

# Crystal structure refinement of the ferroelectric ceramic compound $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$

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$\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$  was synthesized by solid state reaction from  $\text{Sm}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  in molar relation 1:1:3. Title compound is isostructural with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . Products of the reaction were analyzed by X-ray diffraction methods. The crystal structure was refined by the Rietveld Method. Cell parameters are:  $a=5.368(2)$ ,  $b=5.369(2)$ , and  $c=32.71(2)$  Å, space group  $Fmmm$ . The final R value was 9.96% ( $R_w=13.43\%$ ). © 1998 International Centre for Diffraction Data. [S0885-7156(98)00501-6]

Key words: ferroelectric ceramic, Rietveld refinement, perovskite related structure, rare earth bismuth titanates

## INTRODUCTION

The family of oxides with composition  $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$ , where  $n=1, 2, 3, 4$ , and 5 were synthesized and investigated by several authors (Aurivillius, 1950; Newnham *et al.*, 1971; Rae *et al.*, 1990). The cubo-octahedral M site accepts Bi, Ba, Sr, and several rare earth ions, while the smaller, Ti, Nb, Ta, Fe, W, Ga, and Cr ions go into the octahedral R site. The structures consist of  $\text{Bi}_2\text{O}_2$  layers interleaved with perovskite-like  $\text{M}_{n-1}\text{R}_n\text{O}_{3n+1}$  layers. Several empirical rules have emerged regarding the crystal chemistry. The bismuth oxide layer is almost inviolate, however the bismuth atoms in the perovskite layer are readily replaced by a large number of univalent, divalent, and trivalent cations. The size requirements are no more stringent than those of the perovskite structure itself. Ions as small as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Gd}^{3+}$  and as large as  $\text{Ba}^{2+}$  and  $\text{K}^+$  substitute for  $\text{Bi}^{3+}$ , although ions about the size of  $\text{Sr}^{2+}$  and  $\text{La}^{3+}$  form the most extensive solid solutions. Recently we reported the dielectric characterization of  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$  (Alvarez-Fregoso, 1997). In this paper we present the crystal structure determination and refinement using the Rietveld method of this compound.

## EXPERIMENTAL METHODS

### Sample preparation

$\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$  samples were prepared from a mixture of  $\text{Sm}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  (Aldrich Chem. Co. 99.9%) in a molar ratio 1:1:3, respectively. The reaction was carried out in a Pt crucible. Reagents were initially fired at 700 °C for 72 h and then at 800 °C for another 72 h. Finally, these products were sintered at 900 °C for 72 h. Products of this final firing were analyzed by x-ray diffraction powder methods.

### Specimen preparation

The XRD specimen was prepared by grinding the sample in an agate mortar and pestle and smearing the powder on a glass slide.

## DATA COLLECTION

Data were collected with a Siemens (D-5000) instrument equipped with a computer, a line focus Cu tube operated at 40 kV and 35 mA, a graphite monochromator, and a proportional counter. Intensity was measured at every  $0.02^\circ 2\theta/\text{min}$  from 6 to  $100^\circ$ . The counting time per step was 5 s. The data were corrected using an external Si standard with cell parameter  $a=5.4306$  Å at 25 °C. The  $K\alpha_2$  component was subtracted before reading  $2\theta$  and intensities. DIFFRAC/AT Siemens software was used for data reduction.

## RESULTS AND DISCUSSION

TREOR (Werner *et al.*, 1985) was used for indexing the powder pattern. The title compound is isostructural with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (Rae *et al.*, 1990). The crystal data are included in Table I. The refinement of the crystals structure was carried out using the DBWS-9411 program (Sakthivel and Young, 1992); the atomic coordinates are listed in Table II. The final R value was 9.96% ( $R_w=13.43\%$ ). The most important interatomic distances are summarized in Table III. The powder pattern is shown in Fig. 1. The representation of the structure is shown in Fig. 2. (The figure was generated using Cerius<sup>2</sup>TM. This program was developed by BIOSYM/Molecular Simulations.)

By comparing the cell volume and the orthorhombic distortions between  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$ , it is demonstrated that Sm incorporation decreases the cell parameters and also decreases the orthorhombic distortion, since the ionic radius of  $\text{Bi}^{3+}$  is slightly larger than that of  $\text{Sm}^{3+}$  ( $b/a$  BTO\*\*=1.007,  $b/a$  SmBTO=1.0002 and VBTO=967.8 Å<sup>3</sup>,  $V$  SmBTO=943.1 Å<sup>3</sup>). [BTO= $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (Alvarez-Fregoso, 1997.)] Also, the Sm for Bi substitution induces a 100 °C decrease of the ferroelectric Curie temperature, as previously reported (Alvarez-Fregoso, 1997). A comparison between the  $Cmmm$  and  $Fmmm$  space groups in this compound and results will be published elsewhere.

