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A New Layered Bismuthate $(Sr,K)_3Bi_2O_7$: Synthesis and Crystal Structure

J. S. Pshirkov,*,† S. M. Kazakov,*,† C. Bougerol-Chaillout,† P. Bordet,† J. J. Capponi,†
S. N. Putilin,* and E. V. Antipov*

**Department of Chemistry, Moscow State University, Moscow 119899, Russia; and †Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble cedex 9, France*

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A new layered bismuth-based mixed oxide with appropriate composition $Sr_{1.5}K_{1.5}Bi_2O_7$ was synthesized at 300–450°C and $p(O_2) = 40$ bar. This phase is the second member of the Ruddlesden–Popper series $(Sr,K)_{n+1}Bi_nO_{3n+1}$. From X-ray powder diffraction, the structure was refined in the tetragonal space group *I4/mmm* with lattice constants $a = 4.1549(1)$ Å and $c = 21.8273(6)$ Å ($Z = 2$, $R_I = 0.08$, $R_P = 0.066$). However, electron diffraction patterns revealed the existence of additional weak reflections requiring a $\sqrt{2}a_p \times \sqrt{2}a_p \times c$ unit cell to be indexed. No superconducting signal was detected to 1.5 K. © 1999 Academic Press

Key Words: **mixed bismuth-based oxide; layered structure; X-ray powder diffraction; electron diffraction.**

INTRODUCTION

Since the discovery of superconductivity in the $Ba_{1-x}K_xBiO_3$ system with T_c as high as 30 K (1, 2), many synthesis attempts of new superconductors among bismuthates have been undertaken. However, since the structure of these oxides consists of a three-dimensional framework of BiO_6 octahedra, the variety of new possible bismuthates is not very wide. On the contrary, anisotropic layered structures such as those existing in copper-based superconductors would result in a larger number of compounds. Furthermore, a layered structure may favor higher superconducting transition temperatures, T_c, than a three-dimensional structure.

Layered oxides with general composition $Ba_{n+1}(Pb, Bi)_nO_{3n+1}$ were first reported by Fu *et al.* (3). The structure of these tetragonal Ruddlesden–Popper type phases consist of the alternate stacking along the *c* axis of perovskite-type $(Pb, Bi)O_2$ slabs and rocksalt-type BaO bilayers. Initial attempts to induce a metallic behavior and superconductivity in these materials via Bi–Pb substitution have been unsuccessful (4–6). Later on, Cava *et al.* performed the electrochemical synthesis of $Ba_{1.7}K_{1.3}Bi_2O_7$ (7). Even though the doping occurred then on the electronically inactive *A* site (1), no superconductivity was observed in this compound. This may be due to an inappropriate carrier concentration, which could not be changed, the Ba/K final ratio remaining constant whatever the synthesis conditions. Electronic band structure calculations for the $Ba_{1+x}K_{2-x}Bi_2O_7$ solid solution performed by Mattheiss (8) showed that a slight decrease of the Bi valence should provide more favorable conditions for superconductivity in this material.

Recently, we have reported the synthesis of a new family of superconducting bismuth oxides, $Sr_{1-x}M_xBiO_3$ (M = K, Rb, with $T_c \approx 12$ K for $0.45 \le x \le 0.65$, and $T_c \approx 13$ K for $x = 0.5$, respectively) having a three-dimensional perovskite type structure (9). As for the barium bismuthates, we have then focussed on the search for layered compounds in the Sr–K–Bi–O system. We report here the synthesis under high oxygen pressure and the crystal structure of a new layered bismuthate, $Sr_{1+x}K_{2-x}Bi_2O_7$ ($x \approx 0.6$).

