Preparation of Alkaline Earth Bismuth Pyrochlores Containing Bi^{5+} by Low Temperature Hydrothermal Reaction

N. KUMADA, M. HOSODA, AND N. KINOMURA

Faculty of Engineering, Yamanashi University, Miyamae-cho 7, Kofu 400 Japan

New alkaline earth bismuth oxides containing Bi^{5+} with the pyrochlore type structure were prepared by low temperature hydrothermal reaction using a hydrated sodium bismuth oxide NaBiO$_3$ · nH$_2$O as a starting material. The Ca- and Sr-pyrochlores contain CO$_3$ group and the ratios of Ca/Bi and Sr/Bi vary from 0.22 to 0.44 and from 0.24 to 0.46, respectively. The Ba-pyrochlore contains a H$_2$O or OH group instead of a CO$_3$ group and the ratio of Ba/Bi is constant. The chemical compositions of new pyrochlores are represented as A_xBi$_y$O$_{7-3x}$(CO$_3$)δ for A = Ca, Sr, and Ba$_{0.68}$Bi$_{3.05}$O$_{6.41}$(H$_2$O,OH)$_{0.59}$. The X-ray powder patterns for Ca-, Sr-, and Ba-pyrochlores are indexed in the monoclinic, cubic, and tetragonal systems, respectively. All the pyrochlores decompose above 400°C with two steps of weight losses caused by complete reduction from Bi^{5+} to Bi^{3+}. The Ca-pyrochlores change from the monoclinic to cubic symmetry by partial release of CO$_3$ group, though the symmetry for the Sr- and Ba-pyrochlores are not affected by release of CO$_3$ group or water. The electric resistivity of the monoclinic Ca-pyrochlores is ~10^4 ohm · cm and the cubic Ca-, Sr-, and the Ba-pyrochlores exhibit high electric resistivities (~10^7 ohm · cm) at room temperature. © 1993 Academic Press, Inc.

Introduction

The valence of Bi in oxides is known to adopt either 3+ or 5+ and oxides containing Bi^{5+} are rare. Oxides of $(A,$Bi$)_{1.5}$Bi$_2$O$_{6}$(H$_2$O)$_{1}$ (A = Na,K) with the pyrochlore type structure (*1–5*), superconductive (Ba · K)BiO$_3$ and Ba(Bi · Pb)O$_3$ with the perovskite type structure (*6, 7*) are such examples. The mean valence of Bi in the high temperature superconductive alkaline earth bismuth copper oxides was thought to be higher than 3+ (*8*). As seen in these examples oxides containing Bi^{5+} exhibit interesting physical properties; however, the conventional calcination method to prepare oxides containing Bi^{5+} is applicable only to the system including BaO and this may prevent the discovery new oxides containing Bi^{5+}.

Recently, Reis *et al.* reported that tungsten bronze (NH$_4$)$_x$WO$_3$, containing low valence of tungsten, could be prepared by low temperature hydrothermal reaction (*9*). Low temperature hydrothermal reaction can yield new inorganic compounds which are never prepared by conventional calcination methods. We also have been attempting preparation of new inorganic compounds by low temperature hydrothermal reaction and prepared the ilmenite-type NaNbO$_3$ (*10*), the pyrochlore-type $(A$ · H)TaO$_3$ · nH$_2$O (A = Na,K) (*11*), and acid and alkaline niobium phosphates (*12*). In the course of this research we found that new alkaline earth bismuth oxides containing Bi^{5+} with the pyrochlore-type structure were prepared by low temperature hydrothermal reaction using the hydrated sodium bismuth oxide NaBiO$_3$ · nH$_2$O as a starting material.

The pyrochlore type compound, $A_2B_2X_6Y$ (A; alkaline, alkaline earth, or rare earth metal etc., B; transition metal etc., X; O, F, Y; O, OH, S, F) has a large family by various combination of A and B ions; however, the only reported pyrochlore type

oxide containing Bi^{5+} is $(A,Bi)_{\sim 1.5}Bi_2$ $O_{\sim 6}(H_2O)_{\sim 1}$ $(A = Na, K)$ prepared by Tre-houx et al. (1–5). Here, preparation and thermal behavior of new pyrochlore-type oxides containing Bi^{5+} will be described. We refer hereafter to pyrochlore-type bismuth oxides containing K, Na, Ca, Sr, and Ba as K-, Na-, Ca-, Sr-, and Ba-pyro-chlores, respectively.

