JOURNAL OF SOLID STATE CHEMISTRY **92**, 473–479 (1991)

$BaBiO_{2.5}$, a New Bismuth Oxide with a Layered Structure*

P. LIGHTFOOT,†,‡ J. A. HRILJAC,§ SHIYOU PEI,† YING ZHENG,¶
A. W. MITCHELL,¶ D. R. RICHARDS,† B. DABROWSKI,†
J. D. JORGENSEN,¶ AND D. G. HINKS¶

†Science and Technology Center for Superconductivity and ¶Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439; §Department of Physics, Brookhaven National Laboratory, Upton, New York 11973; and ‡Department of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9 ST United Kingdom

Received October 1, 1990

A new Bi(III) oxide, $BaBiO_{2.5}$, has been prepared by slow-cooling of the perovskite-like $BaBiO_3$ in a reducing atmosphere. The structure was solved ab initio from a combination of synchrotron X-ray and pulsed neutron powder diffraction data. The phase crystallizes in the monoclinic space group $P2_1/c$, with $a = 7.3412(1)$ Å, $b = 7.5793(1)$ Å, $c = 6.0722(1)$ Å, and $\beta = 99.187(2)°$. A novel layer-type structure is adopted consisting of double BiO_x sheets in the *bc* plane separated by Ba ions along the *a* direction. Bi is four-coordinated in a pseudotrigonal bipyramidal environment, with the electron lone-pair occupying one of the equatorial sites, similar to that found in β-Bi_2O_3. There are, thus, significant differences from either the Aurivillius phases or the high-T_c bismuth cuprate superconductors, which may also be regarded as layered bismuth oxides.

Introduction

The perovskite-like $BaBiO_3$ has received much interest, initially due to its potential as a selective oxidation catalyst (*1*) and, more recently, since it is the parent compound of two series of superconductors, $BaBi_{1-x}Pb_xO_3$ ($T_c = 13$ K at $x = 0.7$) (*2*) and $Ba_{1-x}K_xBiO_3$ ($T_c = 30$ K at $x = 0.4$) (*3–5*).

$BaBiO_3$ crystallizes in a distortion of the perovskite structure, having a monoclinic cell containing two formula units and two crystallographically distinct Bi sites of different sizes. This may be regarded as a structural manifestation of the presence of a static charge density wave (CDW), or charge disproportionation, such that a more realistic formulation of this compound is $Ba_2Bi(III)Bi(V)O_6$ (*6–9*). Above room temperature, fully oxygenated $BaBiO_3$ undergoes two phase transitions, first to a rhombohedral phase, at about 132°C, and then to a cubic phase, above 500°C (*6, 10–12*). The static CDW is maintained in all of these phases.

Reduction of Bi(V) to Bi(III) may also occur, to give $BaBiO_{3-\delta}$ ($\delta = 0$–0.5) with δ being a function of temperature and oxygen partial pressure. The phase diagram (*10–13*)

---

* The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

0022-4596/91 $3.00

of $BaBiO_{3-\delta}$ shows the existence of three distinct regions of nonstoichiometry, with respect to temperature and oxygen partial pressure, for $\delta \sim 0.0$–0.05 (I), $\delta \sim 0.13$–0.27 (II), and $\delta \sim 0.42$–0.5 (III), respectively. The transition from phase I to phase II represents a change to higher symmetry from a doubled perovskite cell (*Fm*3*m*) to a simple perovskite-type (*Pm*3*m*), and may be associated with the loss of the static charge density wave, resulting from the reduction in oxygen stoichiometry (*10*). The phase II–phase III transformation appears more complex, and the exact nature of this structural change has yet to be elucidated, though phase III appears to be a pseudotetragonal perovskite.

In all of the above transformations, the basic perovskite-type structure of vertex-sharing BiO_6 octahedra is, however, maintained. In this paper we report the synthesis and characterization of a new fully reduced modification, $BaBiO_{2.5}$, where the perovskite substructure is lost completely, and a novel layer-like structure is formed. This new structure type has been solved ab initio by a combination of the complimentary techniques of high-resolution synchrotron X-ray powder diffraction and time-of-flight neutron powder diffraction.

