Rapid Communication

Preparation of a new pyrochlore-type compound $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ by hydrothermal reaction

Qiang Dong, Hong Jiang, Nobuhiro Kumada *, Yoshinori Yonesaki, Takahiro Takei, Nobukazu Kinomura

Department of Research Interdisciplinary, Graduate School of Medicine and Engineering, University of Yamanashi, Miyamae cho-7, Kofu 400-8511, Japan

ABSTRACT

A new pyrochlore-type $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ with the cubic cell of $a = 10.339(5)$ Å was prepared by hydrothermal reaction using TiO_2 (anatase) and Bi_2O_3 in NaOH solution. This compound was obtained when the molar ratio of $NaOH/TiO_2$ was above 2 and the reaction temperature was above 240 °C. The TG-curve of as-prepared sample showed a mass loss of 0.8 mass% which was caused by release of OH group. This compound decomposed to a pyrochlore-type compound and a layered-type $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ above 800 °C. The optical band gap of $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ was estimated to be 2.5 eV.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Pyrochlore-type compounds have received much attention for several decades due to their diverse physical properties, which allow for a broad range of applications, such as storage capacitor [1], insulating layer [2], high-permittivity dielectrics [3], solid electrolytes [4], host materials for the immobilization of fission products [5], catalysis [6], and thermal barrier coatings [7].

Pyrochlore structures have been reviewed extensively [8]. The general formula of oxide pyrochlores can be written as $A_2B_2O_7$. Ideal stoichiometric pyrochlores ($A_2B_2O_7$) are cubic with space group Fd-$3m$ and often described as two interpenetrating networks of B_2O_6 octahedra and A_2O' tetrahedral [8,9]. The overall formula is typically represented as $A_2B_2O_6O'$ to distinguish the oxygen within the two networks. The relative ionic radii or ionic radius ratios are reported that governed the preparation and stability of the oxide pyrochlores [10]. From extensive experimental work on the synthesis and structural characterization of cubic pyrochlores, stability fields have been proposed for allowable substitution into the A and B cation sites based on simple measures such as the ratio of the cation radii size and the cation electronegativity [8,11].

In Bi/Ti/O system, a cubic pyrochlore structure $Bi_2Ti_2O_7$ with static bismuth displacements and probable domains of static O′ displacements has been synthesized via a co-precipitation route [12]. Recently, we reported that a perovskite-type $(Na_{0.5}Bi_{0.5})TiO_3$ was prepared by hydrothermal reaction using TiO_2 (anatase) and Bi_2O_3 in NaOH solution [13]. On the course of this investigation, a new pyrochlore-type $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ (hereafter NBT) was found and this was the first example of a pyrochlore-type oxide with mixed cations at the A site in Na/Bi/Ti/O system. Here, we will describe a facile hydrothermal method for the preparation of a new pyrochlore-type NBT. The crystal structure of this new pyrochlore-type is refined by means of Rietveld analysis.

2. Experimental procedure

Hydrothermal reaction was carried out with a Teflon-lined autoclave (70 mL) and TiO_2 (anatase), Bi_2O_3 and NaOH (molar ratio Na:Bi:Ti=2:0.5:1) were put into an autoclave with a distilled water (40 mL). The autoclave was heated at 240 °C for 48 h. The solid products were filtered, washed with distilled water for several times and dried at 60 °C in air. The powder sample and crystals with size of ∼50 μm were separated by decantation with distilled water and ethanol. At last the crystals and powders were dried at 60 °C. X-ray powder diffraction (XRD) was performed on a Rigaku X-ray diffractometer (RINT2000V Japan) with graphite-monochromatized $CuK\alpha$ radiation ($\lambda = 1.54056$ Å). The diffraction pattern over the range of 20–70° in 2θ was recorded with a scanning speed of 3° min^{-1}. The structural refinement was carried out with the XRD data collected at intervals of 0.05° from 10.00° to 120.00° 2θ at room temperature. The structure parameters were refined by Rietveld method using the program RIETAN-2000 [14,15]. Crystal structure in this report was drawn with VESTA developed by Momma and Izumi [16]. Scanning electron microscopy (SEM) images were obtained with a JEOL JEM-6500F field emission scanning electron microscope. Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000–400 cm^{-1} on a JASCO FT/IR-4100 spectrometer,