Experimental

1. Sample Preparation

The starting material of $NaBiO_3 \cdot nH_2O$ (Kanto Chemical) was put into an autoclave (70 ml) with a Teflon lining with alkaline earth nitrate $A(NO_3)_2 \cdot nH_2O$ $(A = Ca, Sr)$ and H_2O (30 ml) and was heated at 180°C for $2 \sim 15$ days. The molar ratio of the starting material and alkaline earth nitrate was varied from 0.1 to 10. Since by using $NaBiO_3 \cdot nH_2O$ and $Ba(NO_3)_2 \cdot nH_2O$ the pyrochlore type phase was always accom-panied with impurity phases under any pre-parative conditions, two steps of hydrother-mal treatment were adopted in the case of the Ba-pyrochlore. At first the mixture of $NaBiO_3 \cdot nH_2O$ and $Ba(NO_3)_2 \cdot nH_2O$ with the molar ratio of 1 : 10 was put into an auto-clave together with H_2O (30 ml) and was heated at 120°C for 2 days. The product ob-tained here was the compound in which Na ion was partially ion-exchanged with Ba ion and the ratio of Na/Ba in the product was found to be 1.74 by chemical analysis. This ion-exchanged compound, barium nitrate $Ba(NO_3)_2 \cdot nH_2O$ and H_2O (30 ml) were put into an autoclave and were heated at 180°C higher than the temperature for the ion-ex-change for 2 days. The products were sepa-rated by centrifugation, washed with dis-tilled water, and dried at 50°C.

2. Characterization

The products were identified with an X-ray powder diffractometer with $CuK\alpha$ radia-tion. Lattice parameters were determined by least-squares refinement of powder data

taken with a scanning speed of 0.25°/min. Silicon was used as an internal standard. The intensity data for the Rietveld analysis were collected by using Ni-filtered $CuK\alpha$ radiation for 10 sec at 0.05° interval over 2θ angle from 10 to 120°. The Rietveld struc-tural analysis was carried out by using the program RIETAN (13). The thermal stabil-ity was investigated by TG-DTA in air or in a stream of He and the rate of heating was 10°/min. The species evolved during TG-DTA measurement in a He atmosphere was analyzed by mass spectrometry. Samples were completely dissolved with strong HNO_3 solution and the amounts of alkaline earth metal and bismuth in the solution were determined by the inductively coupled plasma emission spectroscopy (ICP). The mean valence of bismuth was determined by the iodometry. Specific gravity was mea-sured with a pycnometer. Electric resisti-vity was measured on pelletized samples by the two-probe method.

Results and Discussion

1. Preparation of Alkaline Earth Bismuth Pyrochlores

The single phases with the pyrochlore-type structure were obtained, when the mo-lar ratio of the starting material and alkaline earth nitrate, $A(NO_3)_2 \cdot nH_2O$, was ≥ 0.25 for $A = Ca, Sr$, and the molar ratio of bismuth in the ion-exchanged compound and barium nitrate was ≥ 0.5 for $A = Ba$. In the case of $A = Ca, Sr$ the ratios of A/Bi in the products were increased with the molar ratio of the starting material and alkaline earth nitrate and got constant values (Ca/Bi = 0.44 and Sr/Bi = 0.46) when the molar ratio ≥ 2.0. In the Ba-pyrochlore the ratio of Ba/Bi was always 0.22 and was independent of the mo-lar ratio of bismuth in the ion-exchanged compound and barium nitrate. In all pyro-chlores no sodium ion was detected. The color of the products is dark brown for the Ca- and Ba-pyrochlores and black for the Sr-pyrochlores. The X-ray powder patterns of the Ca-, Sr-, and Ba-pyrochlores could
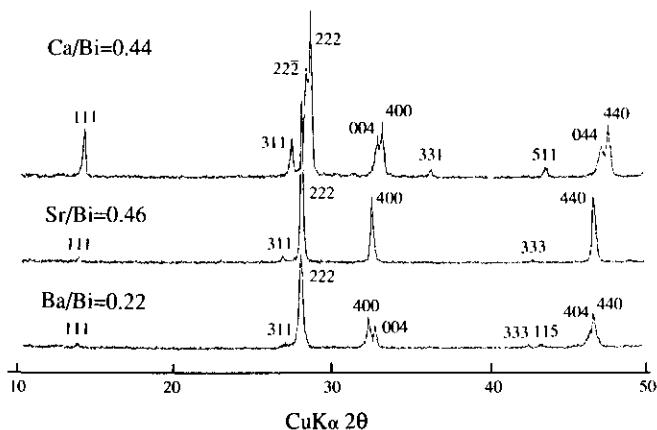
FIG. 1. The X-ray powder patterns of the Ca-, Sr-, and Ba-pyrochlores.

