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Synthesis and Structure of Pyrochlore-Type Bismuth Titanate

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Bismuth titanate with the pyrochlore structure has been prepared for the first time. This phase does not exist in the Bi_2O_3/TiO_2 equilibrium phase diagram, but has now been prepared by a low-temperature synthesis route with a final calcination temperature of 600°C. Structural analysis of pyrochlore bismuth titanate was performed using both synchrotron X-ray and neutron powder diffraction data. The cubic cell edge is 10.357 Å, and the composition based on the refinement of the structure is $Bi_{1.74}Ti_2O_{6.62}$. The Bi^{3+} cations are displaced off the three-fold axis by 0.38 Å in a disordered manner. © 1998 Academic Press

INTRODUCTION

Many $A_2^{3+}M_2^{4+}O_7$ compounds are known to form in the pyrochlore structure (1, 2). The normal pyrochlore structure is sometimes found when A^{3+} is Bi, for example: $Bi_2Ru_2O_7$, $Bi_2Ir_2O_7$, and $Bi_2Pt_2O_7$. The structure of $Bi_2Sn_2O_7$ is apparently pyrochlore related (3), but the actual structure has never been solved. Neither $Bi_2Zr_2O_7$ nor $Bi_2Hf_2O_7$ is known in a pyrochlore structure despite the fact that both $La_2Zr_2O_7$ and $La_2Hf_2O_7$ have the pyrochlore structure. Good evidence for pyrochlore-type $Bi_2Ti_2O_7$ has never been presented. This might not be surprising because $Bi_2Ti_2O_7$ would fall outside the pyrochlore stability field (1, 2) based on the radius ratio of the A and M cations. Pyrochlores of the type $A_2^{3+}Ti_2O_7$, where A^{3+} is Sm through Lu are known to exist. However, the pyrochlore structure has not been produced for the $A_2^{3+}Ti_2O_7$ composition when A^{3+} is Nd, Pr, or La. Because the radius of Bi^{3+} is similar to that of La^{3+}, pyrochlore-type $Bi_2Ti_2O_7$ might not be expected to form. None of the many studies (4–9) of the Bi_2O_3/TiO_2 system indicates a phase close to the $Bi_2Ti_2O_7$ composition. The only equilibrium compounds are $Bi_{12}TiO_{20}$, $Bi_4Ti_3O_{12}$, and $Bi_2Ti_4O_{11}$. Shimada *et al.* (10) reported the formation of pyrochlore bismuth titanate crystals from a $Bi_2O_3/TiO_2/V_2O_5/ZnO$ melt, but the actual composition of the crystals was not determined. The red-brown color of those crystals indicates that they were not a pure bismuth titanate composition. We report here a low-temperature synthesis route to a bismuth titanate with the pyrochlore structure.

EXPERIMENTAL

Titanium(IV) butoxide (Alfa, 99+%) and bismuth(III) nitrate (Aldrich, reagent grade) were separately dissolved in acetone to form 0.1 M solutions. A white precipitate appeared as the Bi solution was added to the Ti solution. This suspension was vigorously stirred and heated to 50°C. Ammonium hydroxide was added dropwise, and the precipitate became gelatinous. After evaporation of the acetone, the sample was ground and heated in air at 600°C for 16 h, producing a light-tan powder.

The X-ray diffraction pattern of samples made in this way at a 1 : 1 Bi : Ti ratio showed that a phase with face-centered cubic symmetry ($a \sim 10.35$ Å) dominated, but peaks of $Bi_4Ti_3O_{12}$ were also present. It was found that these extra peaks could be eliminated by using excess Ti in the synthesis. For the sample used for detailed structural analysis, a 10% molar excess of Ti relative to 1 : 1 Bi : Ti was used. Very weak peaks of $Bi_2Ti_4O_{11}$ and TiO_2 were present in this sample. Heating samples at 650°C or higher resulted in decomposition of the pyrochlore phase to form $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$.

