Synthesis and Crystal Structure of Sr₂ScBiO₆

P. E. Kazin, A. M. Abakumov,[1] D. D. Zaytsev, and Yu. D. Tretyakov

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

N. R. Khasanova and G. Van Tendeloo

EMAT, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium

and

M. Jansen

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

A new complex oxide Sr_2ScBiO_6 was synthesized by a solid state reaction in air. The compound is stable up to 1150°C and acquires the desired oxygen stoichiometry at 850°C. The crystal structure was determined using powder X-ray diffraction, electron diffraction, and high-resolution electron microscopy. Sr_2ScBiO_6 has a perovskite-derived pseudocubic face-centered unit cell ($a = 8.1816(3)$ Å) and a rock-salt ordering of Sc^{3+} and Bi^{5+} over the B positions. Electron microscopy investigation reveals that the real structure is of the La_2NiRuO_6 type, monoclinic with cell parameters $a \approx b = a_{per}\sqrt{2} \approx 5.785$ Å, $c = 2a_{per} \approx 8.182$ Å, and $P2_1/n$ space group. The structure can be described by an $a^+b^-b^-$ system of the BO_6 octahedral tilting. The presence of numerous twin domains is a characteristic feature of this compound. © 2001 Academic Press

INTRODUCTION

Complex oxides with a perovskite structure and containing bismuth in an oxidation state higher than $+3$ attract considerable attention due to superconductivity observed in $Ba_{1-x}K_xBiO_3$ (1, 2) and $Sr_{1-x}K_xBiO_3$ (3). In such compounds a disproportionation into Bi^{3+} and Bi^{5+} is suppressed by doping, leading to metallic behavior and superconductivity. Attainment of bismuth in a high oxidation state requires an oxygen atmosphere or even high oxygen pressure for Sr-based solid solutions. At the same time perovskites with only Bi^{5+} are known in which half of the Bi is substituted by lower charged cations (4–8). In these compounds bismuth appears to be more stable in its highest

oxidation state. For instance, $Sr_6Bi_2O_{11}$ exists up to 1090°C at $P(O_2) = 1$ atm (4), Sr_2LnBiO_6 (Ln = La–Lu) is prepared at 950°C in air (5–7), and Ba_2YBiO_6 is formed at 1075°C in an oxygen atmosphere (8).

In Sr_2LnBiO_6 the cations of Ln and Bi are ordered in the rock-salt manner (6). The perovskite lattice is strongly distorted giving rise to a monoclinic cell. The distortion can be connected with a too big average radius of the B-site cations that gives the Goldshmidt tolerance factor $t < 1$. Sr atoms are too small to be placed into 12-fold coordinated A positions and LnO_6 and BiO_6 octahedra are cooperatively tilted along $[011]_{per}$ and rotated along $[100]_{per}$ to diminish 8 from the original 12 equal Sr–O distances. The ionic radius of Sc^{3+} is close to that of Bi^{5+} and is considerably smaller than that of the Ln^{3+} ions (9). Consequently the tolerance factor for the compound with $Ln = Sc$ has to get closer to 1 and one can expect less structure distortion for this perovskite. Yet to our knowledge this compound has not been described previously.

Recently, by doping the $Bi_2Sr_2CaCu_2O_{8+x}$ superconductor with scandium oxide we observed the formation of a new phase with composition Sr_2ScBiO_6; this phase coexisted with the superconductor and its melt (10). In the present work we consider the synthesis of pure Sr_2ScBiO_6 and determine its crystal structure, oxygen nonstoichiometry, and thermal stability.

EXPERIMENTAL

Chemical grades $SrCO_3$, Bi_2O_3, and Sc_2O_3 taken in appropriate molar ratios were dissolved in an excess of 5 M nitric acid. The solution was evaporated to dryness and decomposed at 200–800°C. The resulting residue was

[1]To whom correspondence should be addressed. Fax: (095) 939-47-88. E-mail: abakumov@icr.chem.msu.ru.

ground, pressed in pellets, annealed at 1050°C for 48 h in air, and air quenched. The samples obtained were further annealed at 850°C for 24 h in air for additional oxidation. This technique allowed the preparation of single-phase Sr_2ScBiO_6 samples.