* Corresponding author. Fax: +81 55 254 3035.
E-mail address: kumada@yamanashi.ac.jp (N. Kumada).

using transparent KBr pellets. Thermo gravimetric analysis (TGA) was carried out in a Rigaku Thermo Plus TG 8120 thermal analysis system with a heating rate of 10 °C min^{-1} from room temperature to 800 °C. Diffuse reflectance spectra were measured with a JASCO V-550 spectrometer. The photocatalytic activities were examined for decomposition of methylene blue (20 ppm solution) under visible light.

3. Results and discussion

The product consisted of homogeneous octahedra with diameters of ~ 50 µm as shown in Fig. 1. Longer reaction time had no effect on the size of the product. From single crystal X-ray diffraction it was found that these crystals were not single crystals. The X-ray powder diffraction patterns for the as-prepared sample was indexed with the cubic cell of $a=10.339(5)$ Å as shown in Fig. 2(a). This value of the lattice parameter was smaller than pyrochlore-type bismuth titanates ($Bi_{1.74}Ti_2O_{6.62}$ (10.3523(2) Å) [17], $Bi_2Ti_2O_7$ (10.3749(2) Å) [12], $Bi_{1.896}Ti_2O_{6.884}$ (10.3735(3) Å) [18]). The Na/Bi ratio in this compound was determined to be 0.19 by the SEM-EDX analysis.

Fig. 1. SEM image of the as-prepared sample.
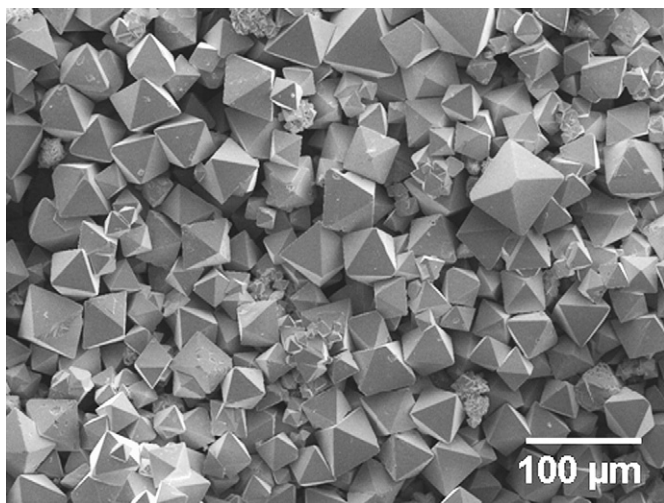
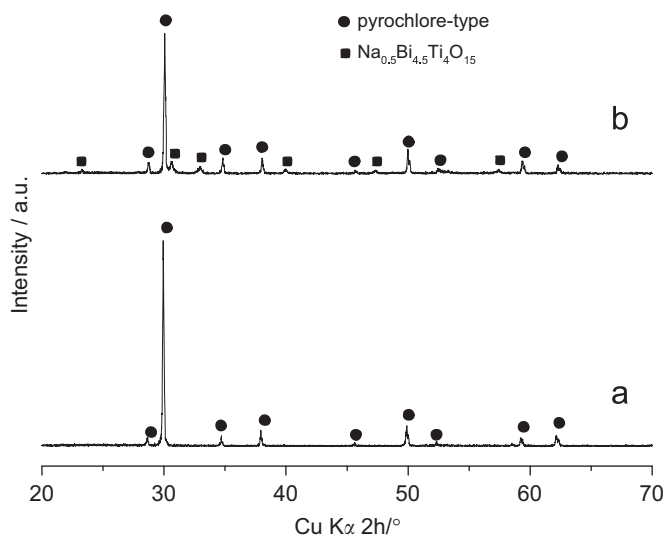The TG-curve of as-prepared sample showed a mass loss of 0.8 mass% which was caused by release of OH group (Fig. 3). The chemical composition is concluded to be $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ from the TG analysis and the ratio of Na/Bi. As shown in Fig. 2(b), the X-ray powder diffraction patterns for the sample heated at 800 °C indicated a small amount of a layered-type $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ as well as a pyrochlore-type compound. As seen in Fig. 4 the FT-IR spectrum of the as-prepared sample show existence of OH group
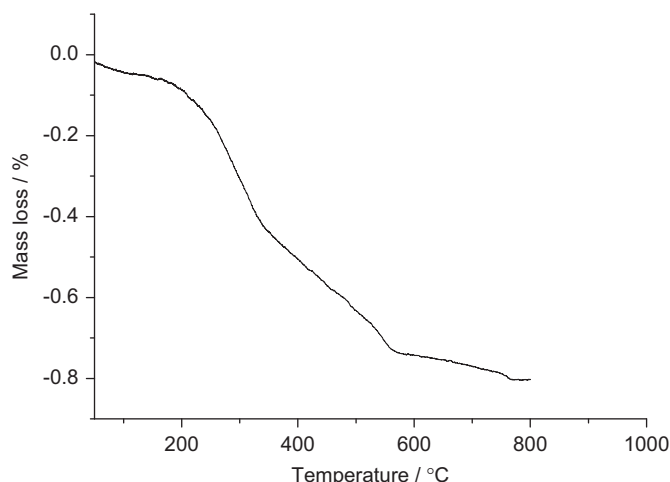