be indexed in the monoclinic, cubic, and tetragonal systems as shown in Fig. 1, respectively. The lattice parameters for the Ca- and Sr-pyrochlores are almost unchanged with the ratio of A/Bi in the products. The TG curves of all pyrochlores indicate a gradual weight loss above 200°C and a steep one at about 400°C which is followed by a small one as shown in Fig. 2. The color of the samples changes to dark brown for the Sr-pyrochlores after the first weight loss, while that of the Ca- and Ba-pyrochlores is almost unchanged. All pyrochlores turn to yellow after the second and third weight losses. The endothermic peaks in the DTA curves correspond to the weight losses in the TG curves and the endothermic peak corresponding to the first weight loss is sharp for the Ca-pyrochlore but broad for the Sr- and Ba-pyrochlores. The endothermic peaks at 756 $\sim$ 792°C will be discussed later.

Mass spectrometry of gas evolved during the TG-DTA measurement shows that O_2 and CO_2 gases are released for the Ca- and Sr-pyrochlores and O_2 and H_2O gases for the Ba-pyrochlore as shown in Fig. 3. The evolution of O_2 gas observed for all the pyrochlores is corresponding to the steep second weight loss in the TG curve and is considered to be caused by the reduction of Bi^{5+} to Bi^{3+}. The evolution of CO_2 gas for the

Ca- and Sr-pyrochlores is observed in the temperature range from 200 to 700°C and is corresponding to all the steps of weight losses. Probably the CO_3 group occupies the site in the tunnel of the pyrochlore-type structure and the determination of precise position of the CO_3 group by using neutron diffraction is planned. The Ba-pyrochlore releases H_2O instead of CO_2 and the evolution is observed at the first and second weight losses. The water molecule is considered to be placed in the tunnel as a OH group and/or water molecule as reported for the Na- and K-pyrochlores (1, 5).