Experimental

Synthesis and Characterization

A pure polycrystalline sample of stoichiometric $BaBiO_3$ was prepared according to our previous two-step procedure (*14*). Subsequent treatment of $BaBiO_3$ at 850°C in 0.1% O_2 overnight, followed by cooling at a rate of $1^\circ\ \mathrm{min}^{-1}$ to room temperature in an atmosphere of 0.05% O_2, resulted in an apparently homogeneous olive-green product. The stoichiometry of this phase was determined to be $BaBiO_{2.52(2)}$ by thermogravimetric reoxidation. The atmosphere for annealing and cooling was chosen to minimize any oxygen uptake on cooling. However, subsequent Rietveld analysis showed that a small amount of reoxidation had occurred on cooling. We also note that $BaBiO_{2.5}$ may be reoxygenated at 400°C in pure O_2, to give pure $BaBiO_3$.

Powder Diffraction Data Collection

Neutron powder diffraction data were collected on the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source, Argonne (*15*). An approximately 10-g sample was loaded in a cylindrical vanadium can, and data were collected for about 2 hr. Only the data from the high-resolution "backscattering" ($2\theta = 150^\circ$) detectors were used for subsequent data analysis.

Synchrotron X-ray powder diffraction data were collected at the Brookhaven National Synchrotron Light Source (NSLS) beamline X7A. A part of the sample of $BaBiO_{2.5}$ which had been used for the neutron diffraction experiment was ground in a glovebox under nitrogen and mounted in a flat-plate sample holder covered with a 2-mil Be foil. Data were collected using a Si(111) channel-cut monochromator and a Ge(220) analyzer crystal, at a wavelength of 1.19971 Å, at 0.008° step intervals over an angular range of 3 to 70° in 2θ. The incident intensity was monitored with an ion chamber located just before the sample, and the data were scaled to counts-per-second relative to a 100-mA ring current.

Structure Solution and Refinement

Initial inspection of the raw neutron diffraction data showed that the phase was considerably different than the original perovskite-like $BaBiO_3$. The powder pattern could not be indexed by any simple distortion of the basic perovskite cell, nor could any apparently isotypic phase be found. Consequently, an attempt was made to index the cell using automated methods. The positions of 22 carefully measured reflections from the neutron data, in the *d*-spacing range 2.3–5.3 Å, were used as input for the autoindexing program ITO (*16*). The first 20 lines were successfully indexed on the basis of a primitive monoclinic cell of approximate dimensions $a = 7.34$ Å, $b = 7.58$ Å, $c = 6.07$ Å, $\beta = 99.23°$, giving a figure-of-merit (*17*), $M_{20} = 29$. Inspection of the whole profile suggested that all the observable peaks could be satisfactorily indexed by this unit cell, in the space group $P2_1/c$. However, due to the relatively limited resolution of the SEPD data, it was anticipated that insufficient individual peak intensities could be extracted to make a structure solution feasible from these data. Therefore, additional high-resolution X-ray data were collected at the NSLS. It was hoped that this would allow the extraction of sufficient unique intensity data to allow at least a partial structure determination, followed by combined use of the X-ray and neutron data to solve and refine the structure completely. Such a technique has recently been used to solve the structure of $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$, for example (*18*).

Close inspection of the X-ray data revealed that there were several weak peaks which were not accounted for by the monoclinic cell. Therefore, those clearly observed reflections with 2θ values less than 50° were individually fitted to pseudo-Voigt peak shapes to obtain accurate positions. Attempts to index all of the reflections on a single cell using the autoindexing programs ITO (*16*) and TREOR-4 (*19*) failed. When the questionable peaks were omitted from the input into TREOR-4, a primitive monoclinic cell with dimensions $a = 7.3417(9)$, $b = 7.5847(6)$, $c = 6.0724(5)$ A, $\beta = 99.19(1)°$ was obtained, with $M_{20} = 67$ and $F_{20} = 118$ (*20*). This cell agrees well with the one obtained from the neutron diffraction data, and was assumed to be correct. All the weaker peaks with an intensity greater than 0.5% of the strongest $BaBiO_{2.5}$ reflection were later assigned to a small amount of $BaBiO_3$ formed during the synthesis.