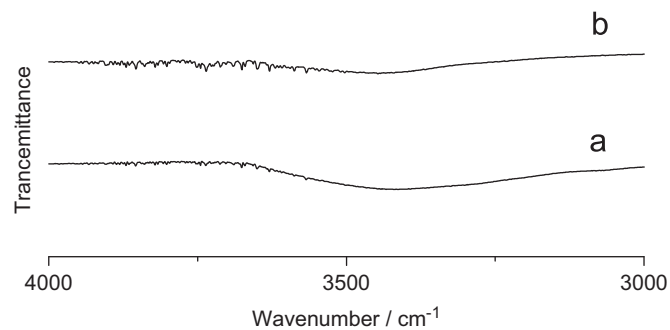
Fig. 3. TG curve of the as-prepared sample.

Fig. 4. FT-IR spectra of (a) the as-prepared sample and (b) sample heated at 800 °C.

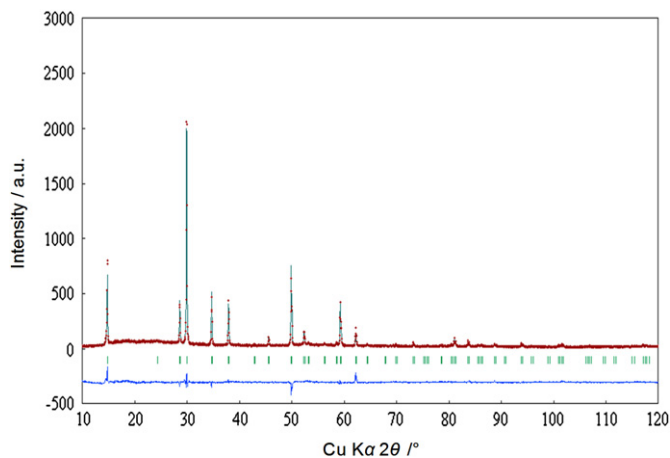**Fig. 2.** X-ray powder diffraction patterns of (a) the as-prepared sample and (b) sample heated at 800 °C.