Total weight loss, mean valence of bismuth, result of chemical analysis, specific gravity, chemical composition, and lattice parameters for the pyrochlores are listed in Table I. The amount of CO_3 or H_2O was estimated by subtracting the weight loss caused by reduction of Bi^{5+} from the total weight loss. The chemical compositions in Table I were determined on the assumption that all anion sites in the pyrochlores prepared in this work were occupied by oxygen, a CO_3 group, or a OH group and water molecule. The calculated specific gravities are in fair agreement with the measured ones. However, small discrepancies seen for the Ca- and Ba-pyrochlores might indicate a small amount of vacancies in the anion sites. By taking into account the fact
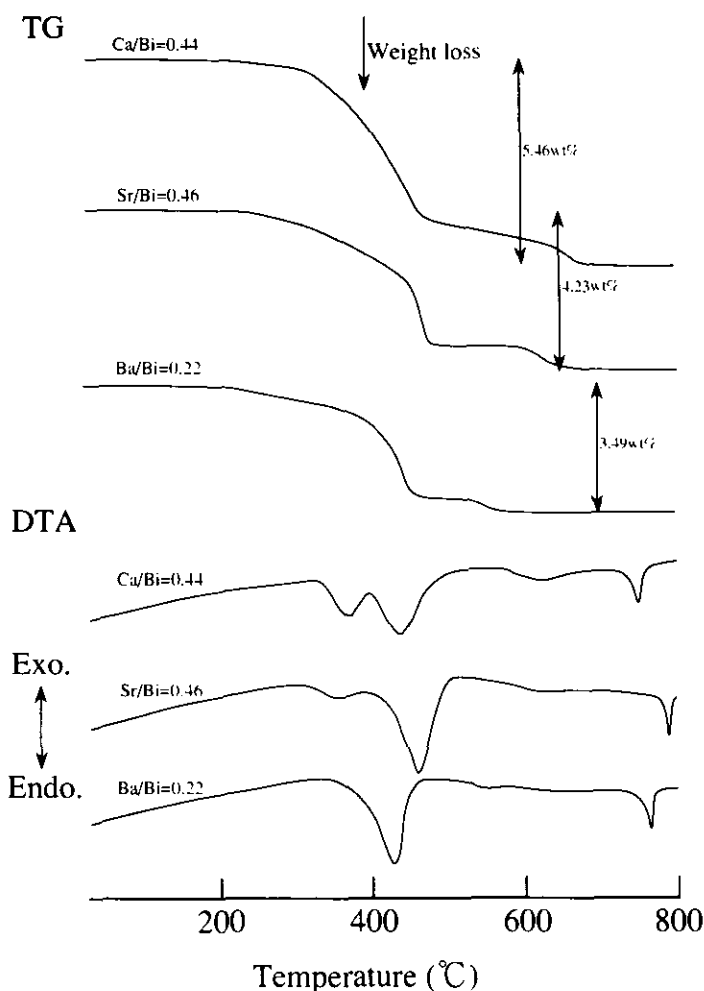
TG

Ca/Bi=0.44

Weight loss

5.46wt%

Sr/Bi=0.46

4.23wt%

Ba/Bi=0.22

3.49wt%

DTA

Ca/Bi=0.44

Exo.

Sr/Bi=0.46

Endo.

Ba/Bi=0.22

200   400   600   800

Temperature (°C)

FIG. 2. The TG-DTA curves of the Ca-, Sr- and Ba-pyrochlores.

that pyrochlores rarely have deficiency at the B site, the site distribution of cations for the alkaline earth pyrochlores prepared here can be represented as $(A_x Bi^{3+}_{y-2} \square_{4-x-y})$ $(Bi^{3+}, Bi^{5+})_2 O_{7-3\delta}(CO_3)_\delta$ for A = Ca, Sr and $(A_x Bi^{3+}_{y-2} \square_{4-x-y})(Bi^{3+}, Bi^{5+})_2 O_{7-\delta}(H_2O, OH)_\delta$ for A = Ba. These alkaline earth pyrochlores are similar to the alkaline pyrochlores, $(A, Bi)_{\sim 1.5} Bi_2 O_{\sim 6}(H_2O)_{\sim 1}$ (A = Na,K) prepared by Trehoux et al. in terms of cation deficiency at the A site and coexistence of Bi^{3+} and Bi^{5+} at the B site (3). Figure 4 shows the mean valence of bismuth and the proportions of Bi^{5+} at the B site and

Bi^{3+} at the A site against the ratio of A/Bi in the product. There is a tendency to increase the mean valence of bismuth with the ratio of A/Bi. The proportion of Bi^{5+} at the B site increases with the mean valence of bismuth, while that of Bi^{3+} at the A site decreases with increase of the mean valence of bismuth.

