JOURNAL OF SOLID STATE CHEMISTRY **116**, 281–285 (1995)

# Crystal Structure of $Bi_2O_4$ with $\beta$-$Sb_2O_4$-Type Structure

N. Kumada[1] and N. Kinomura

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

and

P. M. Woodward and A. W. Sleight

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003*

Received July 25, 1994; in revised form October 19, 1994; accepted October 24, 1994

A new mixed valent bismuth oxide, $Bi^{3+}Bi^{5+}O_4$, was prepared by a low temperature hydrothermal reaction using a hydrated sodium bismuth oxide, $NaBiO_3 \cdot nH_2O$, as a starting material. This oxide is isostructural with $\beta$-$Sb_2O_4$ and the lattice parameters are $a$ = 12.3668(2), $b$ = 5.1180(1), $c$ = 5.5670(1) Å and $\beta$ = 107.838(1)° in the monoclinic system. The crystal structure was refined using high resolution neutron powder diffraction data resulting in $R_{WP}$ = 7.76, $R_P$ = 6.01, $R_E$ = 5.98, and $R_I$ = 2.02%. In this mixed valent bismuth oxide, $Bi^{3+}$ and $Bi^{5+}$ occupy distinct crystallographic sites, $Bi^{3+}$ being coordinated by eight oxygens and $Bi^{5+}$ being octahedrally coordinated by six oxygens. The structure can be related to the $CaF_2$-type structure. This mixed valent bismuth oxide decomposes to $Bi_2O_3$ via an intermediate phase with mixed valent states with weight loss caused by reduction of $Bi^{5+}$ to $Bi^{3+}$ at elevated temperatures.

## INTRODUCTION

Bismuth is known to adopt trivalent or pentavalent states in oxides. Mixed valent states for bismuth have been found in complex alkaline and/or alkaline earth bismuth oxides (1–4), and some of them are superconductors, for example, $(Ba \cdot K)BiO_3$ (3) and $Ba(Bi \cdot Pb)O_3$ (4). Simple mixed valent bismuth oxides, such as $Bi_4O_7$ and $Bi_2O_4$, have been reported (5, 6), but they remain poorly characterized. Begemann and Jansen (6) reported that $Bi_2O_4$ and $Bi_4O_7$, prepared by thermal decomposition of $HBiO_3 \cdot nH_2O$, have cubic $CaF_2$-type and triclinic pyrochlore type structures, respectively. However, structure refinements of these two oxides have not yet been given. In fact, no detailed structure has been reported for any simple mixed valent bismuth oxide. Mixed valent bismuth complex oxides, $BaBiO_3$ (1) and $Na_2Bi_4^{3+}Bi^{5+}AuO_{11}$ (7) are examples of the mixed valent bismuth oxide which was identified with distinct sites of $Bi^{3+}$ and $Bi^{5+}$.

We have reported that new alkaline earth bismuth oxides containing $Bi^{5+}$ with the pyrochlore-type structure were prepared by a low temperature hydrothermal reaction using the hydrated sodium bismuth oxide $NaBiO_3 \cdot nH_2O$ as a starting material (8). Two types of new bismuth oxides, $La_{0.26}Bi_{0.74}OOH$ (9) and $HBi_3(CrO_4)_2O_3$ (10), were also prepared by the same method. During the investigation of this reaction using $NaBiO_3 \cdot nH_2O$, we found a new mixed valent bismuth oxide, $Bi^{3+}Bi^{5+}O_4$ with $\beta$-$Sb_2O_4$-type structure, in contrast to a $CaF_2$-type $Bi_2O_4$ as prepared previously (5, 6). We describe here preparation and thermal behavior of this mixed valent bismuth oxide and its crystal structure refinement using high resolution neutron powder diffraction data.

