

## Study on the crystal and magnetic structures of $\text{SrTbO}_3$ and $\text{BaTbO}_3$ by powder neutron diffraction

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 11703

(<http://iopscience.iop.org/0953-8984/10/50/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 18:13

Please note that [terms and conditions apply](#).

# Study on the crystal and magnetic structures of SrTbO<sub>3</sub> and BaTbO<sub>3</sub> by powder neutron diffraction

Keitaro Tezuka<sup>†</sup>, Yukio Hinatsu<sup>†</sup>, Yutaka Shimojo<sup>‡</sup> and Yukio Morii<sup>‡</sup>

<sup>†</sup> Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>‡</sup> Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-1195, Japan

Received 1 August 1998

**Abstract.** We prepared oxygen stoichiometric SrTbO<sub>3</sub> and BaTbO<sub>3</sub> in which tetravalent terbium ions are stabilized at the B sites of the perovskite ABO<sub>3</sub>. Their crystal structures at room temperature and at 10 K were determined from both x-ray and neutron diffraction measurements. Both SrTbO<sub>3</sub> and BaTbO<sub>3</sub> have an orthorhombic perovskite-type structure with space group *Pnma* (No 62).

Magnetic susceptibility measurements have been performed for both the compounds in the temperature range between 4.5 K and room temperature. Both the compounds show the antiferromagnetic transition at ~33 K. The temperature-dependent magnetic susceptibilities were measured with zero-field-cooled (ZFC) and field-cooled (FC) conditions at an applied field of 1000 G. A dramatic difference between ZFC and FC was observed below the Néel temperatures for both the compounds, which shows the onset of a ferromagnetic moment below those temperatures.

To determine the magnetic structures at the antiferromagnetic state, powder neutron diffraction measurements have been performed at 10 K and room temperature. Both the compounds have the *G*-type magnetic structure in which terbium atoms are antiferromagnetically coupled with the six neighbouring terbium atoms.

## 1. Introduction

It is well known that the most stable oxidation state of rare-earth elements is trivalent. In addition to this state, cerium, praseodymium and terbium have the tetravalent state. As a result, these elements form a series of oxide phases between R<sub>2</sub>O<sub>3</sub> (trivalent) and RO<sub>2</sub> (tetravalent) (R: rare-earth elements). Although cerium dioxide CeO<sub>2</sub> is formed in a flow of oxygen gas atmosphere at high temperatures, the preparative conditions of praseodymium dioxide PrO<sub>2</sub> and terbium dioxide TbO<sub>2</sub> are very severe [1, 2].

It is well known that perovskite-type oxides ABO<sub>3</sub>, where A is a divalent ion (e.g., Sr, Ba), accommodate tetravalent metal ions at the B sites of the crystals. Although many of the transition elements at the B site form perfect or nearly perfect cubic perovskite structures, the rare-earth ions are too large to stabilize the structure, and instead develop distorted perovskite structures. The distortion may be rhombohedral (BaTbO<sub>3</sub>) and orthorhombic (SrTbO<sub>3</sub>, SrPrO<sub>3</sub>, BaPrO<sub>3</sub>, SrCeO<sub>3</sub>, BaCeO<sub>3</sub>) [3–6].

As for magnetic properties, these perovskites show antiferromagnetic ordering at low temperatures. In the ABO<sub>3</sub> perovskite structure, the B site ions are octahedrally coordinated by six oxygen ions and these oxygen polyhedra are three-dimensionally aligned, i.e., a

linear or almost linear B–O–B alignment is found in this structure. Generally, 4f electrons characterizing the magnetic properties of lanthanide compounds are effectively shielded by the outer  $5s^25p^6$  electron shells; the magnetic interactions between 4f electrons are very weak. For the perovskite-type structure containing lanthanide ions at the B sites of the crystal, strong magnetic interactions between lanthanide ions may be operated through oxygen ions intervening between them.

Magnetic properties for the perovskite-type complex oxides containing tetravalent praseodymium ions have been studied some in detail [5, 7–10], those for the compounds containing tetravalent terbium ions have not been investigated yet and even the crystal structure of  $\text{SrTbO}_3$  has not been determined yet.

