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# LETTERS TO THE EDITOR

## Synthesis of $BaTlO_{2.5}$ with Oxygen-Deficient Perovskite Structure

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A new oxygen-deficient perovskite $BaTlO_{2.5}$ was successfully prepared by a solid-state reaction technique. Orthorhombic unit cell dimensions refined from a powder diffraction pattern are $a = 0.6257 \pm 0.0001$, $b = 0.6038 \pm 0.0001$, and $c = 1.7232 \pm 0.0003$ nm. The $BaTlO_{2.5}$ was found to be a semiconductor.

### Introduction

Thallium ion can take a monovalent state ($6s^2$) or a trivalent state ($5d^{10}$). To date, a compound containing a thallium ion with a higher valence, for example, tetravalent thallium ion ($5d^9$), has not been reported. Lead and bismuth, which are neighbor elements of thallium in the periodic table, can form a perovskite with barium ion as an *A*-site partner. We are interested in the structure and properties of the perovskite which is composed of barium ion as *A*-site ion and thallium ion as *B*-site ion. A matter of primary concern is whether the ionic valence of thallium in the *B*-site is +3 or +4 in the perovskite. In the former case, we obtain $Ba^{2+}Tl^{3+}O_{2.5}$. In this case, oxygen vacancies are introduced in the structure in order to compensate the lack of positive charge in a manner similar to $Ca_2Fe_2O_5$ (*1*) and $Sr_2Fe_2O_5$ (*2*). The $Ba^{2+}Tl^{3+}O_{2.5}$ is expected to be an insulator. In the latter case, we obtain $Ba^{2+}Tl^{4+}O_3$.

In order to elucidate the question whether the ionic valence of thallium is trivalent or tetravalent in the perovskite with barium as an *A*-site partner, we synthesized a new perovskite $BaTlO_{3-\delta}$, discussed the structure by the powder X-ray diffraction method, and investigated the electrical resistivity.

### Experimental

$BaTlO_{3-\delta}$ was synthesized by solid-state reaction from a stoichiometric mixture of $Tl_2O_3$ of 99.99% purity and reagent-grade $BaO_2$. In advance of the experiment, the metal content in these reagents was determined by gravimetry. The powders were thoroughly mixed and ground in an agate mortar and pestle. After grinding, the mixture was pressed into a pellet and wrapped in gold foil. To prevent a change in composition of the sample due to vaporization of thallium oxide at high temperatures, the edges of the gold foil were caulked. The

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sample was heated at 923 K for 20 hr in 1 atmosphere of oxygen. The reacted sample was ground, pressed into a pellet, wrapped in a gold foil, and heated at 1000 K for 20 hr. This process was repeated again. Black samples were obtained.

The structure of the sample was characterized by the X-ray diffraction technique. The X-ray diffraction patterns were recorded at room temperature using a Rigaku horizontal $\theta$-$\theta$ scanning diffractometer with a curved graphite monochrometer. The experimental conditions were: Cu target X-ray tube, 40 kV and 25 mA. Diffraction peaks were recorded in a $2\theta$ range from 120 to 5°. Silicon powder was used as an internal standard to determine the lattice constants. To avoid possible errors caused by overlaps, nonoverlapping peaks were used to determine the unit cell dimensions.

## Results and Discussions

The X-ray diffraction pattern of $BaTlO_{3-\delta}$ is plotted in Fig. 1. The X-ray diffraction pattern shows a typical distorted perovskite structure. Additional diffraction peaks, for example, the peak at $2\theta = 10.3°$, due to a superlattice were also observed. These additional peaks are expected to originate from a superstructure caused by a regular shift of ions from their normal lattice sites or through a regular arrangement of oxygen vacancies. Almost all the peaks were indexed with unit cell dimensions of $a = 0.6257 \pm 0.0001$ nm, $b = 0.6038 \pm 0.0001$ nm, and $c = 1.7232 \pm 0.0003$ nm. X-ray diffraction data of the $BaTlO_{3-\delta}$ is given in Table I. These cell dimensions are related to a monoclinic perovskite cell with the dimensions of $a_p = b_p = 0.4347 \pm 0.0001$, $c_p = 0.4308 \pm 0.0001$ nm, and $\gamma = 87.96°$. These two cells are related by $a = 2a_p \cos(\gamma/2)$, $b = 2a_p \sin(\gamma/2)$, and $c = 4c_p$. Some of the peaks could not be indexed in the orthorhombic cell. These peaks were found to be due to $BaCO_3$ and to another phase composed of Ba and Tl oxides. In order to identify this phase, samples with nominal compositions Ba : Tl = 2 : 1 and 1 : 2 were prepared and their X-ray diffraction patterns were recorded. The result re-