## EXPERIMENTAL

The starting material of $NaBiO_3 \cdot nH_2O$ (Kanto Chemical) was put into an autoclave (70 ml) with a Teflon lining with alkaline nitrate $ANO_3$ ($A$ = Li, Na, K) and $H_2O$ (30 ml) and was heated at 120 ~ 200°C for 2 ~ 15 days. The molar ratio of the starting material and alkaline nitrate was varied from 0.1 to 100. The solid products were separated by centrifuging, washing with distilled water, and drying at 50°C. The products were identified by X-ray powder diffraction using Cu$K\alpha$ radiation. The thermal stability was investigated by TG-DTA with a heating rate of 10°/min. The species evolved during TG-DTA measurement in a stream of He was analyzed by mass spectrometry. 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 0.02° intervals in 2$\theta$ from 15° to 115° using a wave length of 1.8857 Å. The

---

[1] To whom correspondence should be addressed.

0022-4596/95 $6.00

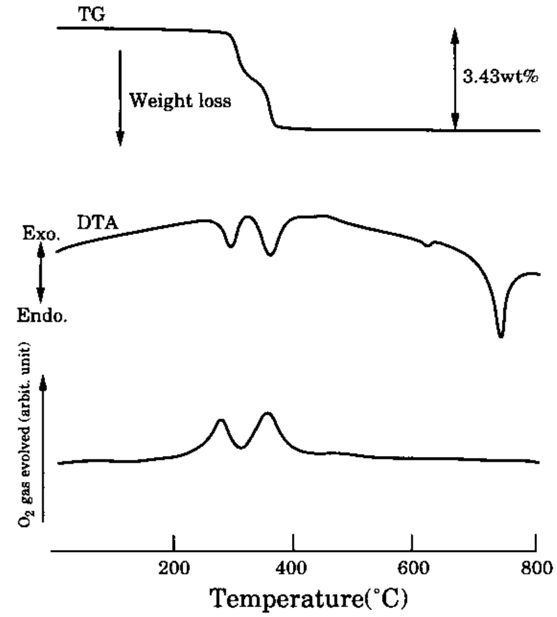

FIG. 1. The TG–DTA curves and temperature dependence of gas evolution during the TG–DTA measurement in a stream of He.

Rietveld structural analysis was performed using the program RIETAN (11).

## RESULTS AND DISCUSSION

### *Preparation*

The new bismuth dioxide, monoclinic $Bi_2O_4$, was obtained under the conditions of the molar ratio of $A$/Bi > 0.5, the reaction temperature of 140°C, and the reaction duration of 4 days. When the reaction temperature was above 160°C, another mixed valent bismuth oxide similar to $Bi_4O_7$ (6) was obtained as described elsewhere (12). Atomic absorption spectrometry indicated that no alkaline metal was detected in a solution formed by dissolution of the product with concentrated $HNO_3$. However, the products always contained a small amount of a second phase. The Rietveld analysis was performed on a selected sample which gave the weakest peaks of the second phase. The powder diffraction pattern of our $Bi_2O_4$ could be indexed on the basis of a monoclinic unit cell similar to that of $\beta$-$Sb_2O_4$.

### *Thermal Behavior*

Figure 1 shows TG–DTA curves of $Bi_2O_4$ and mass spectrometry during TG–DTA measurement. The TG curve indicates two steps of weight losses and only oxygen is evolved in the course of pyrolysis. The observed weight loss (3.43 wt%) agreed well with the value (3.32 wt%) calculated on the assumption that $Bi_2O_4$ changed to $Bi_2O_3$ by release of oxygens caused by complete reduction of $Bi^{5+}$ to $Bi^{3+}$. The X-ray powder pattern of the sample heated up to the first weight loss was similar to that of another mixed valent bismuth oxide prepared at above 160°C (12). Finally this compound decomposed to $\alpha$-$Bi_2O_3$ (13) by complete reduction of $Bi^{5+}$ to $Bi^{3+}$. The small exothermic peak observed at about 600°C in the DTA curve may indicate that the existence of a small amount of impurity and the exothermic peak at 730°C are corresponding to the phase transition from $\alpha$ to $\delta$-$Bi_2O_3$ (14).