The oxygen content was determined by the iodometric method. The cation composition was determined by EDX analysis of the polished sample surface using a Philips ESEM scanning electron microscope and on separate crystallites using a Philips CM20 transmission electron microscope with a LINK2000 attachment.

X-ray diffraction study was performed on a STADI/P diffractometer ($CuK_{\alpha 1}$ radiation, curved Ge monochromator, transmission mode, step 0.01° 2θ, PSD detector). The crystal structure was refined by the Rietveld method using the RIETAN-97 program (11).

Electron diffraction (ED) and high-resolution electron microscopy (HREM) were performed on Philips CM20 and JEOL 4000EX instruments. Image simulation was made using MacTempas software.

RESULTS AND DISCUSSION

1. Sample Characterization

The Sr_2ScBiO_{6-x} samples are homogeneous on the micronscale level, and the cation composition corresponds to the nominal one within 5%. Only small impurities (less than 0.2 vol%) of Bi- and Sc-rich precipitates are found by SEM, but no peaks of foreign phases are detected in the X-ray diffraction pattern. The oxygen content for the sample quenched from 1050°C corresponds to $x = 0.09 \pm 0.01$; after annealing at 850°C the compound becomes almost stoichiometric ($x = 0.02 \pm 0.01$). It will therefore be denoted as Sr_2ScBiO_6.

The compound is stable up to ca. 1150°C in air. The XRD pattern of the sample annealed at 1180°C for 1 h contains only weak lines of the initial compound; however, a set of new lines appears. Some of these lines clearly belong to SrO as well as to an unknown impurity with large d-values of 10.9 Å, 9.38 Å, and 8.04 Å. The weight loss roughly corresponds to the elimination of one oxygen per formula unit, thus implying full reduction of Bi^{5+} to Bi^{3+}. EDX analysis shows that two new phases appear with Sr:Sc:Bi molar ratios 5:3:3 and 10:4:3, as well as a small amount of Bi-rich phase depleted of Sc.

2. X-Ray Diffraction

All strong reflections in the Sr_2ScBiO_6 X-ray diffraction pattern can be indexed in a face-centered cubic lattice with lattice parameter $a = 8.1816(3)$ Å. However, a complete indexing can only be performed on the basis of a tetragonal primitive unit cell with $a = 5.7854(2)$ Å and $c = 8.1818(3)$ Å. The ratio $c/a = \sqrt{2}$ and the weakness of the superlattice

TABLE 1
Selected Parameters from Rietveld Refinement of X-Ray Powder Data for Sr_2ScBiO_6

Space group	$Fm\bar{3}m$
a, Å	8.1895(1)
Z	4
Cell volume, Å^3	549.26
Calculated density, g/cm^3	6.351
2θ range, step, deg	$10 \leq 2\theta \leq 110$, 0.01
Number of reflections	33
Refinable atomic parameters	6
R_I, R_P, R_{wP}	0.029, 0.080, 0.113
Sr	$8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)
B, Å^2	1.03(3)
Bi	$4a$ (0,0,0)
B, Å^2	0.23(2)
g	0.88Bi + 0.12Sc
Sc	$4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)
B, Å^2	0.31(5)
g	0.88Sc + 0.12Bi
O	$24e$ (x,0,0)
x/a	0.2442(7)
B, Å^2	5.6(2)
d(Sr–O), Å	$12 \times 2.8958(1)$
d(Bi–O), Å	$6 \times 2.000(6)$
d(Sc–O), Å	$6 \times 2.095(6)$

reflections suggest that only minor deviations from cubic symmetry are induced. An analysis of the FWHM's dependence on the scattering angle reveals that the half-widths of the hhl reflections are systematically smaller than those of other reflections. It may indicate a small difference in the a and b cell parameters related to a further symmetry decrease. Determination of the extinction conditions on the basis of the X-ray powder pattern seems to be doubtful because of complete overlapping of the reflections caused by the pseudocubic unit cell.