TABLE I. Crystal data of  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$ .

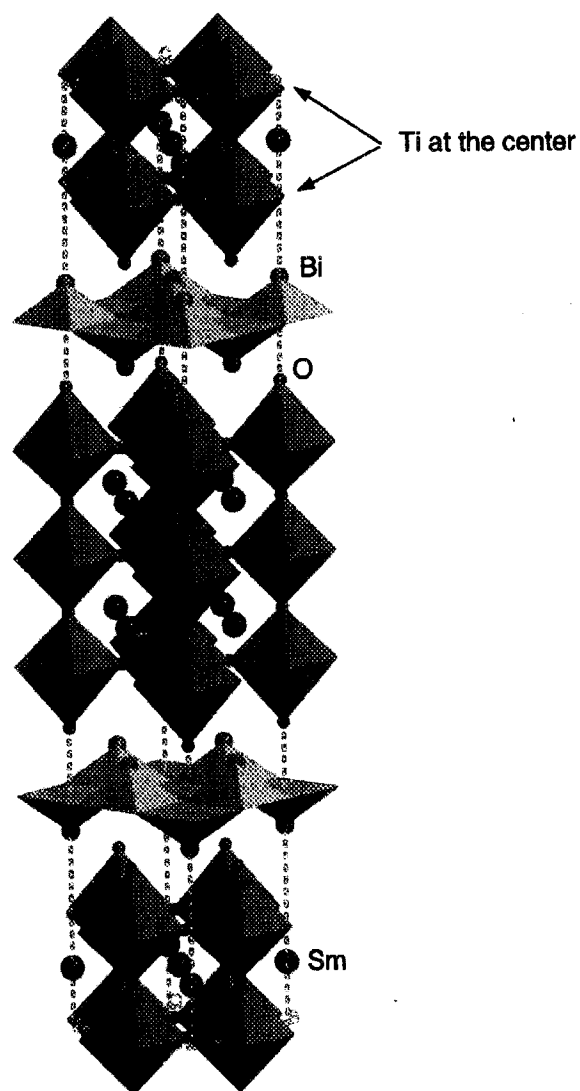
Rad. $\text{CuK}\alpha_1$ $\lambda=1.54062 \text{ \AA}$ Filter Mono			
$a=5.368(2) \text{ \AA}$			
$b=5.369(2) \text{ \AA}$			
$c=32.71(2) \text{ \AA}$			
$V=943.1(7) \text{ \AA}^3$			
Space Group= $Fm\bar{3}m$			
$Z=4$			
$R_w=13.43$			
$R=9.96$			
$S=1.44$			
Number of atoms: 9			
$D_x=8.22 \text{ g/cm}^3$			
$hkl$	$d_{\text{obs}}$ ( $\text{\AA}$ )	$d_{\text{calc}}$ ( $\text{\AA}$ )	$  l_0$
0 0 2	16.247	16.243	4
0 0 4	8.148	8.148	5
0 0 6	5.438	5.438	9
0 0 8	4.081	4.081	4
1 1 1	3.763	3.763	12
1 1 3	3.579	3.578	4
1 1 5	3.281	3.278	9
0 0 1 0	3.269	3.266	3
1 1 7	2.944	2.942	100
0 0 1 2	2.722	2.722	3
0 2 0	2.680	2.681	19
2 0 0	2.680	2.680	19
0 2 2	2.645	2.645	1
2 0 2	2.645	2.645	1
1 1 1 1	2.338	2.338	3
0 0 1 4	2.335	2.334	9
0 2 8	2.241	2.241	8
2 0 8	2.241	2.241	8
2 0 1 0	2.073	2.073	0
2 0 1 2	1.911	1.911	3
2 2 0	1.896	1.896	22
1 1 1 5	1.889	1.889	5
2 2 6	1.791	1.791	2
0 2 1 4	1.761	1.761	10
2 0 1 4	1.761	1.761	10
2 2 8	1.721	1.720	2
1 1 1 7	1.715	1.715	2
1 3 1	1.694	1.694	2
3 1 1	1.694	1.694	2
1 3 5	1.642	1.642	1
3 1 5	1.642	1.642	1
1 3 7	1.594	1.595	15
3 1 7	1.594	1.594	15
1 1 1 9	1.567	1.567	4
2 2 1 4	1.472	1.472	8
1 1 2 1	1.440	1.440	6
0 4 0	1.341	1.342	3
4 0 0	1.341	1.341	3
1 3 1 5	1.339	1.339	2
3 1 1 5	1.339	1.339	2
3 3 7	1.221	1.221	6
2 4 0	1.200	1.200	3
4 2 0	1.200	1.200	3
1 3 2 1	1.148	1.148	3
3 1 2 1	1.148	1.147	3
2 4 1 4	1.068	1.068	3
4 2 1 4	1.068	1.068	3

