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Preparation and Crystal Structure of New Rare Earth Bismuth Oxynitrates: RBi$_2$O$_4$NO$_3$ (R: Y, Sm, Eu, Gd, Tb, Dy, Er, Yb)

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New rare earth bismuth oxynitrates, RBi$_2$O$_4$NO$_3$ (R: Y, Sm, Eu, Gd, Tb, Dy, Er, Yb) were prepared with low temperature hydrothermal reactions using NaBiO$_3\cdot n$H$_2$O and R(NO$_3$)$\cdot n$H$_2$O as starting materials. These rare earth bismuth oxynitrates crystallized in the tetragonal system with space group $P4mm$ and $Z = 1$. The lattice parameters depend on the ionic radius of rare earth atoms and range from $a = 3.8470(1)$ and $c = 10.1762(7)$ Å for R = Yb to $a = 3.9038(1)$ and $c = 10.2370(5)$ Å for R = Sm. The crystal structure for R = Y was refined using neutron powder diffraction data, with the final R factors being $R_{WP} = 4.35$, $R_P = 3.29$, $R_I = 5.39$, and $R_F = 4.40\%$. RBi$_2$O$_4$NO$_3$ is isostructural with R'_xBi$_{3-x}$O$_4X$ (R': La, Ce, Nd, Eu, Gd; X: Cl, Br, Se) having a layered structure based on (RBi$_2$O$_4$)$^+$ and (NO$_3$)$^-$ layers. There are three kinds of metal atom positions, all coordinated by eight oxygens; one is occupied by Y atoms and the other two are filled with Bi atoms. On heating above 500°C this compound decomposes to the solid solution (R,Bi)$_2$O$_3$ accompanied by the evolution of NO and O$_2$.

INTRODUCTION

We have prepared several new bismuth oxides by low temperature hydrothermal reactions using hydrate sodium bismuth oxide, NaBiO$_3\cdot n$H$_2$O, as one of the starting materials (1–7). During these studies a new lanthanum bismuth oxyhydroxide, (La,Bi)OOH with a BiOCl-type related structure was prepared by using lanthanum nitrate as one of the starting materials (2). For other rare earth nitrates, the new rare earth bismuth oxynitrates RBi$_2$O$_4$NO$_3$ (R: Y, Sm, Eu, Gd, Tb, Dy, Er, Yb) were prepared; their crystal structures are isostructural with those of R'_xBi$_{3-x}$O$_4X$ (R': La, Ce, Nd, Eu, Gd; X: Cl, Br, Se).

In the Bi$_2$O$_3$–NO$_3^-$ system, there are two known compounds, BiONO$_3$ (8) and Bi$_5$O$_7$NO$_3$ (9). The crystal structure of BiONO$_3$ has not yet been determined, and Bi$_5$O$_7$NO$_3$ prepared by thermal decomposition of Bi(NO$_3$)$_3\cdot$5H$_2$O is isostructural with Bi$_5$O$_7$I. Recently, a new yttrium oxynitrate, YONO$_3$, was prepared by thermal decomposition of Y(NO$_3$)$_3\cdot$5H$_2$O, and its crystal structure was reported to be similar to that of BiOCl (10). The crystal structure of RBi$_2$O$_4$NO$_3$ is based on (RBi$_2$O$_4$)$^+$ layers and is distinct from the BiOCl type structure, which has (Bi$_2$O$_2$)$^{2+}$ layers. These two structures will be further compared in this paper.

EXPERIMENTAL

1. Sample Preparation and Characterization

Powder of NaBiO$_3\cdot n$H$_2$O (Nacalai Tesque Inc.) was placed in a teflon-lined autoclave (70 ml) with the rare earth nitrate R(NO$_3$)$_3\cdot n$H$_2$O (R: Y, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb) and H$_2$O (30 ml), which was heated at 120–200°C for 4 days. The molar ratio of NaBiO$_3\cdot n$H$_2$O and rare earth nitrate was varied from 0.25 to 8. The solid products were separated by centrifuging, washed with distilled water, and dried at 50°C. The products were identified by X-ray powder diffraction using Ni-filtered Cu$K\alpha$ radiation. The products were completely dissolved in a concentrated HCl and HNO$_3$ mixture, and the amounts of sodium, rare earth, and bismuth in the solution were analyzed by atomic absorption spectroscopy or inductively coupled plasma spectroscopy. The valence of bismuth was determined by idometric titration. The thermal stability was investigated by TG–DTA

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with a heating rate of 10°/min. The species evolved during TG–DTA measurement in a stream of He was analyzed by mass spectrometry.

