*Imma*
0.1	5.940(1)	8.451(3)	5.970(1)	*Imma*
0.2	5.969(4)	17.086(5)	6.052(3)	*Pnma*
0.3	6.002(2)	17.164(5)	6.096(3)	*Pnma*
0.4	6.033(1)	17.208(4)	6.154(2)	*Pnma*
0.5	6.050(3)	17.235(6)	6.230(2)	*Pnma*

terns of $x = 0.2$ to 0.4 samples showed additional reflections; these could be satisfactorily indexed on a larger unit cell, namely *Pnma* of the brownmillerite-type. In fact, the end member ($x = 0.5$), $Ba_2Tl_2O_5$, is known and has a orthorhombic brownmillerite structure (*8*, *9*). The structure is composed of alternating layers of TlO_4 tetrahedra and TlO_6 octahedra stacked along the *b*-axis. The result is to double, approximately, the *b*-axis relative to the orthorhombic $BaPbO_3$-type perovskite structure (Table III). The increase in the pseudo-cubic cell edge with x is consistent with the larger size of Tl^{III} relative to Sb^{V}. The lattice parameters of $Ba_2Tl_2O_5$ are in good agreement with values reported for the polycrystalline sample (*9*) and slightly deviate from the values reported for single crystals (*8*). This discrepancy is probably due to a slight variation in oxygen stoichiometry between single crystals and polycrystalline materials. Our X-ray diffraction data for $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ ($x = 0.2$ to 0.4) did not show any evidence for the formation of $A_3M_3O_8$-type intermediate phases which might also be expected (*10*). Recent neutron diffraction studies on another closely related system, $BaPb_{1-x}Tl_xO_{3-x/2}$, also did not indicate the formation of the $A_2M_3O_8$-type structure during the phase transformation from $BaPbO_3$-type to brownmillerite-type $BaTlO_{2.5}$ (*11*).

The perovskite $BaPbO_3$ is apparently a semimetal (*12*). The isostructural $BaTl_{0.5}Sb_{0.5}O_3$ is an electrical insulator and, in this respect, it resembles $BaBiO_3$. However, the closely related solid solution compounds, $BaTl_{0.5}Pb_{0.5}O_3$ and $BaTl_{0.5}Bi_{0.5}O_3$, are good electrical conductors with semimetallic properties (*13*). This is probably due to the fact that the Sb–O bond (with 5*s* levels) is more ionic than Bi–O or Pb–O bonds. It is interesting to compare $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ compounds with $BaPb_{1-x}Sb_xO_3$ ($x = 0$ to 0.5) phases in which some members are superconducting (*2*). For $BaPb_{1-x}Sb_xO_3$ phases, Sb exists in +3 ($5s^2$) and +5 ($5s^0$) oxidation states, whereas in $BaTl_{0.5}Sb_{0.5}O_3$ as well as in $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ phases, the Sb exists only in the +5 oxidation state. Our attempts to synthesize $BaTl_{0.5-x}Sb_{0.5+x}O_3$ ($x > 0$) phases (mixture of Sb^{3+} and Sb^{5+} at the B-site), in anticipation of obtaining metallic conductivity, always yielded $BaTl_{0.5}Sb_{0.5}O_3$ with $BaSb_2O_6$ as an impurity. This leads us to the conclusion that the perovskite-type structure exists up to the composition $BaTl_{0.5}Sb_{0.5}O_3$.

In the $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ system, the electron count in the 6*s* band would not be expected to change as a function of x. However, it is the overlap of the 6*s* and oxygen 2*p* bands which causes the metallic properties. We might well expect that this overlap will change as a function of x, especially in view of the increasing Tl content and oxygen deficiency with increasing x. Although there is a slight increase in the conductivity with increasing x, the compounds remained semiconducting, which indicates that the thallium 6*s* and oxygen 2*p* bands have indeed separated. It is worthwhile to note that in the case of Tl_2O_3, the overlapping of the Tl 6*s* with the O 2*p* bands gives rise to metallic properties, whereas they are well separated in the oxygen-deficient perovskite-related $Ba_2Tl_2O_5$, which is a semiconductor.

Conclusions

$BaTl_{0.5}Sb_{0.5}O_3$ has been synthesized for the first time. Neutron diffraction studies show that the compound is isostructural with $BaPbO_3$. The perovskite-related solid solution phases of the type $BaTl_{0.5+x}Sb_{0.5-x}O_{3-x}$ could be synthesized for x values in the range 0 to 0.5; all these compounds are electrically semiconducting. Attempts to synthesize antimony-rich phases of the type $BaTl_{0.5-x}Sb_{0.5+x}O_3$ ($x > 0$), with the aim of observing metallic properties by placing Sb^{3+} and Sb^{5+} at the B-site, were not successful.

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