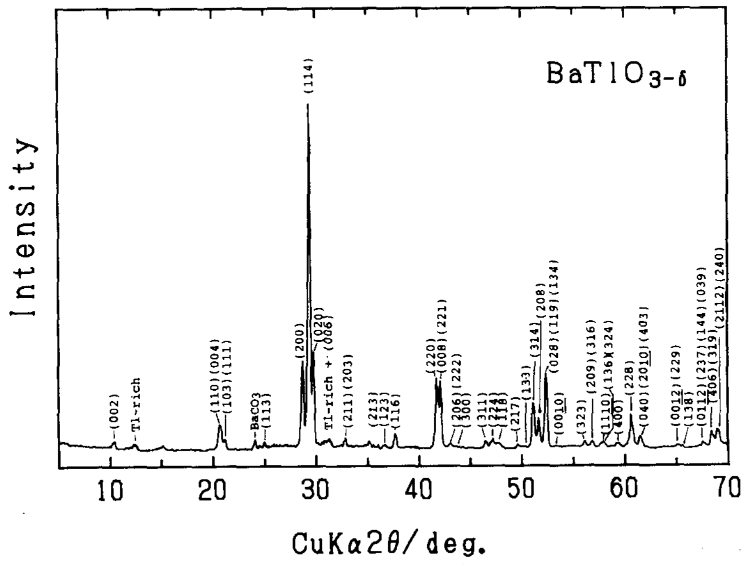

FIG. 1. X-ray diffraction pattern of $BaTlO_{3-\delta}$: "Tl-rich" represents thallium-rich phase composed of thallium and barium oxides.

TABLE I

X-RAY DIFFRACTION DATA OF $BaTlO_{3-\delta}$

| *hkl* | $d_{obs.}$ (nm) | $d_{cal.}$ (nm) | *I* |
|---|---|---|---|
| 0 0 2 | 0.861 | 0.8616 | 2 |
| 1 1 0 | 0.4349 | 0.4345 | 6 |
| 0 0 4 | 0.4312 | 0.4308 | 5 |
| 1 0 3 | 0.4235 | 0.4231 | 3 |
| 1 1 1 | | 0.4213 | |
| 1 1 3 | 0.3460 | 0.3465 | 1 |
| 2 0 0 | 0.3133 | 0.3128 | 24 |
| 1 1 4 | 0.3061 | 0.3059 | 100 |
| 0 2 0 | 0.3022 | 0.3019 | 27 |
| 2 0 3 | 0.2744 | 0.2747 | 2 |
| 2 1 1 | | 0.2742 | |
| 2 1 3 | 0.2503 | 0.2501 | <1 |
| 1 2 3 | 0.2458 | 0.2457 | 1 |
| 1 1 6 | 0.2396 | 0.2396 | 4 |
| 2 2 0 | 0.2174 | 0.2172 | 20 |
| 2 2 1 | 0.2154 | 0.2155 | 18 |
| 0 0 8 | | 0.2154 | |
| 2 0 6 | 0.2114 | 0.2116 | <1 |
| 2 2 2 | 0.2109 | 0.2106 | 1 |
| 3 0 0 | 0.2081 | 0.2086 | <1 |
| 3 1 1 | 0.1956 | 0.1959 | 2 |
| 2 2 4 | 0.1941 | 0.1937 | 1 |
| 1 1 8 | 0.1930 | 0.1930 | 2 |
| 1 3 1 | 0.1903 | 0.1904 | 1 |
| 2 1 7 | 0.1843 | 0.1842 | 1 |
| 1 3 3 | 0.1818 | 0.1818 | <1 |
| 3 1 4 | 0.1793 | 0.1793 | 13 |
| 2 0 8 | 0.1774 | 0.1774 | 10 |
| 0 2 8 | 0.1752 | 0.1752 | 20 |
| 1 1 9 | | 0.1752 | |
| 1 3 4 | | 0.1751 | |
| 0 0 10 | 0.1723 | 0.1723 | <1 |
| 3 2 1 | 0.1708 | 0.1707 | <1 |
| 2 3 1 | 0.1685 | 0.1684 | <1 |
| 3 2 3 | 0.1644 | 0.1644 | 2 |
| 2 0 9 | 0.1632 | 0.1633 | 1 |
| 3 1 6 | 0.1625 | 0.1625 | 1 |
| 1 1 10 | 0.1602 | 0.1602 | 1 |
| 3 2 4 | 0.1594 | 0.1594 | 2 |
| 1 3 6 | | 0.1594 | |
| 4 0 0 | 0.1564 | 0.1564 | 2 |
| 2 2 8 | 0.1530 | 0.1530 | 9 |
| 2 0 10 | 0.1509 | 0.1509 | 3 |
| 0 4 0 | | 0.1509 | |
| 4 0 3 | | 0.1509 | |
| 2 2 9 | 0.1436 | 0.1436 | 1 |
| 0 0 12 | | 0.1436 | |
| 1 3 8 | 0.1432 | 0.1432 | <1 |
| 4 1 4 | 0.1428 | 0.1429 | <1 |
| 1 1 12 | 0.1395 | 0.1397 | <1 |
| 2 3 7 | | 0.1395 | |
| 1 4 4 | 0.1389 | 0.1389 | 1 |
| 4 2 0 | | 0.1389 | |
| 4 0 6 | 0.1373 | 0.1374 | <1 |
| 3 1 9 | | 0.1373 | |
| 2 1 12 | 0.1363 | 0.1363 | 3 |
| 2 4 0 | 0.1360 | 0.1359 | 2 |
| 1 4 5 | 0.1351 | 0.1350 | <1 |
| 2 2 10 | | 0.1350 | |
| 4 2 3 | | 0.1350 | <1 |

vealed that there are at least three phases composed of barium and thallium oxides in the $BaO-Tl_2O_3$ system. X-ray diffraction peaks at $2\theta = 12.3$ and 31.1° are due to a Tl-rich phase whose Tl composition is lower than Ba:Tl = 1:1.