Integrated intensities were obtained by a full pattern decomposition method using a version of the PAWSYN program (*21*) which had been modified to include the Voigt peak shape (*22*). These were corrected for Lorentz polarization and multiplicity factors to obtain a set of 202 structure factors from 8–60° in 2θ, of which 78 were considered observed according to the criterion $F > 4\sigma(F)$. These were input into the SHELXS-86 (*23*) structure solution package, and the direct methods option was used. The positions of the Bi and Ba atoms were obtained from the E-map with the best figure-of-merit. These positions were then used as a starting model for a Rietveld refinement (*24*) of the X-ray data using GSAS (*25*), and subsequent difference Fourier syntheses were used to locate O(1) and O(2). Repeated attempts to locate the third oxygen atom from the X-ray data were unsuccessful. In addition, the positional parameters for O(2) were very unstable in these refinements, and gave unreasonably short (2.2 Å) Ba–O contacts. The agreement factors ($R_{wp} = 25.0\%$, $R_{exp} = 14.4\%$), however, indicated that the gross features of the structure were correct.

At this stage, the model obtained from the

TABLE I

REFINED STRUCTURAL PARAMETERS FOR $BaBiO_{2.5}$

Atom	Site	x	y	z	$B(Å^2)$
Ba	4*e*	0.8640(4)	0.0761(3)	0.2302(4)	0.45(5)
Bi	4*e*	0.3700(2)	0.1210(2)	0.2737(3)	0.49(3)
O1	2*b*	$\frac{1}{2}$	0	0	1.18(8)
O2	4*e*	0.8071(3)	0.0900(3)	0.7208(4)	0.99(5)
O3	4*e*	0.1805(3)	0.2526(3)	0.0404(4)	0.75(4)

Note. Space group $P2_1/c$, $Z = 4$, $a = 7.3412(1)$, $b = 7.5793(1)$, $c = 6.0722(1)$ Å, $\beta = 99.187(2)°$.

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR $BaBiO_{2.5}$

Ba–O1	2.870(3)	Bi–O1	2.241(2)
Ba–O2	3.056(3)	Bi–O2	2.064(3)
Ba–O2	3.076(4)	Bi–O3	2.075(3)
Ba–O2	2.697(4)	Bi–O3	2.489(3)
Ba–O2	2.564(3)		
Ba–O3	3.061(4)	O1–Bi–O2	92.22(9)
Ba–O3	2.973(3)	O1–Bi–O3	90.51(9)
Ba–O3	2.865(4)	O1–Bi–O3	171.39(9)
Ba–O3	3.039(3)	O2–Bi–O3	91.6(1)
		O2–Bi–O3	82.5(1)
		O3–Bi–O3	82.89(9)

Note. Space group $P2_1/c$, $Z = 4$, $a = 7.3412(1)$, $b = 7.5793(1)$, $c = 6.0722(1)$ Å, $\beta = 99.187(2)°$.

X-ray data was used in Rietveld refinements of the neutron data. The positional parameters of O(2) quickly converged to reasonable values, and a different Fourier was used to locate O(3). At this stage it became apparent that a small amount (~5%) of $BaBiO_3$ was present in the sample. Therefore, a two-phase refinement was carried out, using fixed parameters for $BaBiO_3$ in space group $I2/m$. This does not significantly affect the validity of the refinement. The refinement then converged smoothly to final agreement factors $R_{wp} = 5.31\%$, $R_{exp} = 3.32\%$. After completion of the neutron refinement, attempts were made to refine this model using the X-ray data. However, even with the complete structural model the oxygen atom positions could not be refined.

Description of the Structure

Final refined atomic coordinates from the neutron Rietveld refinement are given in Table I, with selected bond distances and angles in Table II. A plot of the final Rietveld profile is shown in Fig. 1. A general view of the structure is given in Fig. 2, from which the layer-like nature is apparent. Bi is coordinated by four O atoms (Fig. 3a) in what may be described as a pseudotrigonal bipyramidal geometry, where one equatorial position may be considered to be occupied by the stereochemically active lone pair of the Bi(III). This coordination is entirely reasonable for Bi(III), and indeed occurs in the binary oxide β-Bi_2O_3 (*26*). As in that case, the axial Bi–O1 and Bi–O3 bonds are significantly longer than the equatorial Bi–O2 and Bi–O3 bonds, and the in-plane O2–Bi–O3 angle (91.5°) is small, in agreement with the observations on a range of Bi(III) and Sb(III) compounds by Aurivillius and Malmros (*27*). A continuous Bi–O network is built up from these units, which are linked to give double BiO_x layers in the *bc* plane. Adjacent layers are separated in the *a* direction by intervening Ba atoms, in 9-coordination (five in-plane neighbors, three above and one below, Fig. 3b).