Fig. 5. Observed and calculated X-ray powder diffraction patterns for $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$. Solid line is the calculated pattern from the refined crystal structure. Residual errors are drawn at the bottom of the figure. Vertical short lines are allowed peak positions satisfying Bragg condition.

at 3400 cm^{-1}; however, for the sample heated at 800 °C no evidence of OH group was observed. From these results as-prepared sample of NBT crystals are considered to decompose to a pyrochlore-type compound and a layered-type $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ at elevated temperatures, accompanying release of OH group.
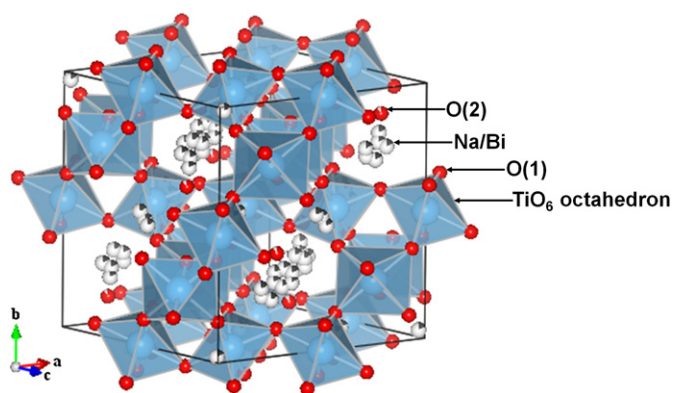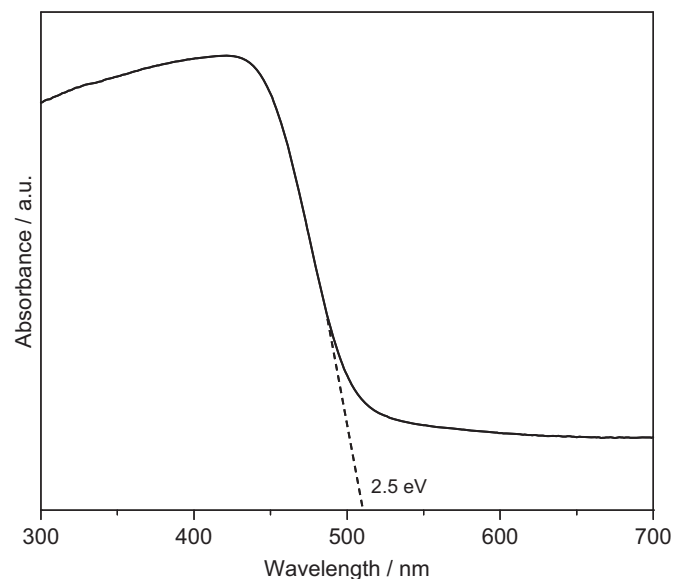
Based on the similarity of the XRD patterns, the structural refinement by Rietveld method was carried out. The final R-factors led to reasonable values ($R_{wp}=11.36\%$, $R_p=8.67\%$). Fig. 5 shows the Rietveld refinement pattern for $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$. The crystal data and atomic parameters are listed in Tables 1 and 2, respectively. Fig. 6 shows the crystal structure of $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$. This compound has a cubic pyrochlore structure, and Na/Bi atom occupies at one crystallographic site (96 g) and its TiO_6 octahedron are slightly tilted. The Ti–O distance (1.998(5) Å) in this compound is slightly longer than those of $Bi_2Ti_2O_7$ (1.964 Å) [12] and $Bi_{1.74}Ti_2O_{6.62}$ (1.9655(3) Å) [17]. The mean interatomic distance of (Na,Bi)–O was 2.49 Å, and this value was shorter than that (2.55 Å) of $Bi_{1.74}Ti_2O_{6.62}$ [17] and longer than that (2.47 Å) of $Bi_2Ti_2O_7$ [12]. Since this refinement was carried out by conventional X-ray powder diffraction data, the detail of the crystal structure could not be discussed. The synchrotron X-ray or neutron

Fig. 7. Optical adsorption spectrum of $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$.

diffraction study is now planning for further discussion of the crystal structure.

Fig. 7 shows optical adsorption spectrum of $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ and its optical band gap was estimated to be 2.5 eV. This value was compatible with that (2.4 eV) of monoclinic $BiVO_4$ which exhibits excellent photocatalytic activity under visible light irradiation [19]. This pyrochlore-type compound $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$, however, indicated no decomposition of methylene blue under visible light irradiation.

Table 1
Crystallographic data for $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$.