For the refinement of the Sr_2ScBiO_6 crystal structure we first assumed an ordered distribution of Sc and Bi over the B positions of the perovskite-type structure. According to the symmetry analysis performed by Woodward (12), the rock-salt-type ordering of the B cations in the $a = 2a_{per}$ face-centered unit cell corresponds to the absence of a tilting distortion of the perovskite framework ($a^0a^0a^0$ tilt system in Glazer's notations (13), space group $Fm\bar{3}m$). However, the thermal parameters for cations obtained after the refinement with fully ordered Sc and Bi indicate probable partial mixing of these cations (-2.9 and 0.8 Å^2 for Sc and Bi positions, respectively). The occupancy values were refined with fixed $B = 0.5$ Å^2 and were found to be equal to 0.88Sc + 0.12Bi for the Sc position and 0.88Bi + 0.12Sc for the Bi one. The final refinement gave a reasonable reliability factor $R_I = 0.029$, whereas the $R_P = 0.080$ and $R_{wP} = 0.113$ show an unsatisfactory matching between the experimental and the calculated profiles. A large value of the thermal parameter of the oxygen atom ($B = 5.6$ Å^2) was observed.
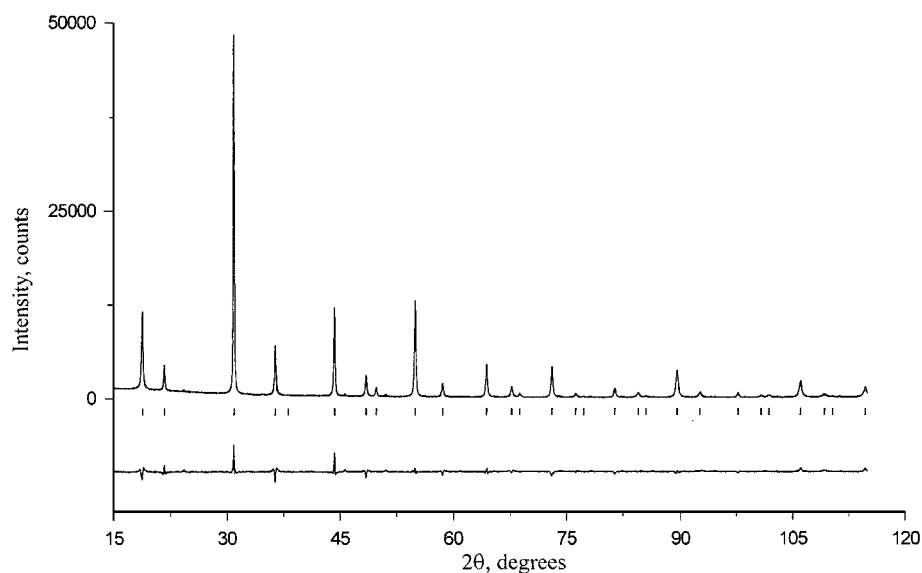
FIG. 1. Observed, calculated, and difference X-ray diffraction patterns for Sr_2ScBiO_6.