In this study, we have paid attention to the Tb-based compounds  $\text{SrTbO}_3$  and  $\text{BaTbO}_3$  and will report their crystal structures, magnetic structures and related magnetic properties through powder x-ray and neutron diffraction measurements and magnetic susceptibility measurements.

## 2. Experiment

Two specimens  $\text{SrTbO}_3$  and  $\text{BaTbO}_3$  were prepared by the standard solid state reaction. The starting materials were  $\text{SrCO}_3$  or  $\text{BaCO}_3$ , and  $\text{Tb}_4\text{O}_7$ . They were ground in an agate mortar, pressed into pellets and fired in a flow of oxygen gas at 1573 K for 24 hours twice. Since these compounds lose a few oxygen atoms at high temperatures and are reoxidized to the stoichiometric composition during cooling, they were reground and fired in a flow of oxygen gas at 1273 K for 48 hours and cooled to room temperature in the furnace.

Powder x-ray diffraction patterns were measured with Cu  $K\alpha$  radiation on a RINT2000 diffractometer (Rigaku, Japan). The structures were refined with the Rietveld analysis method, using the program Rietan [11].

Powder neutron diffraction patterns were measured with a high resolution powder diffractometer (HRPD) in the JRR-3M reactor (Japanese Atomic Energy Research Institute), with a Ge(331) monochromator ( $\lambda = 1.823 \text{ \AA}$ ). The collimators used were  $6'-20'-6'$ , which were placed before and after the monochromator, and between the sample and each detector. The set of 64 detectors and collimators, which were placed every 2.5 degrees, rotate around the sample. The measurements were made at 10 K and room temperature. Crystal and magnetic structures were also determined by the Rietveld technique.

DC magnetic susceptibilities were measured with a SQUID (Quantum Design, MPMS model) after zero field cooling (ZFC) and field cooling (FC) processes in the temperature range 4.5–300 K. The external magnetic field applied was 1000 G. The remnant magnetization measurements were also performed. The samples were cooled to 4.5 K in a zero field. The magnetic field was applied up to 50 000 G and then reduced to zero, and the magnetization measurements were performed in the temperature range from 4.5 K to room temperature. The field dependence of the magnetization was measured at 10 K by changing the magnetic field strength in the range between –50 000 and 50 000 G.