EXPERIMENTAL

The samples were synthesized by a high oxygen pressure technique. First, $Sr_2Bi_2O_5$ was prepared by mixing a stoichiometric amount of $SrCO_3$ (Aldrich, purity > 99%) and Bi_2O_3 (Aldrich, 99.9%) and pelletizing and heating them at 650°C overnight, with repeats at 750°C for 64 h, 800°C for 5 h, and twice more at 850°C overnight. Stoichiometric amounts of $Sr_2Bi_2O_5$, KO_2 and Bi_2O_3 were mixed in a dry box filled with argon. The samples, with initial compositions $Sr_{1+x}K_{2-x}Bi_2O_7$ ($0 \le x \le 1$, $\Delta x = 0.25$), were then subjected to high oxygen pressure experiments performed in a steel autoclave (300–450°C under $p(O_2) = 40$–80 bar for 20 h).

X-ray powder diffraction experiments were carried out with a focusing Guinier camera FR-552 (Cu$K\alpha$ radiation, $\alpha = 1.54056$ Å; Ge was used as an internal standard) in order to identify the phases and determine the lattice

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parameters. X-ray powder diffraction spectra for crystal structure determination were collected on a STADI-P diffractometer (Cu$K\alpha_1$ radiation, curved Ge monochromator, transmission mode, scintillation counter).

Electron microscopy studies were performed with a Philips CM 300 transmission microscope operating at 300 kV and equipped with a Kevex Sigma system for EDS analysis.

The ac magnetic susceptibility was measured in the 1.5–300 K temperature range using a homemade mutual inductance bridge working with an external field of 0.01 Oe at a frequency of 119 Hz.

RESULTS AND DISCUSSION

The variation of the preparation conditions showed that a relatively low temperature (300–450°C) is crucial for a successful synthesis of $(Sr,K)_3Bi_2O_7$. At higher temperatures ($T > 450°C$), other phases (K-doped $SrBi_2O_4$, Bi_2O_3) appeared. Oxygen pressure was found to be an important parameter too. The layered phase was obtained when the oxygen pressure did not exceed 40–50 bar. Increasing the oxygen pressure stabilized the weberite-type structure phase, $Sr_2Bi_2O_7$ in which Bi is pentavalent (10), with a minor replacement of Sr by K. Variations of the synthesis time (10–50 h) did not give any noticeable change in the purity of the phase.

The variation of the K content in $Sr_{1+x}K_{2-x}Bi_2O_7$ ($0 \leq x \leq 1$) did not allow us to prepare pure layered phase. The best results (80% purity) were obtained for the starting composition $Sr_{1.5}K_{1.5}Bi_2O_7$ and the following synthesis conditions: annealing at 400°C for 18 h under oxygen pressure of 80 bar. The main impurities were found to be the perovskite phase $Sr_{1-x}K_xBiO_3$ (with $x \approx 0.7$, determined by EDS analysis), and $SrKBiO_4$. EDX analyses performed on several crystallites showed that the observed stoichiometry was close to $Sr_{1.3(1)}K_{1.8(2)}Bi_{1.9(1)}O_x$ and furthermore did not depend on the starting composition. The lattice parameters were also found to be practically independent on the nominal composition. These facts allow us to conclude that the composition range where the layered phase is formed is very narrow, at least in our synthesis conditions.

Magnetic measurements performed on the prepared samples down to 1.5 K did not show any sign of superconductivity.

The crystal structure of the layered bismuthate was determined from X-ray powder diffraction data. The reflections belonging to the phase were indexed in a body-centered tetragonal unit cell with parameters $a = 4.1549(1)$ Å and $c = 21.8273(6)$ Å. However, electron diffraction patterns showed the presence of weak superstructure reflections requiring a $\sqrt{2}a_p \times \sqrt{2}a_p \times c$ unit cell to be taken into account. Figure 1 gives the example of the ED pattern taking along the $[1\bar{1}1]$ zone axis. All reflections are compatible with the orthorhombic *Bmab* space group if one assumes that the crystallites are twinned in a way similar to that found in La_2CuO_4. As no splitting of the reflections was observed, the orthorhombicity is probably very small. It should be mentioned that similar weak superstructure reflections have been observed in $Ba_3(Pb_{1-x}Bi_x)_2O_7$ (6).