### *Crystal Structure Refinement*

The crystal structure of $Bi_2O_4$ was refined using space group $C2/c$ (No. 15) of $\beta$-$Sb_2O_4$ (15), and the final $R$-factors were $R_{WP}$ = 9.41, $R_P$ = 6.64, $R_E$ = 6.00, and $R_I$ = 2.95% for all the intensity data. By excluding the peaks of the impurity phase, the $R$-factors decreased to $R_{WP}$ = 7.76, $R_P$ = 6.01, $R_E$ = 5.98, and $R_I$ = 2.02%. The crystallographic data is summarized in Table 1. Figure 2 shows the observed and calculated neutron diffraction patterns. Tables 2 and 3 show the atomic parameters and selected interatomic distances and angles, respectively.

There are two crystallographic sites for bismuth (4c and 4e) in this structure. At site 4c, bismuth is octahedrally coordinated by six oxygens at a mean distance of 2.101 Å. At site 4e, bismuth is surrounded by four oxygens located at 2.1–2.3 Å and four more oxygens located at 2.8–3.0 Å. By taking into account the difference in ionic radii of trivalent and pentavalent bismuth and the effect of a stereoactive electron lone pair of $Bi^{3+}$, the 4c site for Bi(1) is considered to be occupied by $Bi^{5+}$ and the 4e site for Bi(2) by $Bi^{3+}$.

In this structure the $Bi^{5+}O_6$ octahedra form layers parallel to (100) by sharing four corners with each other. The $Bi^{3+}$ ions are located in the interlayer positions as shown

TABLE 1

Crystal Data and Intensity Collection for $Bi_2O_4$

| | |
|---|---|
| Color | Reddish brown |
| Crystal system | Monoclinic |
| Space group | $C2/c$ (No. 15) |
| $Z$ | 4 |
| Lattice parameters | $a$ = 12.3668(2), $b$ = 5.1180(1)<br>$c$ = 5.5670(1) Å, $\beta$ = 107.838(1)° |
| Volume | 335.42 Å$^3$ |
| Formula weight | 481.96 |
| Calculated density | 9.55 g/cm$^3$ |
| Wavelength | $\lambda$ = 1.8857 Å |
| Temperature | 23°C |
| $2\theta$ scan range | 15°–115° |
| $R_{WP}$ | 7.76% |
| $R_P$ | 6.01% |
| $R_E$ | 5.98% |
| $R_I$ | 2.02% |