Quantity	X-ray diffraction data
Empirical formula	$Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$
Formula weight	565.08
Crystal system	Cubic
Space group	Fd-$3m$ (no. 227)
Unit cell parameters (Å)	$a=10.336(5)$
Volume (Å^3)	1104.3(9)
Calculated density (g/cm^3)	6.80
R_p (%)	8.67
R_{wp} (%)	11.36
R_I (%)	11.97
R_F (%)	12.61
S	0.77

Table 2
Atomic coordinates and isotropic displacement parameters for $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$.

Atom	Site	g	x	y	z	B (Å^2)
Na/Bi	96g	1/6	0.017(2)	$=x$(Na/Bi)	−0.031(18)	0.2(15)
Ti	16d	1	1/2	1/2	1/2	0.7(18)
O(1)	48f	1	1/8	1/8	0.422(12)	1.0
O(2)	8a	0.9	1/8	1/8	1/8	1.0

4. Conclusions

A new pyrochlore-type $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ with cubic structure is firstly prepared via a facile hydrothermal route in Na/Bi/Ti/O system using TiO_2 (anatase) and Bi_2O_3 in NaOH solution. The chemical composition is concluded to be $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$ from the analysis of experimental results. The crystal data and atomic parameters can compare with those of pyrochlore-type bismuth titanates.

Acknowledgments

References

[1] Y. Hou, T. Lin, Z. Huang, G. Wang, Z. Hu, J. Chu, X. Xu, M. Wang, Appl. Phys. Lett. 85 (2004) 1214–1216.
[2] W.F. Su, Y.T. Lu, Mater. Chem. Phys. 80 (2003) 632–637.
[3] D.P. Cann, C.A. Randall, T.R. Shrout, Solid State Commun. 100 (1996) 529–534.
[4] B.J. Wuensch, K.W. Eberman, C. Heremans, E.M. Ku, P. Onnerud, E.M.E. Yeo, S.M. Haile, J.K. Stalick, J.D. Jorgensen., Solid State Ion. 129 (2000) 111–133.
[5] R.C. Ewing, W.J. Weber, J. Lian, J. Appl. Phys. 95 (2004) 5949–5971.
[6] B.J. Kennedy, J. Solid State Chem. 123 (1996) 14–20.
[7] R.C. Vassen, X. Tietz, T. Basu, D. Stöver, J. Am. Ceram. Soc. 83 (2000) 2023–2028.
[8] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid State Chem. 15 (1983) 55–143.
[9] R.L. Withers, T.R. Welberry, A.K. Larsson, Y. Liu, L. Noren, H. Rundlof, F.J. Brink, J. Solid State Chem. 177 (2004) 231–244.

Fig. 6. Schematic representation of the structure of $Na_{0.32}Bi_{1.68}Ti_2O_{6.46}(OH)_{0.44}$.

[10] N. Wakiya, N. Kieda, A. Saiki, K. Shinozaki, N. Mizutani, J. Solid State Chem. 92 (1991) 320–326.
[11] J.C. Nino, Materials Science and Engineering, The Pennsylvania State University, University Park, PA, 2002.
[12] A.L. Hector, S.B. Wiggin, J. Solid State Chem. 177 (2004) 139–145.
[13] N. Kumada., Y. Morozumi, Y. Yonesaki, T. Takei, N. Kinomura, T. Hayashi, J. Ceram. Soc. Jpn. 116 (2008) 1238–1240.
[14] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65–71.
[15] F. Izumi, T. Ikeda, Mater. Sci. Forum 198 (2000) 321–324.
[16] K. Momma, F. Izumi, J. Appl. Crystallogr. 41 (2008) 653–658.
[17] I. Radosavljevic, J.S.O. Evans, A.W. Sleight, J. Solid State Chem. 136 (1998) 63–66.
[18] S.S. Kim, M.H. Park, J.K. Chung, W.J. Kim, J. Appl. Phys. 105 (2009) 061641–061645.
[19] A. Kudo, K. Omori, H. Kato, J. Am. Chem. Soc. 121 (1999) 11459–11467.