## 3. Results and discussion

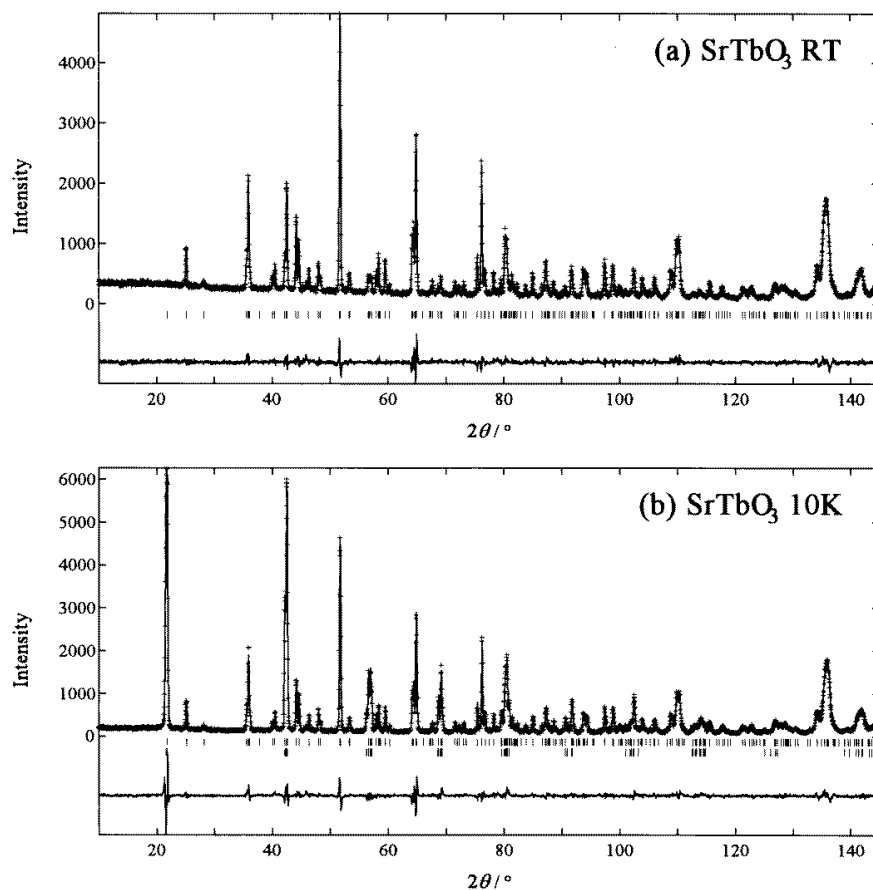
### 3.1. Crystal structure

The  $\text{SrTbO}_3$  and  $\text{BaTbO}_3$  prepared in this study crystallize in single phases. Their x-ray diffraction profiles at room temperature were indexed both with an orthorhombic unit cell, space group  $Pnma$  (No 62).

**Table 1.** Crystal and magnetic structure data for SrTbO<sub>3</sub> and BaTbO<sub>3</sub> from powder neutron diffraction profiles.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
SrTbO <sub>3</sub> , room temperature, space group <i>Pnma</i> (No. 62)					
<i>a</i> = 5.9618(2) Å <i>b</i> = 8.3506(3) Å <i>c</i> = 5.8734(2) Å					
<i>R</i> <sub>wp</sub> = 8.55 <i>R</i> <sub>I</sub> = 2.45 <i>R</i> <sub>F</sub> = 1.66					
Sr	4(c)	−0.040(9)	0.25	0.001(2)	0.20(16)
Tb	4(b)	0.0	0.0	0.5	0.08(12)
O(1)	4(c)	0.528(1)	0.25	−0.090(2)	0.25(18)
O(2)	8(d)	0.208(1)	0.048(1)	0.207(1)	0.14(14)
SrTbO <sub>3</sub> , 10 K, space group <i>Pnma</i> (No. 62)					
<i>a</i> = 5.9621(1) Å <i>b</i> = 8.3478(2) Å <i>c</i> = 5.8715(1) Å					
<i>R</i> <sub>wp</sub> = 10.14 <i>R</i> <sub>I</sub> = 2.04 <i>R</i> <sub>F</sub> = 1.08					
magnetic moment: 6.76(4) μ <sub>B</sub>					
direction of moment: [101] of orthorhombic unit cell					
Sr	4(c)	0.041(1)	0.25	−0.010(2)	0.31(12)
Tb	4(b)	0.0	0.0	0.5	0.03(9)
O(1)	4(c)	0.472(1)	0.25	0.091(1)	0.39(15)
O(2)	8(d)	0.208(1)	−0.048(1)	0.208(1)	0.35(11)
BaTbO <sub>3</sub> , room temperature, space group <i>Pnma</i> (No. 62)					
<i>a</i> = 6.0543(2) Å <i>b</i> = 8.5465(3) Å <i>c</i> = 6.0712(2) Å					
<i>R</i> <sub>wp</sub> = 9.94 <i>R</i> <sub>I</sub> = 3.20 <i>R</i> <sub>F</sub> = 3.67					
Ba	4(c)	0.000(9)	0.25	−0.001(4)	0.89(27)
Tb	4(b)	0.0	0.0	0.5	0.47(23)
O(1)	4(c)	0.507(9)	0.25	0.043(3)	1.48(48)
O(2)	8(d)	0.245(5)	−0.023(1)	0.246(6)	1.12(30)
BaTbO <sub>3</sub> , 10 K, space group <i>Pnma</i> (No. 62)					
<i>a</i> = 6.0447(1) Å <i>b</i> = 8.5260(1) Å <i>c</i> = 6.0747(1) Å					
<i>R</i> <sub>wp</sub> = 10.15 <i>R</i> <sub>I</sub> = 1.70 <i>R</i> <sub>F</sub> = 1.33					
magnetic moment: 6.5 μ <sub>B</sub>					
direction of moment: [100] of orthorhombic unit cell					
Ba	4(c)	0.004(6)	0.25	−0.001(1)	0.01(10)
Tb	4(b)	0.0	0.0	0.5	0.07(7)
O(1)	4(c)	0.501(5)	0.25	0.052(1)	0.49(12)
O(2)	8(d)	0.245(2)	−0.029(1)	0.247(3)	0.29(8)