The structure refinement was performed using RIETAN 97 program (11) in the tetragonal subcell with the $I4/mmm$ space group. The full profile refinement was carried out for three phases simultaneously, namely $Sr_{1+x}K_{2-x}Bi_2O_7$, $Sr_{1-x}K_xBiO_3$ (with $x \approx 0.7$), and $SrKBiO_4$ (Fig. 2) with asymmetric pseudo-Voigt peak profile function. The background was described using a polynomial function including 12 terms. The atomic coordinates of $Ba_{1.7}K_{1.3}Bi_2O_7$ (7) were taken as starting coordinates for the Sr analog. $Sr_{1-x}K_xBiO_3$ was described as a cubic perovskite. $SrKBiO_4$ has a trigonal structure (space group $P321$); structural information about this phase will be published elsewhere (12). For the impurity phases, the scale factor, the lattice constants, and two profile parameters were the only parameters allowed to vary. The crystallographic data collection parameters are presented in Table 1. The final structural information about $Sr_{1+x}K_{2-x}Bi_2O_7$ and the main interatomic distances are listed in Tables 2 and 3, respectively.

The crystal structure of $Sr_{1+x}K_{2-x}Bi_2O_7$ ($x \approx 0.6$) is shown in Fig. 3. It can be described as an intergrowth of perovskite and rock-salt blocks. There are two kinds of positions for *A* (Sr,K) cations. One, labeled Sr1 in Table 2 (12-coordinated to oxygen) is located within the perovskite block, whereas the second position Sr2 (9-coordinated to

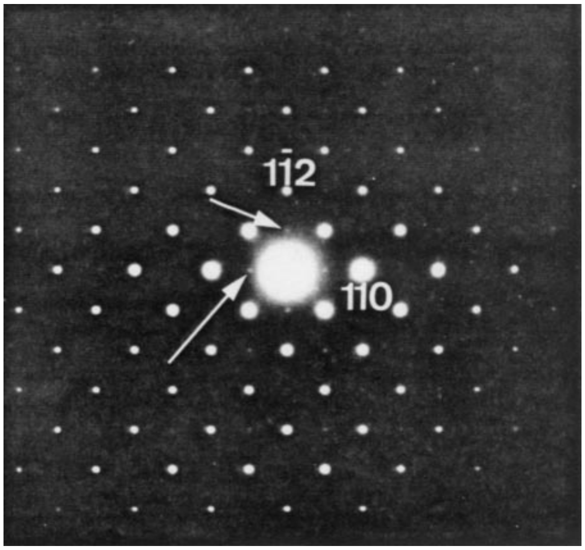

FIG. 1. Electron diffraction pattern taken along the $[1\bar{1}1]$ zone axis showing the presence of additional weak reflections (arrow) with respect to the $a_p \times a_p \times c$ unit cell.