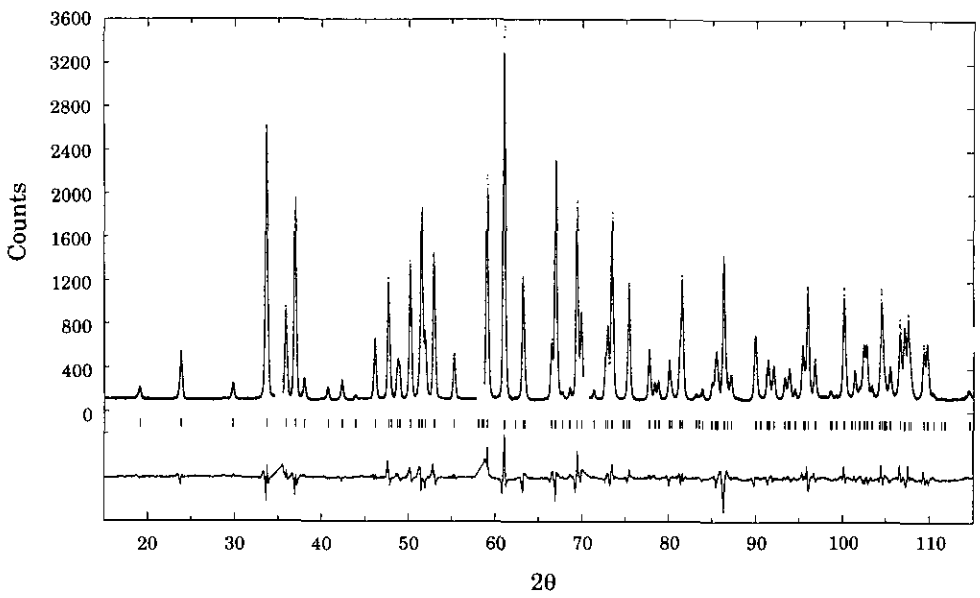

*FIG. 2. Observed (dots), calculated (solid line), and difference (at the bottom) neutron diffraction profiles for $Bi_2O_4$.*

in Fig. 3. The structure projected on (001) is shown in Fig. 4. The dotted lines forming a square in this figure indicate one half of the unit cell. By comparing this half cell and the structure of $CaF_2$ shown on the right side, one can see the close relationship between the two structural types. In the structure of the monoclinic $Bi_2O_4$, oxygens which are superposed in the projection of the $CaF_2$-type structure are displaced so that the $Bi^{5+}$ ion is octahedrally coordinated and the coordination polyhedron of $Bi^{3+}$ is distorted cubic. The octahedral coordination for the $Bi^{5+}$ ion is derived from the cubic coordination in the $CaF_2$-type structure by a strong displacement of two cubic neighbors sited body-diagonally. Removal of such oxygens from the fluorite structure result in octahedral coordination in the C-type rare earth sesquioxides structure. As the average coordination number of bismuth decreases, so must the average coordination number of oxygen decrease. In the $CaF_2$ structure, the anion is surrounded by a perfect tetrahedron of cations. In monoclinic $Bi_2O_4$, the coordination number of one oxygen (O1) remains four as a highly distorted tetrahedron. The coordination of the other oxygen (O2) has, however, dropped to three. It thus appears that many simple bismuth oxides have structures which may be considered as fluorite related. Cubic cell edges reported are $a$ = 5.6595 Å for $\delta$-$Bi_2O_3$ (*14*), 5.4754 Å for $BiO_{2-x}$, and 5.5390 Å for $BiO_2$ (*6*).The relevant edges of monoclinic $Bi_2O_4$ are $(a \times \sin \beta)/2$ = 5.8861, $b$ = 5.1180, and $c$ = 5.5670 Å which give a $(V/2)^{1/3}$ of 5.515 Å.

The coordinations of $Bi^{3+}$ and $Bi^{5+}$ and the interatomic distances between bismuth and oxygen in mixed valent bismuth oxides are summarized in Table 4. The mean interatomic distance (2.101 Å) of $Bi^{5+}$–O in monoclinic $Bi_2O_4$ corresponds to those of other mixed valent bismuth oxides, and these values also agree well with that (2.10 Å) in $KBiO_3$ (*16*). The coordination polyhedron around

TABLE 2

**Positional and Thermal Parameters (Å$^2$) of $Bi_2O_4$**

| Atom | Site | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|---|
| Bi(1) | 4c | $\frac{1}{4}$ | $\frac{1}{4}$ | 0 | 0.6(1) |
| Bi(2) | 4e | 0 | 0.268(1) | $\frac{1}{4}$ | 1.2(1) |
| O(1) | 8f | 0.1787(5) | 0.063(1) | 0.652(1) | 1.5(2) |
| O(2) | 8f | 0.0933(5) | 0.416(1) | 0.973(1) | 1.3(1) |