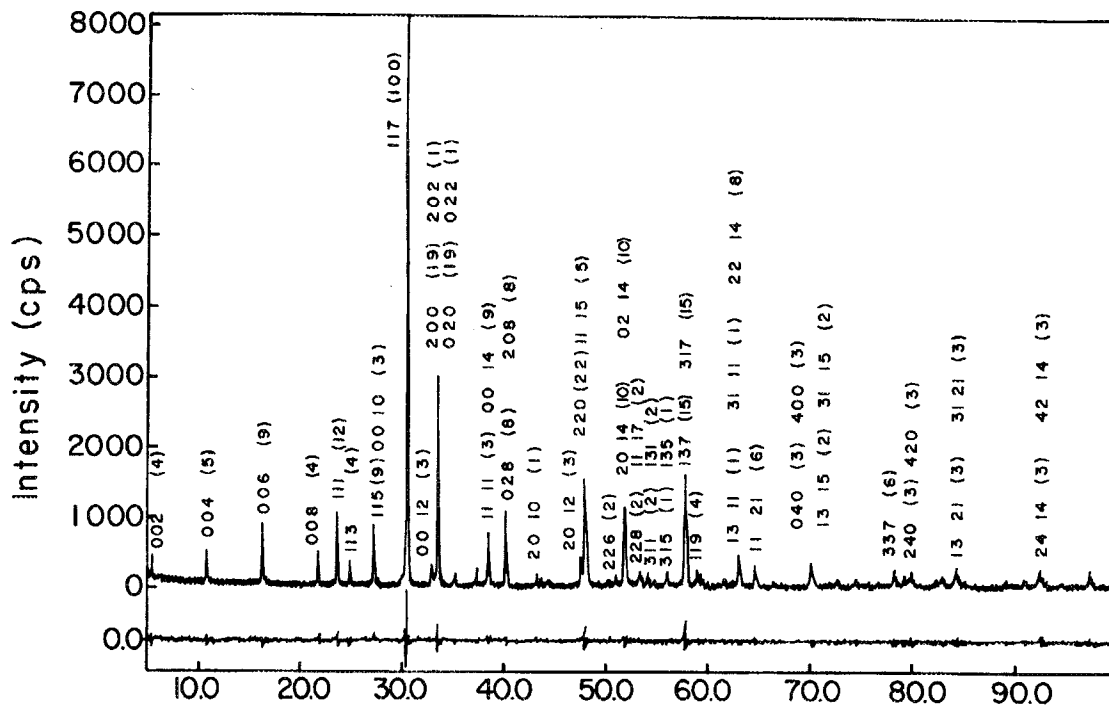
TABLE II. Atomic coordinates of  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$ .

Atom	$X/a$	$Y/b$	$Z/c$	$B(\text{\AA}^2)$	$N$
Sm	0.0000	0.0000	0.0662(1)	0.43(10)	0.3(1)
Bi	0.0000	0.0000	0.2108(1)	0.03(10)	0.3(1)
Ti <sub>1</sub>	0.0000	0.0000	0.5000	0.48(15)	0.16(9)
Ti <sub>2</sub>	0.0000	0.0000	0.3724(2)	0.72(14)	0.3(1)
O <sub>1</sub>	0.2500	0.2500	0.0000	2.04(64)	0.3(1)
O <sub>2</sub>	0.2500	0.2500	0.2500	0.26(67)	0.2(1)
O <sub>3</sub>	0.0000	0.0000	0.4409(8)	3.30(78)	0.2(1)
O <sub>4</sub>	0.0000	0.0000	0.3195(9)	2.54(64)	0.3(1)
O <sub>5</sub>	0.2500	0.2500	0.1141(4)	0.65(31)	0.6(3)

TABLE III. Interatomic distances.

	Distance ( $\text{\AA}$ )
Sm-O <sub>5</sub>	2.462(2)
Bi-O <sub>2</sub>	2.291(2)
Ti <sub>1</sub> -O <sub>3</sub>	1.934(1)
Ti <sub>2</sub> -O <sub>3</sub>	2.241(1)
Ti <sub>2</sub> -O <sub>4</sub>	1.731(1)

Figure 1. Coordination polyhedral representation of the structure of  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$ .



2 θ

Figure 2. X-ray powder diffraction pattern of  $\text{Sm}_2\text{Bi}_2\text{Ti}_3\text{O}_{12}$ .

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