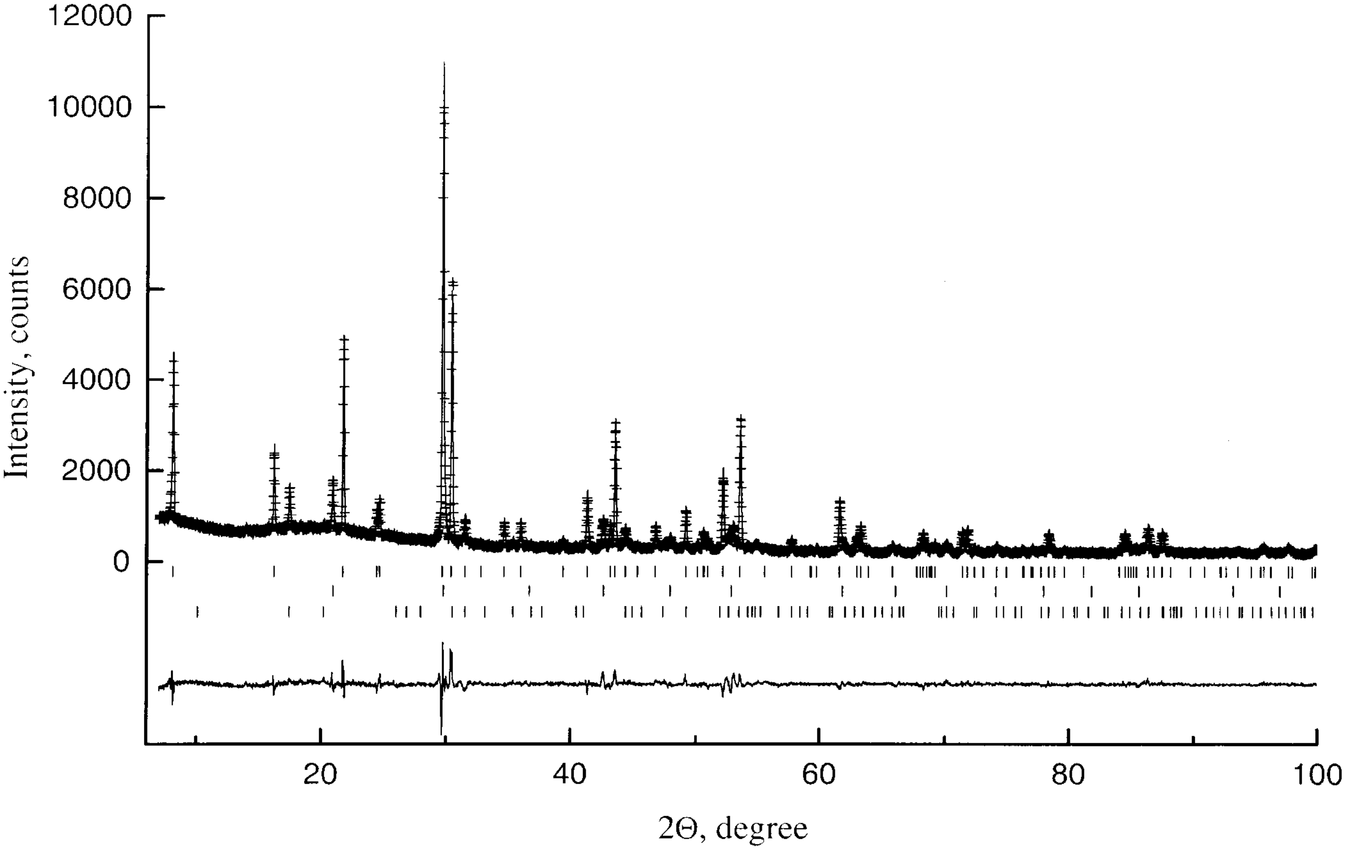

FIG. 2. Observed, calculated, and difference X-ray diffraction patterns for the $Sr_{1.6}K_{1.4}Bi_2O_7$ sample. Theoretical reflection positions of $Sr_{1.6}K_{1.4}Bi_2O_7$ as well as of $Sr_{0.3}K_{0.7}BiO_3$ and $SrKBiO_4$ are shown below the profile (from top to bottom).

oxygen) is within the rock-salt block. The refinement of the Sr : K ratio for the two types of sites revealed that Sr1 contains only Sr, while the other, Sr2, is occupied by Sr and K in a 0.3 : 0.7 ratio. Therefore, the overall composition could be expressed as $Sr_{1.6}K_{1.4}Bi_2O_7$, in reasonable agreement with the nominal composition ($Sr_{1.5}K_{1.5}Bi_2O_7$) and