TABLE 3

**Selected Interatomic Distances (Å) and Angles (°) of $Bi_2O_4$**

| | |
|---|---|
| Bi(1)–O(1) 2.080(5) × 2 | Bi(2)–O(2) 2.145(7) × 2 |
| –O(1) 2.100(6) × 2 | –O(2) 2.316(5) × 2 |
| –O(2) 2.123(5) × 2 | –O(1) 2.823(6) × 2 |
| mean 2.101 | –O(1) 2.965(7) × 2 |
| | mean 2.562 |
| O(1)–Bi(1)–O(1) 85.1(1) | O(1)–Bi(2)–O(1) 59.1(1) |
| O(1)–Bi(1)–O(1) 94.9(1) | O(1)–Bi(2)–O(1) 95.0(2) |
| O(1)–Bi(1)–O(2) 81.1(2) | O(1)–Bi(2)–O(2) 60.8(2) |
| O(1)–Bi(1)–O(2) 89.9(2) | O(1)–Bi(2)–O(2) 70.0(3) |
| O(1)–Bi(1)–O(2) 90.1(2) | O(1)–Bi(2)–O(2) 70.7(2) |
| O(1)–Bi(1)–O(2) 98.9(2) | O(1)–Bi(2)–O(2) 81.4(2) |
| | O(1)–Bi(2)–O(2) 82.5(4) |
| | O(1)–Bi(2)–O(2) 91.4(2) |

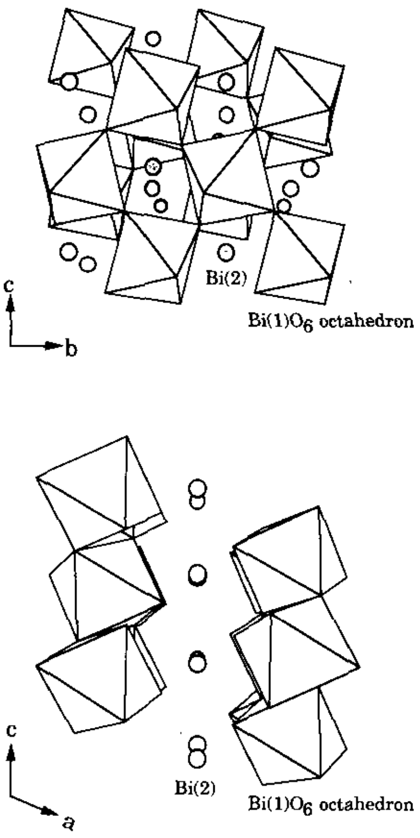

FIG. 3. Crystal structure of $Bi_2O_4$.

$Bi^{5+}$ in oxides is generally a regular octahedron with the $Bi^{5+}$–O distance of ~2 Å.

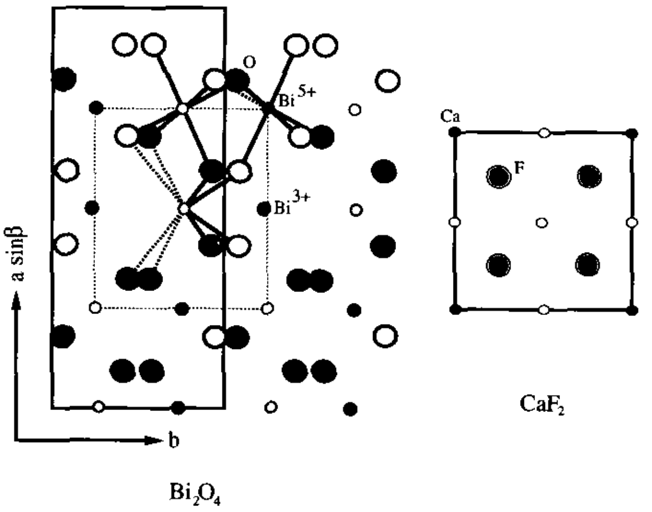

FIG. 4. Comparison of crystal structures between $Bi_2O_4$ and $CaF_2$. Solid lines denote the unit cell.