The layer-like nature of this structure invites comparison with two previously well-documented series of layered mixed oxides of Bi(III), namely the Aurivillius phases (*28*), formulated as $(Bi_2O_2)A_{m-1}B_mO_{3m+1}$, for example $Bi_2SrNb_2O_9$, and the high-T_c superconductors, $(BiO)_mSr_2Ca_{n-1}Cu_nO_{2n+2}$ (*29*) where m = 1or 2 and n = 1, 2, 3. In the Aurivillius phases, Bi lies at the apex of a square pyramid with four oxygen atoms, and these units are linked by sharing "edges" to form continuous Bi_2O_2 sheets. This contrasts significantly with the pseudotrigonal bipyramidal geometry found in the present phase, although both are clearly manifestations of the requirements of the Bi(III) lone pair. In the high-T_c superconductors, Bi is nominally in octahedral coordination in a rocksalt-like layer, although the environment is highly distorted and complicated by the presence of structural modulations and variable oxygen content (*30–32*). Although the layer sequence Ba–Bi–Bi–Ba, along the *a* direction in $BaBiO_{2.5}$, is reminiscent of the Sr–Bi–Bi–Sr

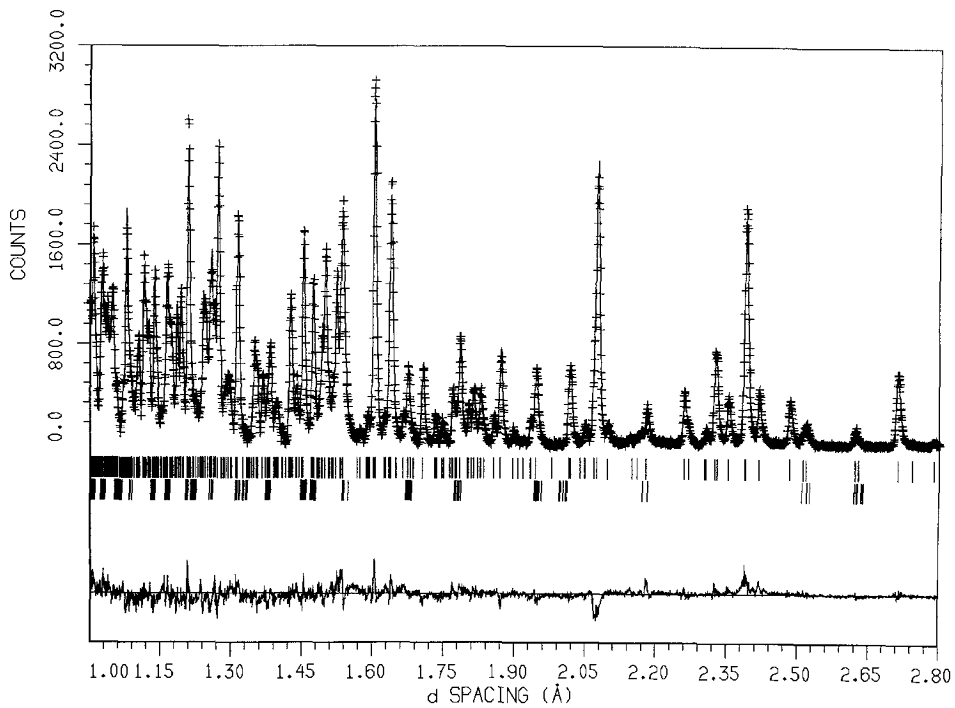

FIG. 1. Portion of the final Rietveld profile for $BaBiO_{2.5}$ neutron data. Plus marks (+) are the raw data, the solid line is the calculated profile. A difference (obs-calc) plot is shown beneath. Tick marks represent the positions of allowed reflections for $BaBiO_{2.5}$ (upper) and $BaBiO_3$ (lower). $BaBiO_3$ represents about 5% of the sample.

sequence in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, there is no further structural relationship apparent between the two.

Conclusions

A new Bi(III) oxide has been prepared by slow-cooling of the perovskite-like $BaBiO_3$ in a reducing atmosphere. Other highly reduced phases in this system have been synthesized (*13*), but are reported to be yellow or magenta colored. Unfortunately, since no X-ray powder diffraction patterns were reported for those phases, we are unable to say how they are related to the phase reported here.