2. Phase Change on Heating for Alkaline Earth Bismuth Pyrochlores

The pyrochlores release CO_2 or H_2O and continuously decompose on heating in the temperature range from 200 to 800°C, ac-
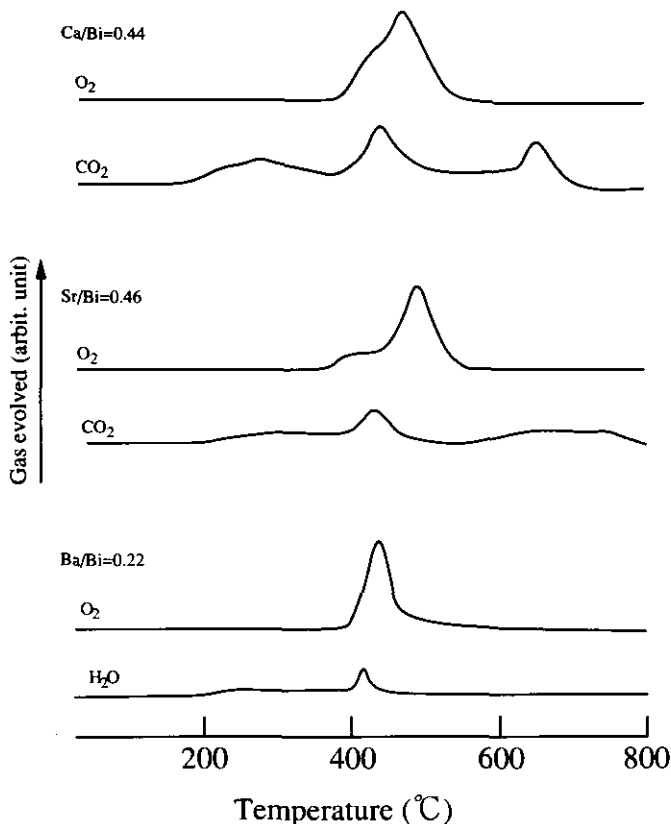
FIG. 3. Temperature dependence of gas evolution during the TG-DTA measurement in a stream of He.

companying three steps of weight losses as mentioned above. The Ca-pyrochlores were found to change from the monoclinic to cubic symmetry prior to the thermal decomposition as shown by X-ray powder patterns in Fig. 5. The lattice parameter of the cubic Ca-pyrochlore with Ca/Bi = 0.44 is a = 10.83 Å and the unit cell volume decreases by 0.7% during this change. However, the Sr- and Ba-pyrochlores keep their symmetry after the first weight loss and the lattice parameters are almost unchanged (a = 11.00 Å for the Sr-pyrochlores and a = 11.07, c = 10.96 Å for the Ba-pyrochlore). The first endothermic peak observed for the monoclinic Ca-pyrochlores at about 340°C disappears from the DTA curves of the cubic Ca-pyrochlores and the monoclinic symmetry is not recovered even by leaving the sample in air for a long time. Also, for the

Ca- and Sr-pyrochlores the total weight loss of the samples heated up to the first weight loss is always smaller than that of the as-prepared pyrochlores. These facts suggest that release of CO_3 or OH groups is not reversible unlike the case of the defect pyrochlores, $(A,H)TaO_3 \cdot nH_2O$ (A = Na,K) (11).

The decomposition products of the Ca-pyrochlores were found to be a rhombohedral solid solution, $CaO \cdot mBi_2O_3$ ($0.14 \leq$ Ca/Bi ≤ 0.32) (14) for the pyrochlore with Ca/Bi = 0.22 and a mixture of the rhombohedral phase and $CaBi_2O_4$ for the pyrochlores with Ca/Bi ≥ 0.33. (The X-ray powder pattern of $CaBi_2O_4$ mentioned here is not identified with the reported one for $CaBi_2O_4$ in the ASTM cards (No. 30-232) but coincided with the product obtained by calcination of $Ca(NO_3)_2 \cdot nH_2O$ and

TABLE I

TOTAL WEIGHT LOSS, MEAN VALENCE OF BISMUTH, RESULT OF CHEMICAL ANALYSIS, CHEMICAL COMPOSITION, SPECIFIC GRAVITY AND LATTICE PARAMETERS FOR THE ALKALINE EARTH PYROCHLORES