TABLE 4
**Coordinations of $Bi^{3+}$ and $Bi^{5+}$ in Mixed Valent Bismuth Oxides**

| Compounds | Structural type | Coordination of $Bi^{3+}$ | Coordination of $Bi^{5+}$ | Reference |
|---|---|---|---|---|
| $BaBiO_3$ | Perovskite | Octahedral 2.26–2.29 Å | Octahedral 2.11–2.14 Å | (1) |
| K–Bi–O | Pyrochlore | Octahedral 2.10 Å<br>Eightfold 2.37–3.14 Å | Octahedral 2.10 Å | (2) |
| Sr–Bi–O | Pyrochlore | Octahedral 2.23 Å<br>Eightfold 2.38–2.57 Å | Octahedral 2.23 Å | (8) |
| $Na_2Bi_5AuO_{11}$ | Tetragonal bronze-related structure | Sevenfold 2.10–3.21 Å | Octahedral 1.932–2.03 Å | (7) |
| $Bi_2O_4$ | $\beta$-$Sb_2O_4$ | Eightfold 2.145–2.965 Å | Octahedral 2.080–2.123 Å | This work |

The interatomic distances of $Bi^{3+}$–O in the irregular cubic coordination of monoclinic $Bi_2O_4$ are classified in two groups; one has short distances of 2.145 (×2) and 2.316 Å (×2) and the other longer distances of 2.823 (×2) and 2.965 Å (×2). These values correspond to the two distinct ranges, 2.08–2.29 and 2.48–2.80 Å, observed in $\alpha$-$Bi_2O_3$ (13). This irregular coordination for $Bi^{3+}$ ion is observed also in many compounds containing $Bi^{3+}$ ion such as $Na_2Bi_5AuO_{11}$ (7) and is caused by the lone pair of electrons on $Bi^{3+}$. In contrast with this, the coordination of $Bi^{3+}$ ion in pyrochlore-type compounds and $BaBiO_3$ is unusual, because $Bi^{3+}$ ion is not located at the coordination polyhedron mentioned above and has unusually short $Bi^{3+}$–O distances. In pyrochlore-type compounds, the $Bi^{3+}$ ion is distributed over the octahedral *B* site and the eightfold *A* sites, coexisting with $Bi^{5+}$ ion at the *B* sites and alkaline or alkaline earth ions at the *A* site, respectively. On the other hand, an octahedral site in $BaBiO_3$ is occupied only by $Bi^{3+}$ ion.

As seen in Table 5, the crystal structures of $A^{3+}B^{5+}O_4$-type compounds (*A* = Sb and Bi; B = Nb, Sb, Ta, and Bi) are classified into three groups of orthorhombic $\alpha$-, monoclinic $\beta$-, and triclinic $\beta$-phases (17), and also the high temperature $\gamma$-phase is found in $BiNbO_4$ and $BiTaO_4$ (18). The unit cell volume of the monoclinic $Bi_2O_4$ is largest in this family. The crystal structures of orthorhombic $\alpha$- and monoclinic $\beta$-phases are closely related to each other; however, the triclinic $\beta$-phase has a quite different structure from the other two (17). Thus there is a possibility of the existence of an $\alpha$-phase for $Bi_2O_4$ and a low temperature hydrothermal reaction may be a promising method to prepare it.

## CONCLUSION

A new mixed valent bismuth oxide, $Bi^{3+}Bi^{5+}O_4$ prepared by a low temperature hydrothermal reaction, was found to be isostructural with $\beta$-$Sb_2O_4$. It is noteworthy

TABLE 5

Crystal Structures of $A^{3+}B^{5+}O_4$-Type Compounds ($A$ = Sb, Bi; $B$ = Nb, Sb, Ta, Bi)