In order to determine the oxygen content $3 - \delta$ in $BaTlO_{3-\delta}$, weight changes of the sample pellets were measured after a series of heat-treatment procedures. An averaged value of $3 - \delta$ was calculated to be $2.53 \pm 0.02$. This result corresponds to a trivalent state of thallium ions in $BaTlO_{3-\delta}$.

A perovskite parameter $a$, defined by the cubic root of the cell volume of the perovskite unit, for the perovskite-type compounds $BaBO_3$ ($B$ = Mo, Hf, Sn, Zr, Pb, Pr, Ce (*3*), and Th (*4*)) was plotted against their ionic radii of $B^{4+}$ at the six coordination site (*5*) (Fig. 2). Since a linear relationship holds between the ionic radii and the perovskite parameter, we can evaluate the perovskite parameter of an unknown compound using the known ionic radii of $B^{4+}$ at the six coordination site or vice versa. However, the ionic radius of thallium is available only for the monovalent and trivalent state (*6*). The ionic radius of thallium ion in $BaTlO_{3-\delta}$ is estimated to be 0.0825 nm from the linear relationship, using as observed perovskite parameter of $BaTlO_{3-\delta}$ the value 0.4333 nm. This value is smaller than the radius, 0.0885 nm, of the $Tl^{3+}$ ion at the six coordination site. On the

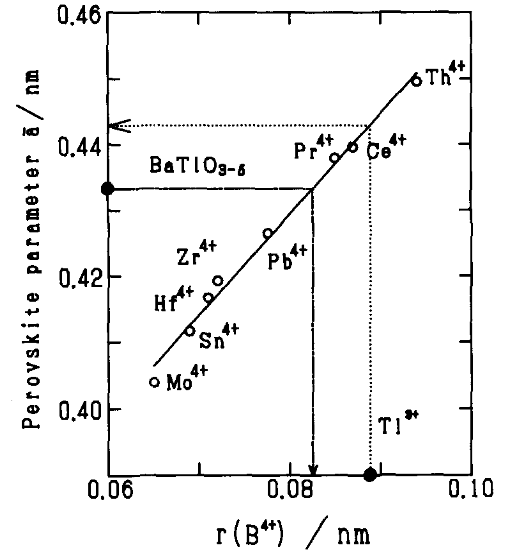

FIG. 2. Perovskite parameter versus Shannon radius of $B^{4+}$ ions at the six coordination site.

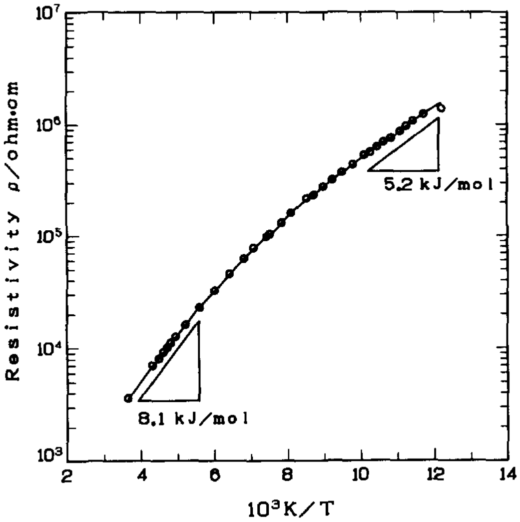

FIG. 3. Temperature dependence of electrical resistivity of $BaTlO_{3-\delta}$.

other hand, the perovskite parameter is estimated to be 0.443 nm from the linear relation using an ionic radius of 0.0885 nm for $Tl^{3+}$. This value is greater than the observed value of 0.4333 nm. This apparent discrepancy could be due to a contraction of the ionic distance between thallium and oxygen ions caused by a stronger coulombic attraction through the existence of tetravalent thallium ions or a formation of five- or four-coordinated trivalent thallium ions which originate from the formation of oxygen vacancies. The value of 2.53 for $3 - \delta$ in $BaTlO_{3-\delta}$ supports the latter case. The quadruple period of the perovskite unit along the *c*-axis may be explained by the alternate sheets of octahedra and tetrahedra observed in $Ca_2Fe_2O_5$ (*1*) or $Sr_2Fe_2O_5$ (*2*) with the brownmillerite structure.

Figure 3 shows the electrical resistivity of $BaTlO_{3-\delta}$ measured by an ac 2-probe method using 1 kHz. Semiconducting behavior was observed. The electrical resistivity of $BaTlO_{3-\delta}$ is comparable to that of $BaBiO_3$ (*6*). As the temperature increased, the activation energy increases as shown in Fig. 3.

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