Neutron diffraction measurements were also performed for the SrTbO<sub>3</sub> and BaTbO<sub>3</sub> both at room temperature and at 10 K, to determine their precise crystal structures and magnetic structures at low temperature. Figure 1 shows the neutron diffraction profiles for SrTbO<sub>3</sub> and BaTbO<sub>3</sub>. The results were analysed with the Rietveld method, and they are shown in table 1. The result on the SrTbO<sub>3</sub> by the neutron diffraction measurements at room temperature agrees well with that by the x-ray diffraction measurements, i.e., it has an orthorhombic perovskite with space group *Pnma*. Figure 2 shows the crystal structure of SrTbO<sub>3</sub> at room temperature. The crystal structure of SrTbO<sub>3</sub> at 10 K has the same as that at room temperature, and the cell volume at 10 K is smaller than that at room temperature. In the previous work for BaTbO<sub>3</sub> at both room temperature and 10 K, the nuclear Bragg peaks were indexed with a rhombohedral unit cell, space group *R* $\bar{3}$ *c* (No 167) [3, 10]. The magnetic peaks were analysed and it had the *G*-type magnetic structure [10]. In this study, we have shown that BaTbO<sub>3</sub> has an orthorhombic symmetry at both room temperature and 10 K, from both the x-ray and the neutron diffraction measurements.



**Figure 1.** Powder neutron diffraction pattern fitting for SrTbO<sub>3</sub> and BaTbO<sub>3</sub>. The calculated and observed patterns are shown on the top solid line and the markers above the peaks, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities: (a) SrTbO<sub>3</sub> at room temperature. (b) SrTbO<sub>3</sub> at 10 K. The second vertical marks show the positions calculated for magnetic reflections. (c) BaTbO<sub>3</sub> at room temperature. In this case the wavelength of incident neutrons is 2.300 Å. (d) BaTbO<sub>3</sub> at 10 K. In this case, the second vertical marks show the positions calculated for magnetic reflections, and the third vertical marks show the positions calculated for Al metal which exists as a part of the sample container.

### 3.2. Magnetic properties

**3.2.1. Magnetic susceptibility.** The temperature dependence of the magnetic susceptibilities for the samples SrTbO<sub>3</sub> and BaTbO<sub>3</sub> prepared in this study is shown in figure 3. Both SrTbO<sub>3</sub> and BaTbO<sub>3</sub> show the antiferromagnetic transition at 32.0 and 33.4 K, respectively. It is found that dramatic differences between ZFC and FC are observed below Néel temperatures for both the SrTbO<sub>3</sub> and BaTbO<sub>3</sub>. These results suggest that the magnetic moments of Tb in SrTbO<sub>3</sub> and BaTbO<sub>3</sub> order with a slight ferromagnetic component below Néel temperatures.

To study the existence of the ferromagnetic moment, the remnant magnetization measurements were performed. Figure 4 shows that it confirmed that the weak ferromagnetic