2. Crystal Structure Refinement

For the structural refinement by neutron diffraction, intensity data were collected at 295 K on a high-resolution powder diffractometer at the Brookhaven National Laboratory. The data were recorded at intervals of 0.05° in 2θ from 10.00 to 156.75° using a wavelength of 1.8857 Å. Rietveld structural analysis was performed using the program RIETAN (11).

RESULTS AND DISCUSSION

1. Preparation

Single-phase $R\mathrm{Bi_2O_4NO_3}$ phases were obtained by reactions at 140–200°C for 2 days using the molar ratios of $R/\mathrm{Bi} = 0.5$–8 for R = Y, Sm, Eu, Gd, Tb, Dy, Er, Yb. The X-ray powder patterns were indexed in the tetragonal system with $a \sim 3.8$ Å and $c \sim 10.2$ Å as summarized in Table 1. The lattice parameters depend on the ionic radius of rare earth as shown in Fig. 1. From the chemical analysis, the molar ratio of Bi/R in the products was found to be two, and no sodium was detected. The mean valence of bismuth was determined to be three. Figure 2 shows the IR spectrum for the product of R = Y, and the strong absorption at 1380 $\mathrm{cm^{-1}}$ was assigned to the $(\mathrm{NO_3})^-$ group. The chemical analysis for R = Y is summarized in Table 2. The molar ratio of Bi/Y was independent of the preparative condition. As mentioned later, the weight loss was caused by the release of the nitrate group. Therefore, the chemical composition may be represented as $R\mathrm{Bi_2O_4NO_3}$.

The X-ray powder pattern of the product for R = Nd indicated that this product is isostructural with the lanthanum bismuth oxyhydroxide, $\mathrm{La_{0.26}Bi_{0.74}OOH}$ (2). The X-ray powder pattern of the product for R = Pr was similar to that of $R\mathrm{Bi_2O_4NO_3}$, however, several weak unindexed peaks were observed. The products for R = Ce were not well crystallized.

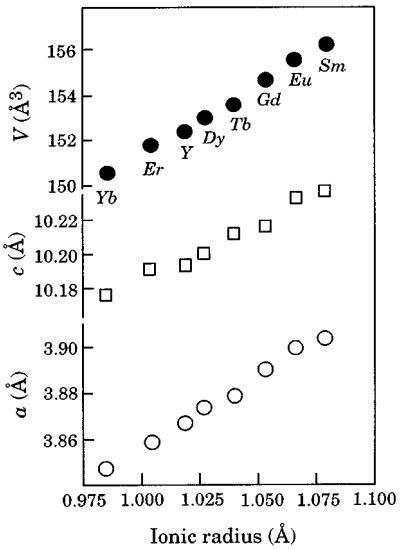

FIG. 1. Lattice parameters and unit cell volumes plotted against ionic radius of R ions for $R\mathrm{Bi_2O_4NO_3}$.

2. Thermal Behavior

Figure 3 shows the TG–DTA curves and gas evolution during the TG–DTA measurement for $\mathrm{YBi_2O_4NO_3}$. The one-step weight loss is observed above 400°C and is caused by the release of NO and $\mathrm{O_2}$. The observed weight loss (8.63 wt%) agrees well with the value (8.53 wt%) calculated on the assumption that the $\mathrm{NO_3}$ group is released from $\mathrm{YBi_2O_4NO_3}$. The X-ray powder pattern of the sample heated to 800°C corresponds to that of the cubic $\mathrm{(Y,Bi)_2O_3}$ (12).