X-ray diffraction data were collected at the National Synchrotron Light Source at Brookhaven National Laboratory. The sample was in a 0.2-mm capillary, and an absorption correction was applied. Neutron data were collected on BT-1 at the NIST Center for Neutron Research. Details of data collection are in Table 1.

STRUCTURAL ANALYSIS

Refinements of both the X-ray and neutron diffraction data were initiated using GSAS software (11) and assuming the ideal structure in space group $Fd3m$ with a composition of $Bi_2Ti_2O_7$. A three-phase refinement was used to account

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TABLE 1
Details of X-ray and Neutron Diffraction Data Collection

Quantity	X-ray diffraction data	Neutron diffraction data
Empirical formula	$Bi_{1.74}Ti_2O_{6.62}$	$Bi_{1.74}Ti_2O_{6.62}$
Formula weight (amu)	565.302	565.302
Z	8	8
Calculated density (g/cm^3)	6.762	6.771
Space group	*Fd*3*m*	*Fd*3*m*
a (Å)	10.3569(1)	10.3523(2)
Wavelength (λ)	0.50275	1.5402
Data range (° 2θ)	4.5–38	10–150
Zero point (° 2θ)	0.0087(2)	− 0.050(2)
Step size (° 2θ)	0.005	0.05
Number of variables	35	27
R_p (%)	1.88	4.11
wR_p (%)	1.80	5.03
R_F^2 (%)	6.07	5.50
χ^2 (%)	2.204	1.059

TABLE 2
Atomic Fractional Coordinates, Occupancies, and Isotropic Thermal Parameters[a]

Atom	Site	x/a	y/b	z/c	Occupancy	U_{iso} (Å)
Bi (1)	96h	0	0.02745(4)	0.97255(4)	0.145(1)	0.0129(2)
Ti (2)	16d	0.5	0.5	0.5	1	0.0189(4)
O (3)	48f	0.125	0.125	0.43126(9)	1	0.0181(2)
O (4)	8a	0.125	0.125	0.125	0.624(1)	0.0234(1)

[a] Cation parameters from X-ray data and oxygen parameters from neutron data.

for the very weak peaks of $Bi_2Ti_4O_{11}$ and TiO_2. It became apparent immediately that the Bi site was not fully occupied. Furthermore, peaks normally forbidden in the pyrochlore structure were clearly present. These reflections are forbidden in the sense that isotropic atoms in positions *a*, *b*, *c*, *d*, and *f* of *Fd*3*m* will not contribute to reflections such as 442 and 644. These reflections become possible for anisotropic atoms or for isotropic atoms in positions *e*, *g*, *h*, or *i*. In the case of $Sn^{2+}_{2-x}(Nb^{5+}_{2-y}Sn^{4+}_{y})O_{7-x-y/2}$ and $Sn^{2+}_{2-x}(Ta^{5+}_{2-y}Sn^{4+}_{y})O_{7-x-y/2}$ pyrochlores, Sn^{2+} cations placed in either position *h* or *g* gave a good fit to all reflections, including those "forbidden" in the ideal pyrochlore structure (12). Position *h* moves the *A* cation off the three-fold axis in a direction halfway between two of the six equatorial oxygens. Position *g* moves the *A* cation off the three-fold axis directly toward one of these six oxygens. Both models were refined for our bismuth titanate sample. Agreement factors were significantly better with Bi in position *h*; therefore, only that model is presented here. In both the *g* and *h* refinements, Bi moves 0.38(2) Å off the three-fold axis. Refinement was also attempted with Bi in the ideal (0, 0, 0) site with anisotropic thermal parameters, but this failed due to a nonpositive definite problem.