| | $Sb^{3+}$ | | | $Bi^{3+}$ | | | |
|---|---|---|---|---|---|---|---|
| | $Nb^{5+}$ | $Sb^{5+}$ | $Ta^{5+}$ | $Nb^{5+}$ | $Sb^{5+}$ | $Ta^{5+}$ | $Bi^{5+}$ |
| α-type | $SbNbO_4$<br>Orthorhombic<br>$V$ = 324.4 Å$^3$ | α-$Sb_2O_4$<br>Orthorhombic<br>$V$ = 307.5 Å$^3$ | $SbTaO_4$<br>Orthorhombic<br>$V$ = 321.0 Å$^3$ | α-$BiNbO_4$<br>Orthorhombic<br>$V$ = 330.9 Å$^3$ | | α-$BiTaO_4$<br>Orthorhombic<br>$V$ = 328.5 Å$^3$ | |
| β-type | | β-$Sb_2O_4$<br>Monoclinic<br>$V$ = 303.7 Å$^3$ | | β-$BiNbO_4$<br>Monoclinic<br>$V$ = 324.0 Å$^3$ | $BiSbO_4$<br>Monoclinic<br>$V$ = 309.6 Å$^3$ | β-$BiTaO_4$<br>Triclinic<br>$V$ = 323.1 Å$^3$ | $Bi_2O_4$<br>Monoclinic<br>$V$ = 335.42 Å$^3$ |
| γ-type | | | | γ-$BiNbO_4$<br>Monoclinic | | γ-$BiTaO_4$<br>Monoclinic<br>$V$ = 328.2 Å$^3$ | |

that monoclinic $Bi_2O_4$ is structurally related to other bismuth oxides, with or without mixed valence. This is the first crystal structure determination for any simple mixed valent bismuth oxide. These results indicate that low temperature hydrothermal reactions using $Bi^{5+}$-containing starting materials to prepare new bismuth oxides with mixed valence are effective.

## ACKNOWLEDGMENT

The neutron diffraction data were collected at the high flux beam reactor at Brookhaven National Laboratory which is supported by the Division of Materials Sciences, U.S. Department of Energy under Contract DE-AC02-76CH0016. This work was supported in part by NSF Grant DMR-9308530.

## REFERENCES

1. D. E. Cox and A. W. Sleight, *Solid State Commun.* **19,** 969 (1976).
2. J. Trehoux, F. Abraham, D. Thomas, C. Doremieux-Morin, and H. Arribart, *J. Solid State Chem.* **73,** 80 (1988).
3. R. Mattheiss, E. M. Gyorgy, and D. W. Johnson, *Phys. Rev. B* **37,** 3745(1988).
4. A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, *Solid State Commun.* **17,** 27 (1975).
5. G. Gattow and W. Klippel, *Z. Anorg. Allg. Chem.* **470,** 25 (1980).
6. B. Begemann and M. Jansen, *J. Less-Common Metals* **156,** 123 (1989).
7. J. Pannetier, D. Tranqui, and A. W. Sleight, *Mater. Res. Bull.* **27,** 1379 (1992).
8. N. Kumada, M. Hosoda, and N. Kinomura, *J. Solid State Chem.* **106,** 476 (1993).
9. N. Kumada, N. Kinomura, S. Kodialam, and A. W. Sleight, *Mater. Res. Bull.* **29,** 497 (1994).
10. S. Kodialam, N. Kumada, R. Mackey, and A. W. Sleight, *Eur. J. Solid State Inorg. Chem.* **31,** 739 (1994).
11. F. Izumi, *Kobutsugaku Zasshi* **17,** 37 (1985).
12. N. Kinomura and N. Kumada, *Mater. Res. Bull.*, in press.
13. G. Malmros, *Acta Chem. Scand.* **24,** 384 (1970).
14. H. A. Harwig, *Z. Anorg. Allg. Chem.* **444,** 151 (1978).
15. J. Amador, E. G. Puebla, M. A. Monge, I. Rasines, and C. R. Valero, *Inorg. Chem.* **27,** 1367 (1988).
16. S. Kodialam, V. C. Korthius, R. D. Hoffmann, and A. W. Sleight, *Mater. Res. Bull.* **27,** 1379 (1992).
17. E. T. Keve and A. C. Skapski, *J. Solid State Chem.* **8,** 159 (1973).
18. A. W. Sleight and G. A. Jones, *Acta Crystallogr. Sect. B* **37,** 2748 (1975).