TABLE 1
The Lattice Parameters and Unit Cell Volumes for $R\mathrm{Bi_2O_4NO_3}$

R	a (Å)	c (Å)	V (Å^3)
Sm	3.9038(1)	10.2370(5)	156.19
Eu	3.8996(1)	10.2331(7)	155.61
Gd	3.8905(1)	10.2163(6)	154.63
Tb	3.8790(2)	10.212(1)	153.66
Dy	3.8740(1)	10.2003(7)	153.08
Y	3.8671(1)	10.1930(3)	152.43
Er	3.8587(2)	10.1914(7)	151.75
Yb	3.8470(1)	10.1762(7)	150.60

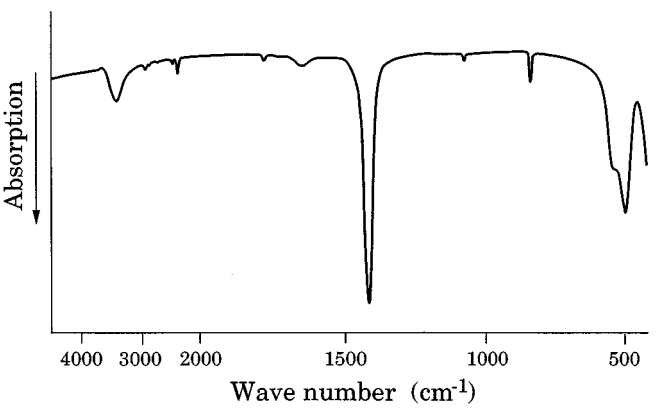

FIG. 2. Infrared spectrum for $\mathrm{YBi_2O_4NO_3}$.

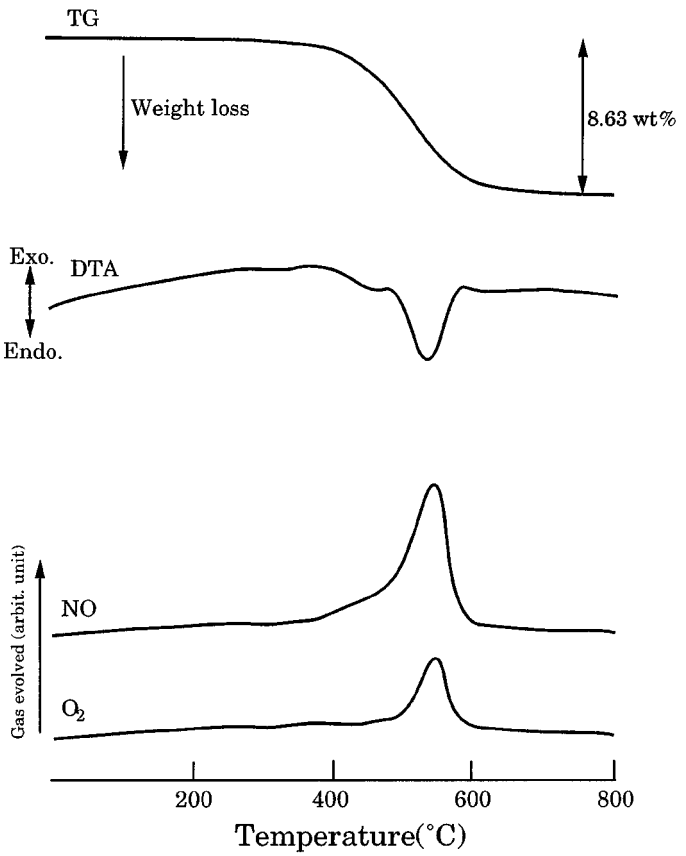

FIG. 3. TG–DTA curves and gas evolution during TG–DTA measurement for $YBi_2O_4NO_3$.

TABLE 2
Chemical Analysis $(Y, Bi)_3O_4NO_3$

	Y_2O_3	Bi_2O_3	Weight loss	Total
Calculated (wt%)	17.84	73.63	8.53	100.0
Observed (wt%)	17.00	74.28	8.63	99.91

3. *Crystal Structure*

The $RBi_2O_4NO_3$ composition may be considered a member of the M_3O_4X (M, metal; X, halogen) family in which $R'_xBi_{3-x}O_4X$ (R': La, Ce, Nd, Eu, Gd; X: Cl, Br, Se) and Bi_3O_4X (X: Cl, Br) are known (13). Their crystal structures are built up from a fluorite-type $(M_3O_4)^+$ layer and a single halogen layer. The former has the tetragonal cell with $a \sim 3.9$ Å and $c \sim 8.9$ Å and the latter is distorted to monoclinic. The similarity of cell dimensions of $RBi_2O_4NO_3$ and $R'_xBi_{3-x}O_4X$ suggests that the crystal structure of $RBi_2O_4NO_3$ can be derived by replacing the halogen atom in $R'_xBi_{3-x}O_4X$ with the $(NO_3)^-$ group.