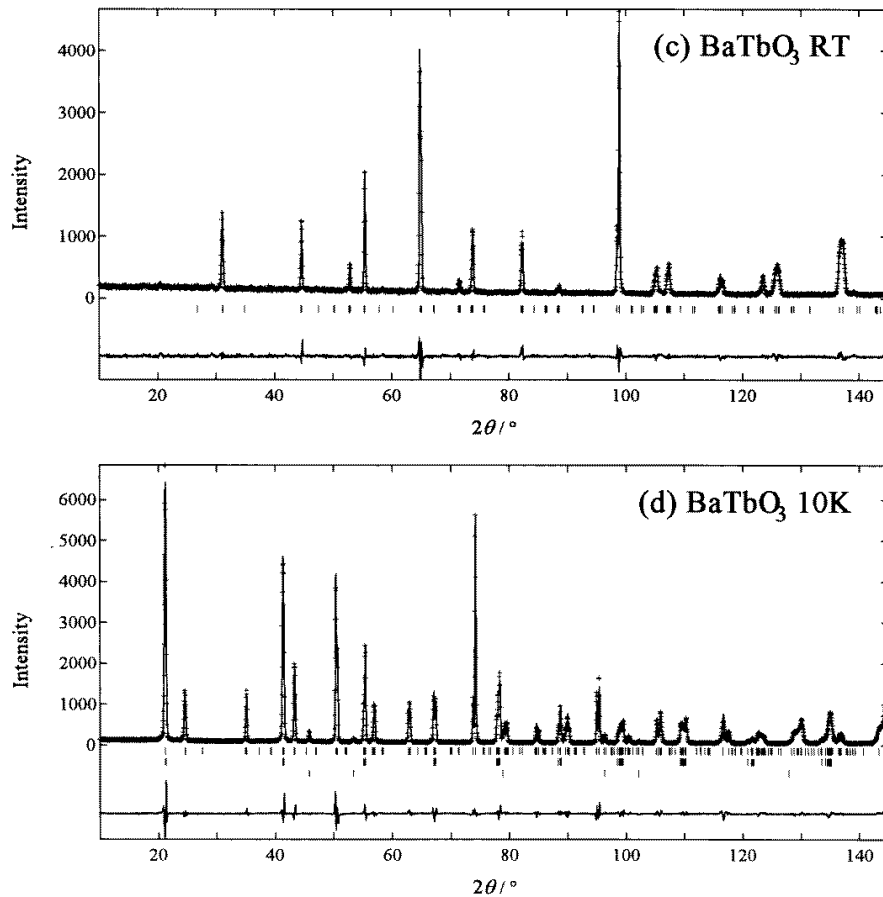


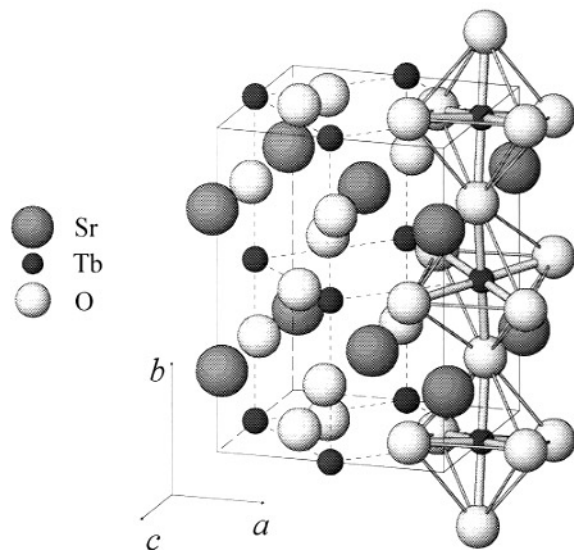
Figure 1. (Continued)

moments for both SrTbO<sub>3</sub> and BaTbO<sub>3</sub> disappear above Néel temperatures, i.e., it has been confirmed that the magnetic moments of Tb<sup>4+</sup> ions showing antiferromagnetic interactions at low temperatures have a weak ferromagnetic component below the Néel temperatures.

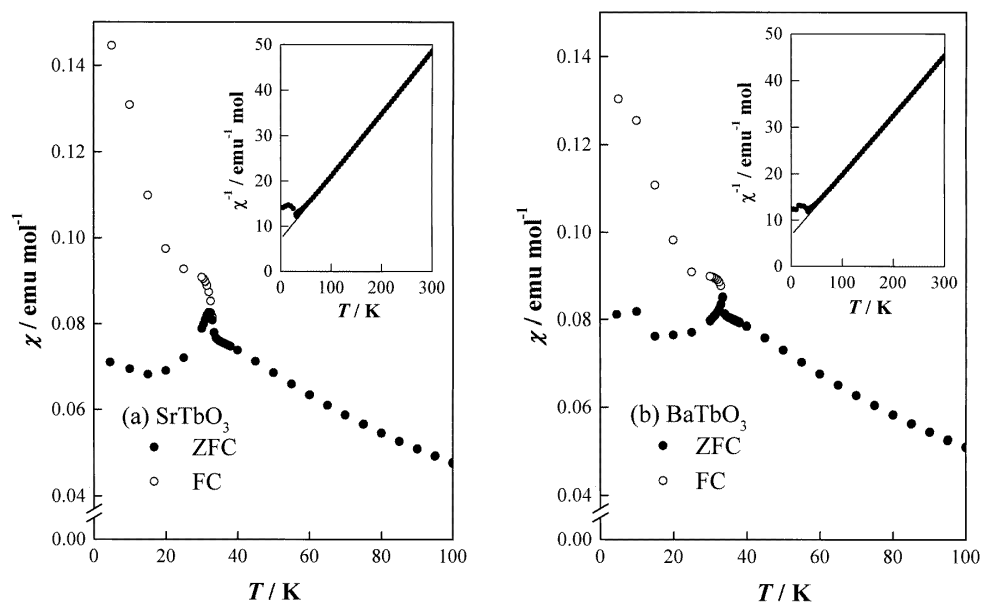
A small magnetic hysteresis has been found at 10 K for both the compounds (figure 5), which means that there exists a ferromagnetic component in the magnetic moment of terbium. It is calculated to be  $\sim 0.1 \mu_B/\text{Tb}$  for both the samples from the magnetization curve.