The refinements based on the X-ray and neutron data gave very similar results for the bismuth positional and occupational parameters. Neither set of data would give a stable refinement if the occupation factor and thermal parameter value for O(4) were simultaneously refined. The occupation factor for this oxygen was therefore constrained to achieve charge balance, but its thermal parameter was refined. The agreement between observed and calculated diffraction patterns is shown in Figs. 1a and 1b. Final parameters are shown in Table 2, and some interatomic distances and angles are given in Table 3.

DISCUSSION

Apparently, previous attempts to prepare pyrochlore-type bismuth titanate were made at high temperatures

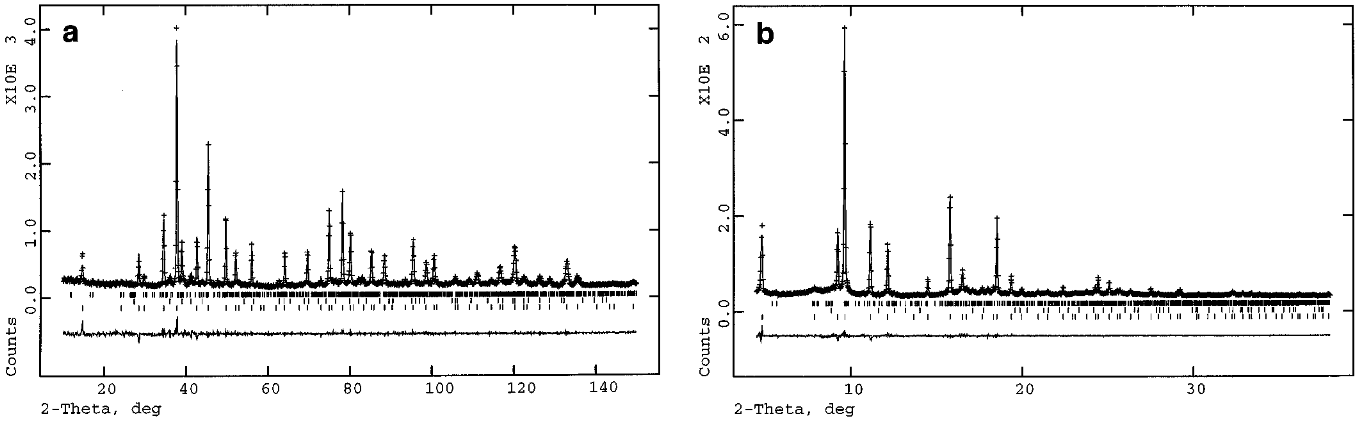

FIG. 1. Neutron (a) and X-ray (b) powder patterns for bismuth titanate. Observed (+), calculated (solid lines), and differences patterns are shown. Upper ticks are $Bi_2Ti_4O_{11}$; middle ticks are rutile TiO_2; and lower ticks are bismuth titanate.

TABLE 3
Selected Interatomic Distances (Å) and Bond Angles (°)

	O(3)	O(4)
Bi(1)	2.2868(6) × 2 2.6517(7) × 2 2.9722(7) × 2	2.27710(3) × 2
Ti(2)	1.9655(3) × 6	
O(3)–Bi(1)–O(3)	72.86(1)	
O(3)–Bi(1)–O(4)	88.00(2) × 2 108.60(2) × 2	
O(4)–Bi(1)–O(4)	159.667(1)	
O(3)–Ti(2)–O(3)	92.49(4) 87.51(4)	

where only the equilibrium phases are obtained. Knop *et al.* (13, 14) attempted and failed to prepare pyrochlore-type bismuth titanate at 1000°C. However, a $(Y_{1-x}Bi_x)_2Ti_2O_7$ solid was prepared with x as high as 0.75. Extrapolation of the cell edge vs x gives a value of 10.354 Å for hypothetical $Bi_2Ti_2O_7$ with the pyrochlore structure. Bamberger *et al.* (15) studied several other $(A_{1-x}Bi_x)_2Ti_2O_7$ solid solutions and also concluded that the cubic cell edge of $Bi_2Ti_2O_7$ would be about 10.354 Å. This value falls very close to the cell edge we find for $Bi_{1.74}Ti_2O_{6.62}$.