The structure of the new phase has been solved ab initio by a combination of synchrotron X-ray and pulsed neutron powder

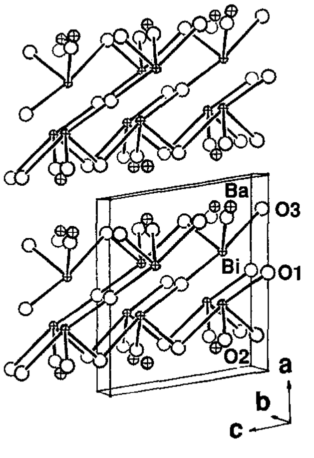

FIG. 2. Structure of $BaBiO_{2.5}$ viewed approximately along *b*.

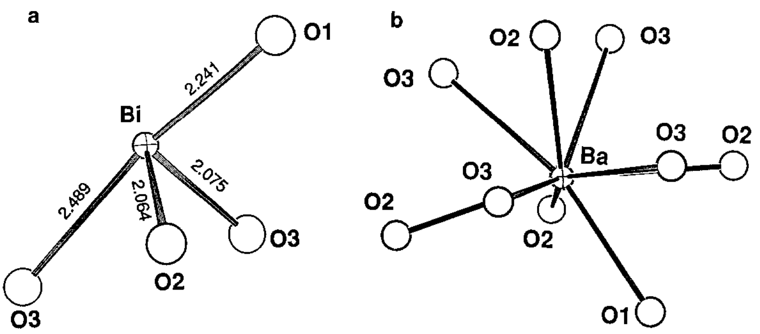

FIG. 3. (a) Local environment around Bi in $BaBiO_{2.5}$. The coordination polyhedron may be regarded as a trigonal bipyramid with one equatorial position occupied by the Bi $6s^2$ lone pair. (b) Local environment around Ba in $BaBiO_{2.5}$.

diffraction techniques. Both have been used independently in the past to solve structures from powder data; however, the inability of either technique alone to successfully determine and refine this structure emphasizes the complementarity of the two methods. We may note, in particular, the strength of the high-resolution X-ray data for locating the heavy atoms, but its lack of sensitivity to the determination of the oxygen atom positions in this case. The neutron diffraction data were essential to the *refinement* of the structure, but inadequate to *solve* the structure, due to the resolution limitations. However, given sufficient resolution, neutrons can be successful in structure solution by powder methods, as shown by Cheetham *et al.* in the case of $FeAsO_4$ (*33*).

The phase adopts a new layered structure type, unrelated to that of perovskite. Although the phase is not directly related structurally to the high-T_c bismuth cuprates, it represents a material where the bismuth environment is well characterized, and hence serves as a useful model to help understand the complex structural modulations and local bismuth–oxygen coordination environments present in those systems.

Acknowledgments

Work at Argonne is supported by the US Department of Energy, Division of Basic Energy Sciences, under Contract W-31-109-ENG-38 (J.D.J., D.G.H., Y.Z., A.W.M.) and the National Science Foundation, Science and Technology Center for Superconductivity, under Grant DMR-88-09854 (P.L., S.P., D.R.R., B.D.). J.A.H. acknowledges the U.S. Department of Energy, Division of Materials Sciences, under Contract DE-AC02-76CH00016. We also thank D. E. Cox for useful comments and for critically reviewing the manuscript.

References

1. R. A. BEYERLEIN, K. R. POEPPELMEIER, AND A. J. JACOBSON, 23rd Annual Spring Symposium of the Pittsburgh–Cleveland Catalysis Society, Paper B-2, Beachwood, Ohio, May 16–18, 1984.
2. A. W. SLEIGHT, J. L. GILLSON, AND P. E. BIERSTEDT, *Solid State Commun.* **17**, 27 (1975).
3. L. F. MATTHEISS, E. M. GYORGY, AND D. W. JOHNSON JR., *Phys. Rev. B* **37**, 3745 (1988).
4. R. J. CAVA, B. BATLOGG, J. J. KRAJEWSKI, R. C. FARROW, L. W. RUPP JR., A. E. WHITE, K. T. SHORT, W. F. PECK JR., AND T. Y. KOMETANI, *Nature* **332**, 814 (1988).
5. D. G. HINKS, B. DABROWSKI, J. D. JORGENSEN, A. W. MITCHELL, D. R. RICHARDS, SHIYOU PEI, AND DONGLU SHI, *Nature* **333**, 836 (1988).
6. D. E. COX AND A. W. SLEIGHT, *Solid State Commun.* **19**, 969 (1976).
7. G. THORNTON AND A. J. JACOBSON, *Acta Crystallogr. Sect. B* **34**, 351 (1978).
8. D. E. COX AND A. W. SLEIGHT, *Acta Crystallogr. Sect. B* **35**, 1 (1979).
9. C. CHAILLOUT, A. SANTORO, J. P. REMEIKA, A. S. COOPER, G. P. ESPINOSA, AND M. MAREZIO, *Solid State Commun.*, **65**, 1363 (1988).
10. S. PEI, J. D. JORGENSEN, D. C. HINKS, P. LIGHTFOOT, Y. ZHENG, D. R. RICHARDS, B. DABROW-