In the case of an orthorhombically distorted perovskite type compound with space group *Pnma*, the Dzyaloshinsky–Moriya interaction can exist between the magnetic ordered elements at 4b sites, from the point of crystalline symmetry. The experimental results that these compounds have the weak ferromagnetic component are consistent with this theory.

Both SrTbO<sub>3</sub> and BaTbO<sub>3</sub> exhibit normal paramagnetic behaviour above  $T_N$ . The fit of the Curie–Weiss law to  $\chi$ – $T$  curves for SrTbO<sub>3</sub> and BaTbO<sub>3</sub> gives  $\mu_{eff} = 7.83 \mu_B$  and  $\Theta = -56.7$  K, and  $\mu_{eff} = 7.88 \mu_B$  and  $\Theta = -54.1$  K, respectively. The ground state of the tetravalent terbium free ion is  $^8S_{7/2}$  and the theoretical magnetic moment is  $7.94 \mu_B$ . The effective magnetic moments obtained from this experiment are slightly lower than  $7.94 \mu_B$ , which may suggest that the tetravalent terbium ions in these compounds are affected by the crystal field to some extent.



**Figure 2.** Crystal structure of SrTbO<sub>3</sub>: an orthorhombic structure with space group *Pnma*.



**Figure 3.** Magnetic susceptibilities. Inset shows the inverse magnetic susceptibility against temperature: (a) SrTbO<sub>3</sub> and (b) BaTbO<sub>3</sub>.

**3.2.2. Magnetic structure.** In the powder neutron diffraction profiles measured at 10 K for both the SrTbO<sub>3</sub> and BaTbO<sub>3</sub> (figure 1(b) and (d)), magnetic Bragg peaks are present. We will consider the magnetic structures for SrTbO<sub>3</sub> and BaTbO<sub>3</sub> at 10 K. The crystal structures of these compounds at this temperature are both orthorhombic with space group

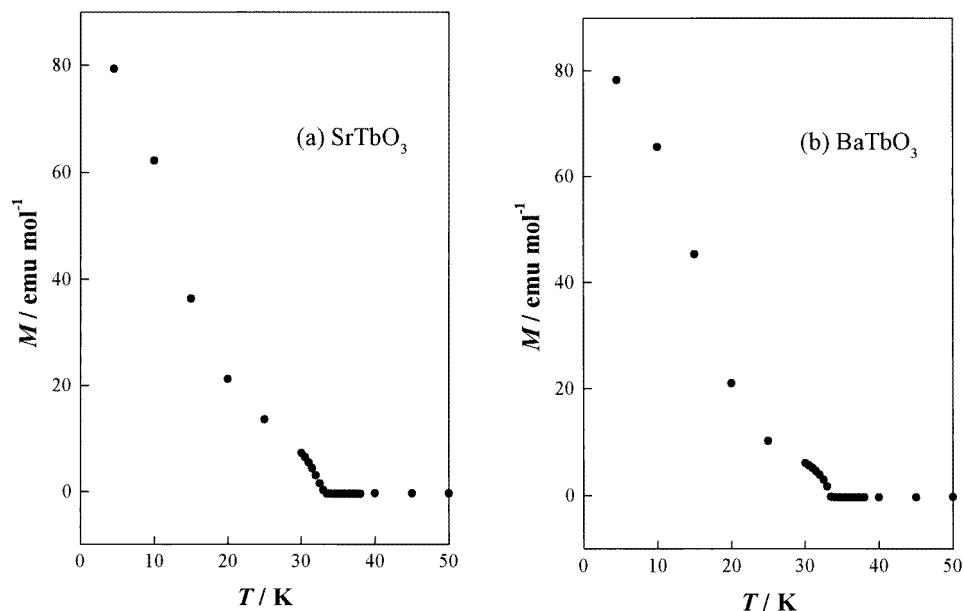


Figure 4. Remnant magnetizations: (a) SrTbO<sub>3</sub> and (b) BaTbO<sub>3</sub>.