TABLE 1
Results of the Rietveld Refinement

Phase	$Sr_{1.6}K_{1.4}Bi_2O_7$	$Sr_{0.3}K_{0.7}BiO_3$	$SrKBiO_4$
Space group	*I*4/*mmm*	*Pm*3*m*	*P*321
Lattice constants	$a = 4.1549(1)$ Å $c = 21.8273(6)$ Å	$a = 4.2396(3)$ Å	$a = 10.149(2)$ Å $c = 3.4248(8)$ Å
V	376.93(2) $Å^3$	76.21(1) $Å^3$	305.5(1) $Å^3$
Z	2	1	3
ρ_{cal}, g/cm^3	6.39	7.03	6.08
Number of refinement parameters	17	5	6
Numbers of phase reflections	81	17	135
Refined phase mass fractions (%)	77	15	8
R_I, R_F	0.046, 0.033	0.036, 0.022	0.128, 0.061
Radiation	$CuK\alpha_1 = 1.54056$ Å		
Diffractometer	STADI-P		
2Θ range, step (°)	$2\Theta = 7.0–100.0$, $\Delta(2\Theta) = 0.02$		
R_{wp}, R_p	0.085, 0.067		

Note. The R factors are defined as $R_{wp} = ([\sum w[y_i(\text{obs}) - y_i(\text{calc})]^2]/\{\sum w[y_i(\text{obs})]^2\})^{1/2}$, $R_p = \sum|y_i(\text{obs}) - y_i(\text{calc})|/\sum y_i(\text{obs})$, $R_I = \sum|I_j(\text{obs}) - I_j(\text{calc})|/\sum I_j(\text{obs})$, $R_F = \sum|\sqrt{I_j}(\text{obs}) - \sqrt{I_j}(\text{calc})|/\sum\sqrt{I_j}(\text{obs})$.

TABLE 2
Positional and Thermal Atomic Parameters for $Sr_{1.6}K_{1.4}Bi_2O_7$

Atom	Position	*x*	*y*	*z*	B (Å^2)	*g*
Sr1	2*b*	0	0	0.5	1.1(2)	
Sr2(K)	4*e*	0	0	0.3066(3)	0.9(2)	0.30(1)/0.70(1)
Bi	4*e*	0	0	0.0987(1)	0.56(6)	
O1	2*a*	0	0	0	0.9(3)	
O2	8*g*	0	0.5	0.0850(7)	0.9(3)	
O3	4*e*	0	0	0.193(1)	0.9(3)	

TABLE 3
Main Interatomic Distances (Å) and Angles (°) for $Sr_{1.6}K_{1.4}Bi_2O_7$

Sr1–O1	2.938(1) × 4
Sr1–O2	2.79(1) × 8
Sr2(K)–O2	3.14(1) × 4
Sr2(K)–O3	2.938(1) × 4
Sr2(K)–O3	2.50(2)
Bi–O1	2.154(2)
Bi–O2	2.098(2) × 4
Bi–O3	2.04(2)
Average	2.10
Bi–O2–Bi = 165.15°	

the EDS data ($Sr_{1.3}K_{1.8}Bi_{1.9}O_7$). It is interesting to note that a similar distribution of the cations on the different crytallographic sites was found for $Ba_{1.7}K_{1.3}Bi_2O_7$ from an X-ray single-crystal experiment (7). The Bi cations occupy only one crystallographic position in a slightly distorted octahedron. The in-plane Bi–O2 distance is 2.098(2) Å (× 4); the distance to the oxygen shared between the 2 successive Bi–O layers is d(Bi–O1) = 2.154(2) Å, while the distance to the oxygen in the rock-salt block is rather short, d(Bi–O3) = 2.04(2) Å. The Bi–O distances in the Sr-layered compound (2.10 Å in average) are similar to those found in the oxide of pentavalent bismuth $KBiO_3$ and slightly shorter than the corresponding distances in the Ba analogue (2.12 Å in average) (7). Such a shrinkage of the Bi–O bond lengths is probably due to the slightly higher valence of Bi in the Sr-layered compound, related in turn to the higher potassium content. The Bi–O distances in the present layered phase are also slightly shorter than the distances found in the superconducting $Sr_{1-x}K_xBiO_3$ perovskite phases (2.11 Å), in correlation with a higher Bi valence state. Such a high Bi valence may be responsible for the absence of superconductivity in the samples we prepared.