SKI, AND A. W. MITCHELL, *Mater. Res. Bull,* **25,** 1467 (1990).

11. H. SAKUMA, H. HASHIZUME, AND A. YAMANAKA, *Acta Crystallogr. Sect. B,* in press.
12. H. KUSUHARA, A. YAMANAKA, H. SAKUMA, AND H. HASHIZUME, *Jpn. J. Appl. Phys.* **28,** 678 (1989).
13. R. A. BEYERLEIN, A. J. JACOBSON, AND L. N. YACULLO, *Mater. Res. Bull.* **20,** 877 (1985).
14. D. G. HINKS, A. W. MITCHELL, Y. ZHENG, D. R. RICHARDS, AND B. DABROWSKI, *Appl. Phys. Lett.* **54,** 1595 (1989).
15. J. D. JORGENSEN, J. FABER JR., J. M. CARPENTER, R. K. CRAWFORD, J. R. HAUMANN, R. L. HITTERMANN, R. KLEB, G. E. OSTROWSKI, F. J. ROTELLA, AND T. G. WORLTON, *J. Appl. Crystallogr.* **22,** 321 (1989).
16. J. M. VISSER, *J. Appl. Crystallogr.* **2,** 89 (1969).
17. P. M. DEWOLFF, *J. Appl. Crystallogr.* **1,** 108 (1968).
18. M. A. LAFONTAINE, A. LEBAIL, AND G. FEREY, *J. Solid State Chem.* **85,** 220 (1990).
19. P.-E. WERNER, *Z. Kristallogr.* **120,** 375 (1964).
20. G. S. SMITH AND R. L. SNYDER, *J. Appl. Crystallogr.* **12,** 60 (1979).
21. G. S. PAWLEY, *J. Appl. Crystallogr.* **14,** 357 (1981).
22. M. S. LEHMANN, private communication.
23. G. M. SHELDRICK, *in* "Crystallographic Computing 3," (G. M. Sheldrick, C. Kruger and R. Goddard, Eds.), pp. 175–189, Oxford University Press, 1985.
24. H. M. RIETVELD, *J. Appl. Crystallogr.* **2,** 65 (1969).
25. A. C. LARSON AND R. B. VON DREELE, Los Alamos National Laboratory Report No. LA-UR-86-748 (1987).
26. S. K. BLOWER AND C. GREAVES, *Acta Crystallogr Sect. C* **44,** 587 (1988).
27. B. AURIVILLIUS AND G. MALMROS, *K. Tekn. Hogsk. Handl.* **291,** 544 (1972).
28. B. AURIVILLIUS, *Ark. Kemi* **2,** 519 (1950).
29. K. YVON AND M. FRANCOIS, *Z. Phys. B* **76,** 413 (1989).
30. C. C. TORARDI, J. B. PARISE, M. A. SUBRAMANIAN, J. GOPALAKRISHNAN, AND A. W. SLEIGHT, *Physica C* **157,** 115 (1989).
31. Y. LEPAGE, W. R. MCKINNON, J.-M. TARASCON, AND P. BARBOUX, *Phys. Rev. B* **40,** 6810 (1989).
32. Y. GAO, P. LEE, P. COPPENS, M. A. SUBRAMANIAN, AND A. W. SLEIGHT, *Science* **241,** 954 (1988).
33. A. K. CHEETHAM, W. I. F. DAVID, M. M. EDDY, R. J. B. JAKEMAN, M. W. JOHNSON, AND C. C. TORARDI, *Nature* **320,** (1986).