The neutron diffraction pattern for $YBi_2O_4NO_3$ was indexed with the same tetragonal cell used for the X-ray powder pattern, and no extra diffraction peaks due to a superstructure were observed. No systematic absences for reflections were observed in the X-ray and neutron powder diffraction patterns; therefore, eight space groups with tetragonal symmetry are possible. Of these space groups $P4$ (No. 75) and $P4mm$ (No. 99) allow a structural model having a set of $(M_3O_4)^+$ layers and $(NO_3)^-$ groups as in the crystal structure of $R'_xBi_{3-x}O_4X$. The Rietveld structural refinement using the neutron diffraction data led to reasonable R factors; $R_{WP} = 4.47$, $R_P = 3.40$, $R_I = 5.67$, and $R_F = 4.68\%$ for $P4$ and $R_{WP} = 4.35$, $R_P = 3.29$, $R_I = 5.39$, and $R_F = 4.40\%$ for $P4mm$. However, in the case of $P4$ the refined positional parameters of one oxygen in the $(NO_3)^-$ group, in which the starting positions of oxygen atoms were estimated from N–O distance, had unreasonable values. Therefore, the structural model using the space group $P4mm$

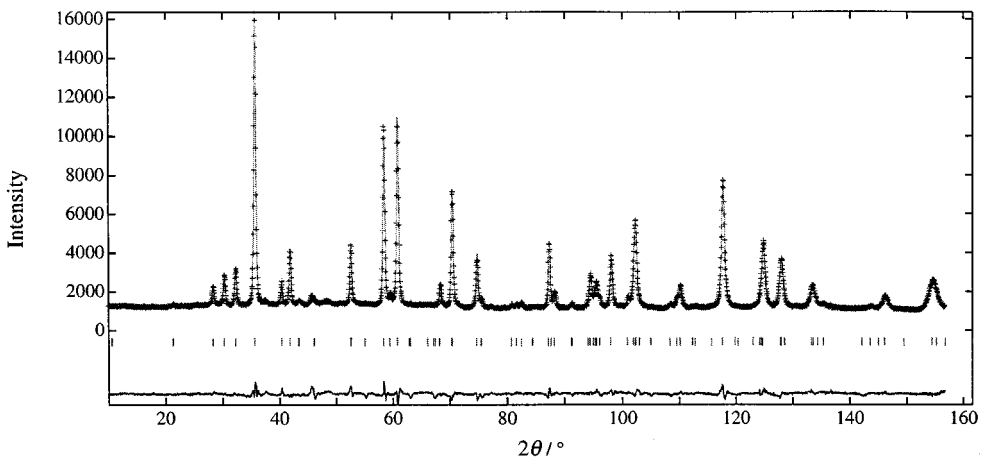

FIG. 4. Observed (dots), calculated (solid line), and difference (bottom) neutron diffraction profiles for $YBi_2O_4NO_3$.

TABLE 3
Crystal Data and Intensity Collection for $YBi_2O_4NO_3$

Color	Yellow
Crystal system	Tetragonal
Space group	*P*4*mm* (No. 99)
Z	1
Lattice parameters	$a = 3.8671(1)$, $c = 10.1930(3)$ Å
Volume	152.43 Å^3
Formula weight	632.83
Calculated density	6.89 g/cm^3
Wavelength	$\lambda = 1.8857$ Å
Temperature	23°C
2θ scan range	10.00–156.75°
R_{WP}	4.35%
R_P	3.29%
R_I	5.39%
R_F	4.40%

was adopted. Since the twofold axis of the $(NO_3)^-$ is parallel to the *c* axis (fourfold axis), two oxygen atoms of the $(NO_3)^-$ group in the *ab* plane must be statistically distributed in the 4*e* site. The occupancy of the oxygen atom at the 4*e* site refined to 0.48(6). Thus, the orientation of the $(NO_3)^-$ groups is an average in which the adjacent $(NO_3)^-$ groups stand at right angles to each other, and in this case the shortest O–O distance has a reasonable value of 2.98(2) Å as mentioned later. A similar average structure for $(NO_3)^-$ groups is also observed in $YONO_3$ (10).