Ca/Bi in preparation	Weight loss (%)	Mean valence of Bi	CaO (wt%)	Bi$_2$O$_3$ (wt%)	Bi$_2$O$_5$ (wt%)	CO$_2$ (wt%)	Total (wt%)	Chemical composition	Specific gravity (g/cm^3) Calc.	Specific gravity (g/cm^3) Meas.	Lattice parameters
0.25	3.78	4.03	4.74	44.01	50.23	0.55	99.53	Ca$_{0.66}$Bi$_{3.04}$O$_{6.78}$(CO$_3$)$_{0.10}$	8.05	7.86	$a = 10.77(1)$, $b = 10.90(2)$, $c = 10.92(1)$ Å, $\beta = 91.99(3)°$
0.50	4.93	4.25	7.16	33.22	59.39	1.11	100.88	Ca$_{0.90}$Bi$_{2.70}$O$_{6.46}$(CO$_3$)$_{0.18}$	7.46	7.29	$a = 10.77(1)$, $b = 10.81(1)$, $c = 10.91(1)$ Å, $\beta = 91.12(4)°$
1.00	4.99	4.34	8.84	28.80	62.51	0.97	101.12	Ca$_{1.09}$Bi$_{2.58}$O$_{6.55}$(CO$_3$)$_{0.15}$	7.26	7.08	$a = 10.80(1)$, $b = 10.79(1)$, $c = 10.96(2)$ Å, $\beta = 90.69(8)°$
2.00	5.46	4.33	9.22	29.30	61.72	1.49	101.73	Ca$_{1.11}$Bi$_{2.52}$O$_{6.31}$(CO$_3$)$_{0.23}$	7.12	6.84	$a = 10.81(1)$, $b = 10.80(1)$, $c = 10.96(2)$ Å, $\beta = 90.58(7)°$

Sr/Bi in preparation	Weight loss (%)	Mean valence of Bi	SrO (wt%)	Bi$_2$O$_3$ (wt%)	Bi$_2$O$_5$ (wt%)	CO$_2$ (wt%)	Total (wt%)	Chemical composition	Specific gravity (g/cm^3) Calc.	Specific gravity (g/cm^3) Meas.	Lattice parameters
0.25	3.13	3.84	9.64	51.72	39.80	0.57	101.73	Sr$_{0.76}$Bi$_{3.13}$O$_{6.67}$(CO$_3$)$_{0.11}$	8.32	8.20	$a = 11.02(1)$ Å
0.50	3.83	4.06	13.83	39.65	47.41	0.78	101.67	Sr$_{1.03}$Bi$_{2.80}$O$_{6.58}$(CO$_3$)$_{0.14}$	7.85	7.74	$a = 11.01(1)$ Å
1.00	4.26	4.19	15.25	32.84	51.94	0.92	100.95	Sr$_{1.11}$Bi$_{2.65}$O$_{6.52}$(CO$_3$)$_{0.16}$	7.61	7.50	$a = 11.01(1)$ Å
2.00	4.23	4.19	16.19	32.42	50.76	0.96	100.33	Sr$_{1.20}$Bi$_{2.61}$O$_{6.49}$(CO$_3$)$_{0.17}$	7.60	7.49	$a = 11.01(1)$ Å