$Pnma$  and the magnetic Bragg peaks can be indexed in the crystallographic unit cell, with both  $h + l$  and  $k$  odd.

In the orthorhombic space group  $Pnma$ , with Tb atoms in the 4b Wyckoff position, four magnetic sites are available in the unit cell, namely:

Position	$x$	$y$	$z$
Tb1	1/2	0	0
Tb2	1/2	1/2	0
Tb3	0	1/2	1/2
Tb4	0	0	1/2

with respective magnetic moments  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4$ . Four types of magnetic arrangement are possible [12]:

$$F = S_1 + S_2 + S_3 + S_4$$

$$G = S_1 - S_2 + S_3 - S_4$$

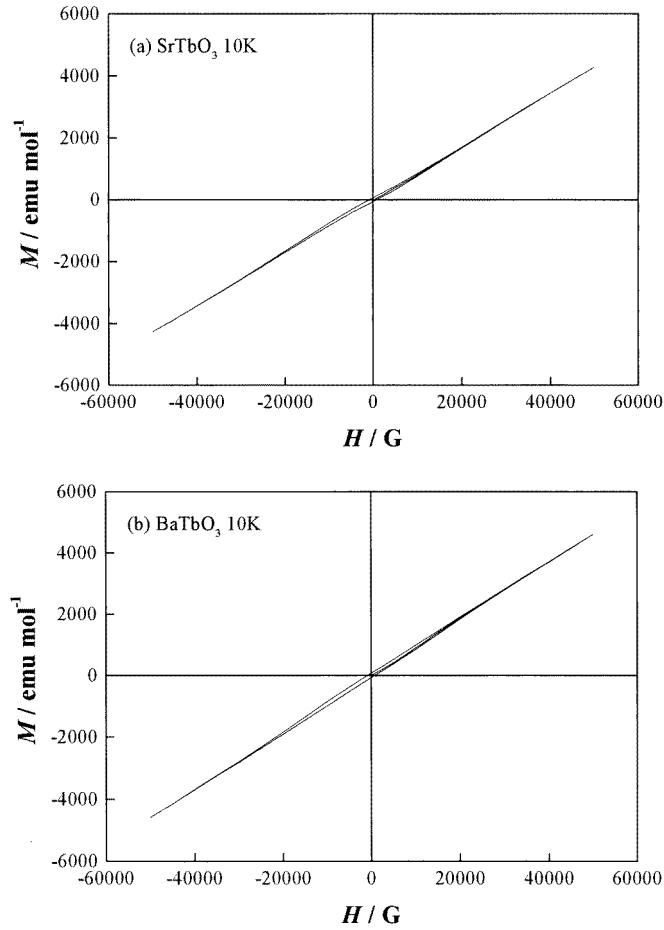
$$C = S_1 + S_2 - S_3 - S_4$$

$$A = S_1 - S_2 - S_3 + S_4.$$

It is known that for magnetic atoms in the 4b sites, some simple selection rules correspond to the  $F$ ,  $G$ ,  $C$  and  $A$  types of magnetic moment arrangement as shown in table 2. In the case of an  $F$ -type (ferromagnetic) magnetic arrangement, the selection rule for the  $F$  type is equal to that of the nuclear diffraction at the 4b site; both the magnetic and nuclear Bragg reflections are found at the same diffraction angles. It is, therefore, difficult to detect the intensity of  $F$ -type magnetic reflection from the mixed peaks if the value of the ferromagnetic moment is not so large.

From the selection rules in table 2, the type of magnetic structure at 10 K is determined to be the  $G$  type shown in figure 6. Magnetic Bragg peaks corresponding to  $C$  or  $A$  type of magnetic arrangements were not observed.