Figure 4 shows observed and calculated neutron diffraction patterns. The crystallographic data and atomic parameters are summarized in Tables 3 and 4, respectively. Selected interatomic distances are listed in Table 5. As shown in Fig. 5, the crystal structure of $YBi_2O_4NO_3$ is built up by alternate stacking of $(M_3O_4)^+$ layers and $(NO_3)^-$ groups along the *c* axis. There are three kinds of metal atom sites in the $(M_3O_4)^+$ layer. Yttrium atoms at the center of the layer are coordinated by eight oxygen atoms to form a cube with interatomic distances of 2.38(3) and 2.40(3) Å. Two bismuth atoms have similar environments with eight

TABLE 4
Positional and Thermal Parameters (Å) for $YBi_2O_4NO_3$

Atom	Site	Occupancy	*x*	*y*	*z*	B_{iso}
Y	1a	1	0	0	0	0.4(2)
Bi(1)	1*b*	1	0.5	0.5	0.240(5)	0.9(7)
Bi(2)	1*b*	1	0.5	0.5	0.748(5)	0.7(9)
O(1)	2*c*	1	0.5	0	0.864(5)	0.8(7)
O(2)	2*c*	1	0.5	0	0.139(6)	0.5(6)
O(3)	1*a*	1	0	0	0.369(6)	2.8(8)
O(4)	4*e*	0.48(6)	0.284(9)	0	0.550(6)	3(1)
N	1*a*	1	0	0	0.497(6)	0.3(4)

TABLE 5
Selected Interatomic Distances (Å) for $YBi_2O_4NO_3$

Y–O(1)	2.38(3) ×4	Bi(1)–O(2)	2.19(2) ×4
O(2)	2.40(3) ×4	O(3)	3.03(2) ×4
mean	2.39	mean	2.61
O(1)–O(1)	2.734 ×4	O(2)–O(2)	2.734
O(2)–O(2)	2.734 ×4	O(3)–O(3)	3.867
Bi(2)–O(1)	2.27(3) ×4	N–O(3)	1.30(6)
O(4)	2.92(4) ×4	O(4)	1.23(4) ×2
mean	2.60	mean	1.25
O(1)–O(1)	2.734 ×4	O(3)–O(4)	2.15(6) ×2
O(4)–O(4)	2.98(2) ×4	O(4)–O(4)	2.19(7)

oxygen atoms to form square antiprism. The square antiprism around the Bi(1) atom is formed by O(2) from the $(M_3O_4)^+$ layer and O(3) from the $(NO_3)^-$ group, and the interatomic distances are 2.19(2) and 3.03(2) Å, respectively. The square antiprism around the Bi(2) atom formed by O(1) and O(4) atoms is somewhat distorted, as shown in Fig. 6. The Bi(2)–O(1) and O(4) distances are 2.27(3) and 2.92(2) Å, and the O(4)–O(4) distance in this polyhedron corresponds to the shortest O–O distance between the adjacent $(NO_3)^-$ groups. In the $(NO_3)^-$ group, the N–O distances are 1.23(4) and 1.30(6) Å, agreeing well with the N–O distances of 1.23(3)–1.28(2) in $Bi(NO_3)_3 \cdot 5H_2O$, which were determined by using single-crystal X-ray diffraction data (14).