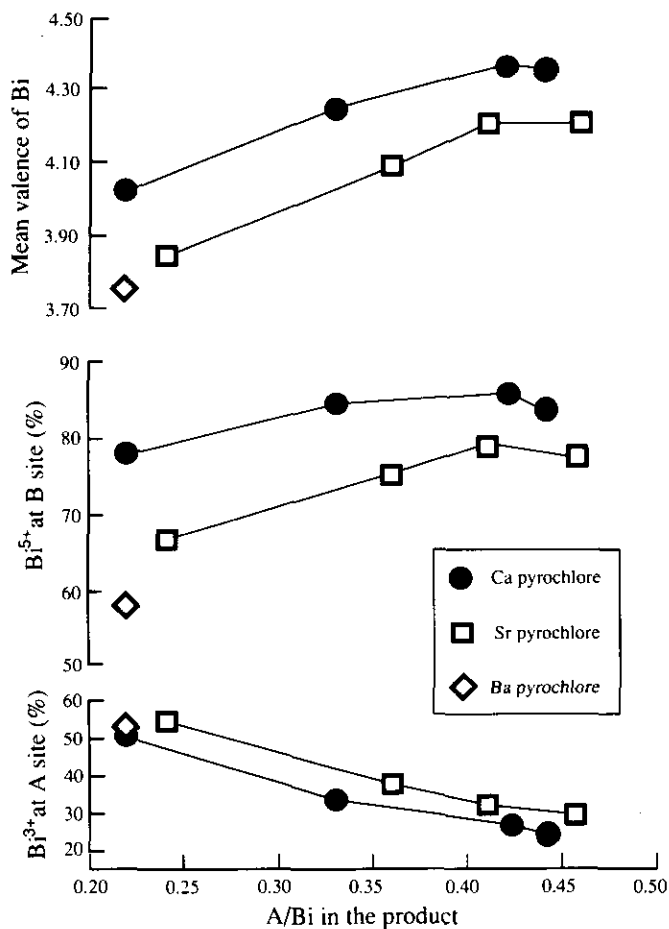| Ba/Bi in preparation	Weight loss (%)	Mean valence of Bi	BaO (wt%)	Bi$_2$O$_3$ (wt%)	Bi$_2$O$_5$ (wt%)	H$_2$O (wt%)	Total (wt%)	Chemical composition	Specific gravity (g/cm^3) Calc.	Specific gravity (g/cm^3) Meas.	Lattice parameters
—	3.49	3.76	12.55	53.00	34.55	1.27	101.37	Ba$_{0.68}$Bi$_{3.05}$O$_{6.41}$(H$_2$O,OH)$_{0.59}$	8.35	8.24	$a = 11.09(1)$, $c = 10.92(1)$ Å

FIG. 4. The mean valence of bismuth and the proportions of Bi^{5+} at the B site and Bi^{3+} at the A site against the ratio of A/Bi (A = Ca, Sr, Ba) in the product.
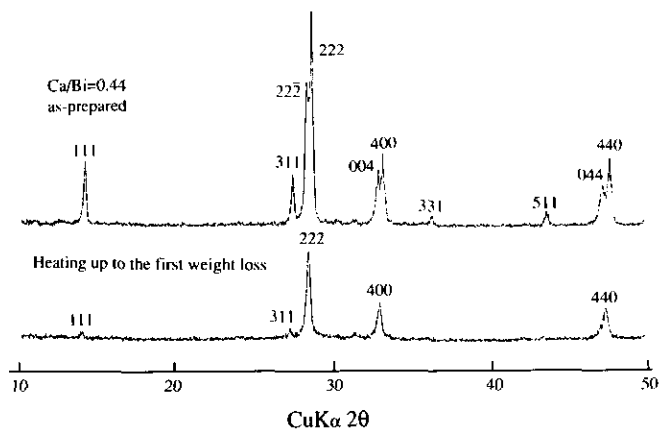

FIG. 5. The change of the X-ray powder pattern by heating up to the first weight loss for the Ca-pyrochlore with Ca/Bi = 0.44.

$Bi(NO_3)_3 \cdot 5H_2O$ with molar ratio of $1:2$ at 750°C.) All the Sr-pyrochlores partially decompose at the second weight loss (~500°C) and the decomposition products are similar to those of the Ca-pyrochlores; the pyrochlore with Sr/Bi = 0.24 changes to a rhombohedral solid solution, $SrO \cdot mBi_2O_3$ ($0.14 \leq$ Sr/Bi ≤ 0.32) (*15*) and the pyrochlores with Sr/Bi ≥ 0.36 to a mixture of the rhombohedral phase and $SrBi_2O_4$. The Ba-pyrochlore also decomposes at the second weight loss and the X-ray powder pattern of the decomposition product is similar to that of the rhombohedral solid solution for $AO \cdot mBi_2O_3$ (A = Ca,Sr) (*16*). The rhombohedral solid solution is reported to have a phase transition at $735 \sim 740$°C for $A = Ca$ (*14*) and at $680 \sim 715$°C for $A = Sr$ (*15*). The endothermic peak for the Ca-pyrochlore at 756°C in heating process in Fig. 2 and the corresponding exothermic peak at 740°C in cooling process is considered to indicate the phase transition of the rhombohedral solid solution. An endothermic peak was observed at 792°C for the Sr-pyrochlore with Sr/Bi = 0.46 in heating process (but not in cooling process) and no endothermic peak was observed for the pyrochlore with Sr/Bi = 0.24 which decomposed only to the rhombohedral solid solution. As $SrBi_2O_4$ decomposes to two solid solutions at about 790°C (*15*), the endothermic peaks at 792°C observed for pyrochlores with Sr/Bi > 0.24 is thought to be due to the decomposition of $SrBi_2O_4$. The endothermic peak at 775°C on heating and the exothermic one at 771°C on cooling for the Ba-pyrochlore correspond to melting and solidification of the rhombohedral phase.