The Ti–O distances of 1.96 Å in $Bi_{1.74}Ti_2O_{6.62}$ are in good agreement with the 1.97 Å Ti–O distances reported for $Sm_2Ti_2O_7$, which has the ideal pyrochlore structure (13). The O–Ti–O angles of the Ti–O antiprism are 87.5° and 92.5°, indicating a relatively small distortion from an octahedron. The A cation site of the pyrochlore structure is not a typical site for a lone pair cation such as Bi^{3+}. The movement of Bi^{3+} off the three-fold site is a way of creating a better environment for Bi^{3+} and its lone pair of electrons (Figs. 2 and 3). The result of this disordered displacement is that Bi^{3+} has four short Bi–O distances of about 2.28 Å and then longer distances of 2.65 and 2.97 Å. Presumably, the orbital with the lone pair of electrons points between the two oxygens at 2.97 Å. The O(4)–Bi–O(4) angle, which would be 180° in the ideal pyrochlore structure, has dropped to 160°.

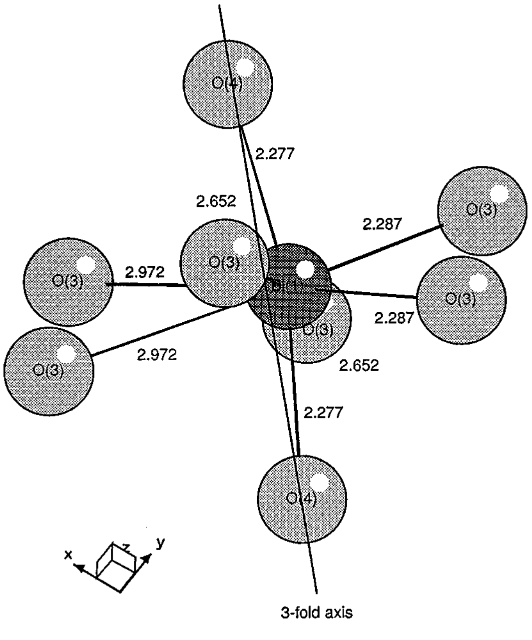

FIG. 2. Complete oxygen environment of bismuth.

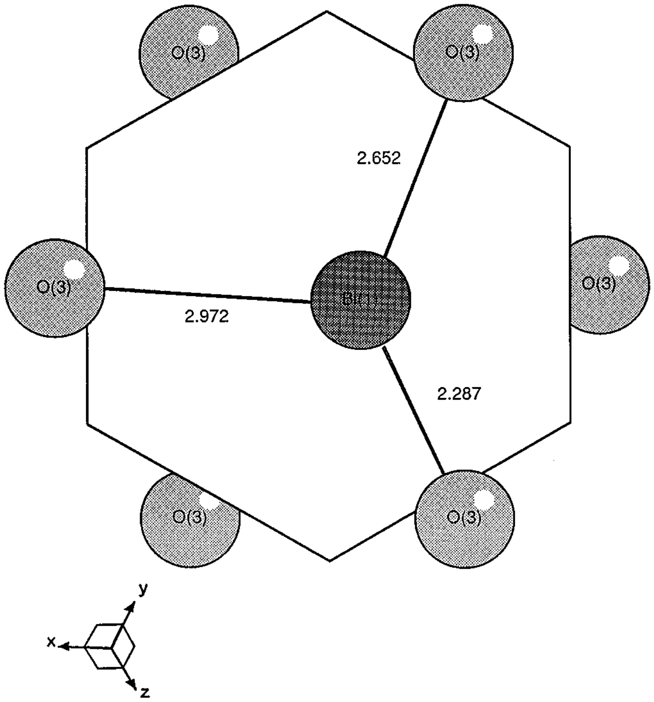

FIG. 3. Projection of bismuth environment looking down the three-fold axis.

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