The $R'_xBi_{3-x}O_4X$ solid solution has a wide range ($1 \le x \le 2$) in contrast to $YBi_2O_4NO_3$. In the case of $Nd_{0.5}Bi_{2.5}O_4Cl$ ($x = 0.5$), neodymium and bismuth atoms are statistically distributed at the site with the eightfold coordination. The refinement of the disordered model for $YBi_2O_4NO_3$ led to $R_{WP} = 4.20$, $R_P = 3.18$, $R_I = 4.16$, and $R_F = 3.03\%$, being somewhat better than those for the ordered model. However, the mean metal–oxygen distance

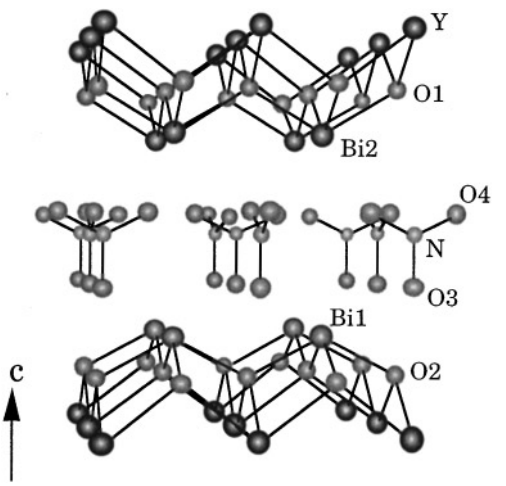

FIG. 5. Crystal structure of $YBi_2O_4NO_3$.

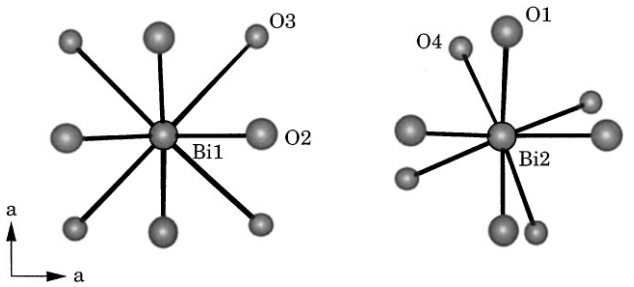

FIG. 6. Coordination environments around Bi(1) and Bi(2) atoms.

(2.39 Å) for one of three metal sites was shorter than those (2.60 and 2.63 Å) for the other sites as observed in the ordered model. By taking into account the difference between ionic radii of yttrium and bismuth and the chemical composition of Bi/Y = 2, the ordered model is considered to be reasonable.

The Sillen structures are based on $(Bi_2O_2)^{2+}$ layers and are classified by the way of stacking $(Bi_2O_2)^{2+}$ layers (M) and halide layers (X); for example, the $X1$ structure can be described as the stacking of layers in sequence -M–X–M- as found in $CaBiO_2Cl$, and the $X2$ has the -M–X–X–M- sequence as in BiOCl (15). A bismuth oxycarbonate, $Bi_2O_2CO_3$, also has the Sillen structure and belongs to the $X1$ structure (16). There are many bismuth oxyhalides distinct from the Sillen structures, such as, $BiM_3O_3Cl_3$ (M = Ca, Sr) (17) and Bi_3PbWO_8Cl (18). Tha latter is one of bipox structure series compounds with a mixed Aurivillius–Sillen structure. Also, $R'_xBi_{3-x}O_4X$ and $RBi_2O_4NO_3$ do not have the Sillen structure, however, the $(M_3O_4)^+$ layer in $R'_xBi_{3-x}O_4X$ and $RBi_2O_4NO_3$ can be derived by insertion of $(MO)^-$ layers into the $(Bi_2O_2)^{2+}$ layers of the Sillen structure. In this respect these compounds may be regarded as a derivative of the Sillen structure.

CONCLUSION

New rare earth bismuth oxynitrates $RBi_2O_4NO_3$ (R: Y, Sm, Eu, Gd, Tb, Dy, Er, Yb) were prepared with low temperature hydrothermal reactions. The crystal structure of $RBi_2O_4NO_3$ is based on $(RBi_2O_4)^+$ and $(NO_3)^-$ layers and is derived by replacing the halogen atoms in $R'_xBi_{3-x}O_4X$ with $(NO_3)^-$ groups. $RBi_2O_4NO_3$ phases are the first examples of a $R'_xBi_{3-x}O_4X$-type structure where X is a $(NO_3)^-$ group.

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