3. Crystal Structure and Electric Resistivity of Pyrochlores

The Rietveld structural refinement of the Sr-pyrochlore with Sr/Bi = 0.46 was carried out on the assumption of the space group of $Fd3m$. The refinements of the Ca- and Ba-pyrochlores were not attempted because the space group of the distorted pyrochlore type structure is unknown. The final R-fac-

TABLE II

ATOMIC PARAMETERS OF THE Sr-PYROCHLORE

Atom	Site	Occupancy	x	y	z	B (Å²)
Sr,Bi	16(*d*)	0.905^a	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.0^a
Bi	16(*c*)	1.0	0	0	0	0.9(2)
O	48(*f*)	1.0	0.348(4)	$\frac{1}{8}$	$\frac{1}{8}$	1.0^a
O	8(*b*)	1.0	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	1.0^a

^{a} Denotes a fixed parameter.

tors (R_{WP}, R_P, R_B) defined in the reference (*17*) were 14.3, 9.2, and 11.4%, respectively, by neglecting carbons and fixing the thermal parameters of A site cations and oxygens to 1.0. The atomic parameters are listed in Table II. The positional and thermal parameters of the atoms in the tunnel can not be determined precisely by using the X-ray powder pattern and determination of these parameters may require neutron diffraction data. In the case of the K-pyrochlore the precise positions of the OH groups and water molecules in the tunnel were determined by neutron diffraction and NMR studies (*5*).

The metal–oxygen distances for the Sr-pyrochlore are listed in Table III. The Bi–O distance in the BiO_6 octahedron for the Sr-pyrochlore is slightly larger than 2.10 Å for the K-pyrochlore (*5*), because the proportion (23%) of large Bi^{3+} ions in the BiO_6 octahedra for the Sr-pyrochlore is higher than that (14%) for the K-pyrochlore (*5*). On the other hand the (Sr,Bi)–O(48(*f*)) distance in the Sr-pyrochlore is smaller than (K,Bi)–O(48)(*f*)) distance in the K-pyrochlore (*4*) because of the difference between ionic radii of K and Sr ions.

TABLE III

THE METAL–OXYGEN DISTANCES (Å) OF THE Sr-PYROCHLORE

Bi–O48(*f*)	2.23
(Sr,Bi)–O48(*f*)	2.57
(Sr,Bi)–O8(b)	2.38

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The electric resistivity of the monoclinic Ca-pyrochlore with Ca/Bi = 0.44 is $\sim 10^4$ ohm · cm and that of the cubic one exhibits higher electric resistivity ($\sim 10^7$ ohm · cm) at room temperature, and the Sr- and Ba-pyrochlores also show high electric resistivity ($\sim 10^7$ ohm · cm) at room temperature.

Conclusion

The alkaline earth bismuth pyrochlores containing Bi^{5+} were prepared by the low temperature hydrothermal reaction by using $NaBiO_3 \cdot nH_2O$ as a starting material. The ratios of Ca/Bi and Sr/Bi are ranged from 0.22 to 0.44 and from 0.24 to 0.46, respectively while the ratio is 0.22 for the Ba-pyrochlore. Then the mean valence of bismuth is ranged from 4.03 to 4.34 and from 3.84 to 4.19 for the Ca- and Sr-pyrochlores, respectively and is 3.76 for the Ba-pyrochlore. All the pyrochlores decompose on heating in the temperature range from 200 to 800°C, accompanying the release of O_2 and CO_2 or H_2O with the three steps of weight losses.

Acknowledgment

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