**Figure 5.** Magnetic hysteresis curves at 10 K: (a) SrTbO<sub>3</sub> and (b) BaTbO<sub>3</sub>.

**Table 2.** Selection rule of magnetic Bragg peaks.

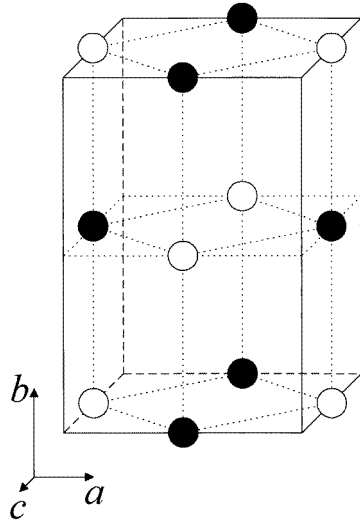
Type	1	2	3	4 <sup>a</sup>	$h+l$	$k$
<i>F</i>	+	+	+	+	even	even
<i>G</i>	+	-	+	-	odd	odd
<i>C</i>	+	+	-	-	odd	even
<i>A</i>	+	-	-	+	even	odd

<sup>a</sup> The numbers correspond to site number below.

Position	$x$	$y$	$z$
Tb1	1/2	0	0
Tb2	1/2	1/2	0
Tb3	0	1/2	1/2
Tb4	0	0	1/2

+ and - represent direction of magnetic moment and + is antiparallel to -.

Next, we will consider the *F* type. From magnetization measurements, we have found that there exists the ferromagnetic component in the magnetic moment of terbium (*F* type)



**Figure 6.** Magnetic structure for SrTbO<sub>3</sub> and BaTbO<sub>3</sub> at 10 K. ○ and ● represent the direction of magnetic moment of the terbium element and ○ is antiparallel to ●.

at 10 K. However, the reflection intensity due to the magnetic diffraction is too small (the ferromagnetic moment is  $\sim 0.1 \mu_B/\text{Tb}$  from the hysteresis curve) compared with that due to the nuclear diffraction to estimate the component of the magnetic moment with  $F$  type from this powder neutron scattering pattern.

It has been determined that the magnetic moment of SrTbO<sub>3</sub> has been directed to be [101] of the orthorhombic unit cell, from the Rietveld analysis. There may exist a magnetic component of  $b$ -axis direction, but for this type of antiferromagnet, it is difficult to determine that by the powder neutron diffraction method. The direction of the magnetic moment of BaTbO<sub>3</sub> is [100]. To determine the further precise directions of the magnetic moments, the neutron diffraction technique using a single crystal is needed.

### Acknowledgment

The present work was supported by the Asahi Glass Foundation.

### References

- [1] MacChesney J B, Williams H J, Sherwood R C and Potter J F 1964 *J. Chem. Phys.* **41** 3177
- [2] MacChesney J B, Williams H J, Sherwood R C and Potter J F 1966 *J. Chem. Phys.* **44** 596
- [3] Jacobson A, Tofield B C and Fender B E F 1972 *Acta Crystallogr. B* **28** 956
- [4] Hinatsu Y 1992 *J. Solid State Chem.* **100** 136
- [5] Hinatsu Y, Itoh M and Edelstein N 1996 *J. Solid State Chem.* **132** 337
- [6] Horyń R, Wolcyz M and Bukowski Z 1996 *J. Solid State Chem.* **124** 176. These authors report that SrPrO<sub>3</sub> is monoclinic. The reason for the difference in the crystal system of SrPrO<sub>3</sub> among researchers is probably due to some difference of the cooling condition of specimens when prepared.
- [7] Rosov N, Lynn J W and Lin Q 1992 *Phys. Rev. B* **45** 982
- [8] Felner I, Yeshurun Y, Hilscher G, Holubar T, Schaudy G, Yaron U, Cohen O, Wolfus Y, Yacoby E R, Klein L, Potter F H, Rastomjee C S and Egdell R G 1992 *Phys. Rev. B* **46** 9132

- [9] Itoh M and Hinatsu Y 1998 *J. Alloys Compounds* **264** 119
- [10] Tofield B C, Jacobson A C and Fender B E F 1972 *J. Phys. C: Solid State Phys.* **5** 2887
- [11] Izumi F 1993 *The Rietveld Method* ed R A Young (Oxford: Oxford University Press) ch 13
- [12] Bertaut E F 1968 *Acta Crystallogr. A* **24** 217