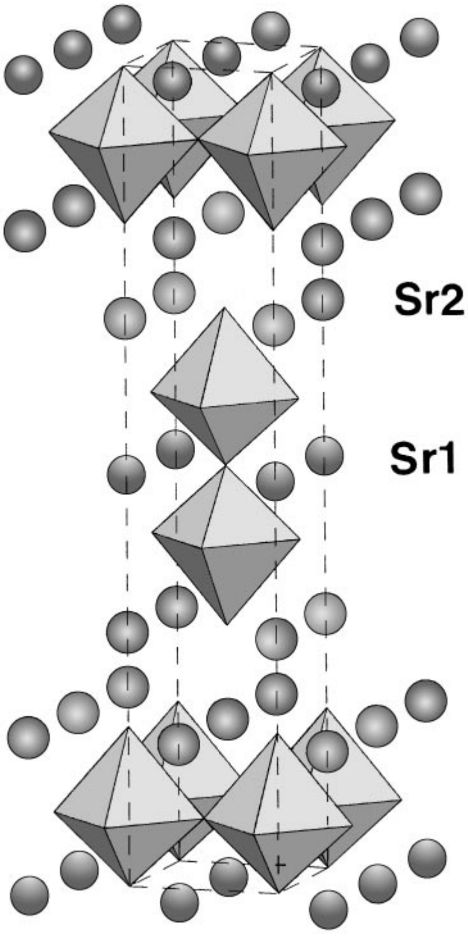

FIG. 3. Crystal structure of $Sr_{1.6}K_{1.4}Bi_2O_7$.

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REFERENCES

1. L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson Jr., *Phys. Rev. B*, **37,** 3745 (1988).
2. R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp Jr., A. E. White, K. Short, W. F. Peck, and T. Kometani, *Nature* **332,** 814 (1988).
3. W. T. Fu, H. W. Zandbergen, Q. Xu, J. M. van Ruitenbeek, L. J. de Jongh, and G. Van Tendeloo, *Solid State Commun.* **70,** 1117 (1989).
4. Q. Xu, W. T. Fu., J. M. van Ruitenbeek, and L. J. de Jongh, *Physica C* **167,** 271 (1990).
5. Q. Xu, W. T. Fu, J. M. van Ruitenbeek, L. J. de Jongh, M. Drillon, and Y. Bruynseraede, *J. Less-Common Met.* **164–165,** 948 (1990).
6. R. J. Cava, H. Takagi, H. W. Zandbergen, B. Hessen, J. J. Krajewski, and W. F. Peck, *Phys. Rev. B* **46,** 14,101 (1992).
7. R. J. Cava, T. Siegrist, W. F. Peck Jr., J. J. Krajewski, B. Batlogg, and J. Rosamilia, *Phys. Rev. B* **44,** 9746 (1991).
8. L. F. Mattheiss, *Phys. Rev. B* **45,** 12,528 (1992).
9. S. M. Kazakov, C. Chaillout, P. Bordet, J. J. Capponi, M. Nunez-Regueiro, A. Rysak, J. L. Tholence, P. G. Radaelli, S. N. Putilin, and E. V. Antipov, *Nature* **390,** 148 (1997).
10. O. Knop, G. Demazeau, and P. Hagenmuller, *Can. J. Chem.* **58,** 2221 (1980).
11. Izumi F., *in* "The Rietveld Method" (R. A. Young Ed.)," Chap. 13. Oxford Univ. Press, Oxford, 1993.
12. S. M. Kazakov, in preparation.