This value can be caused by an oxygen displacement away from the ideal position due to a small rotation and a tilt of the BiO_6 and ScO_6 octahedra; this cannot be described in the frame of the face-centered cubic cell. The crystallographic parameters, parameters of the Rietveld refinement, atomic coordinates, and interatomic distances for Sr_2
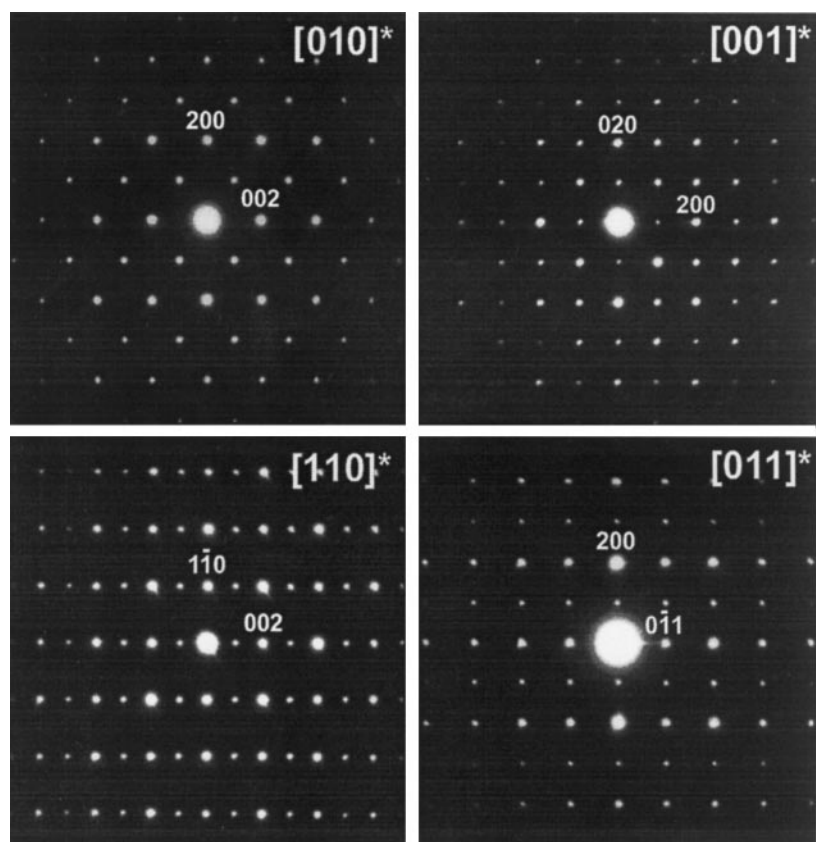

FIG. 2. [010]*, [001]*, [110]*, and [011]* electron diffraction patterns from single domains of Sr_2ScBiO_6.
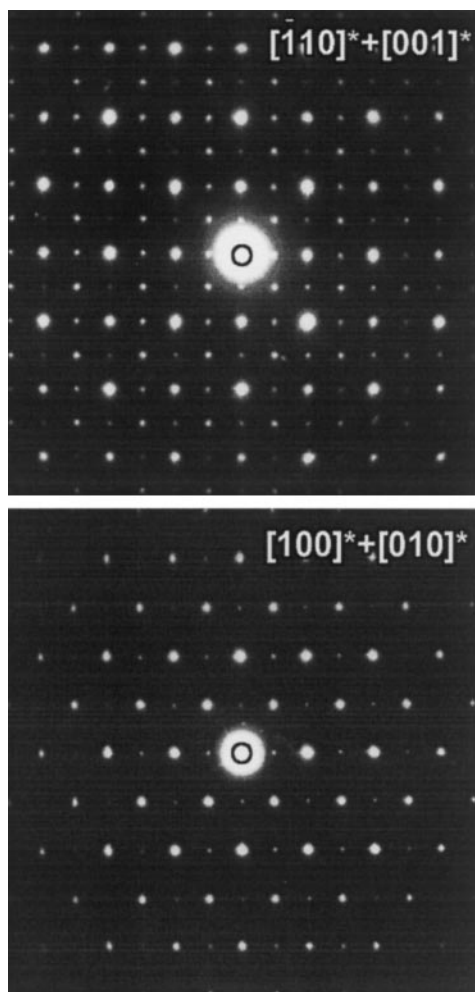
FIG. 3. Composite electron diffraction patterns from regions containing two or more orientation domains.

$ScBiO_6$ are given in Table 1. The observed, calculated, and difference X-ray diffraction patterns are shown in Fig. 1. Sc and Bi have an octahedral oxygen environment. The Sc–O (2.095(6) Å) and Bi–O (2.000(6) Å) distances correlate well with the observed occupancies of these positions and ionic radii of Sc^{3+} (0.81 Å) and Bi^{5+} (0.74 Å). Sr atoms are situated in cuboctahedra with $d(Sr–O) = 2.8958(1)$ Å.

Different tilt systems proposed by Woodward (12) with a decrease of symmetry to tetragonal, orthorhombic, and monoclinic were also tested but none resulted in a stable refinement and gave reasonable values of the interatomic distances and the thermal parameters.

3. Electron Microscopy

The ED patterns along the main zone axes are shown in Fig. 2. The indexing of these patterns is performed using a unit cell with $a \approx b = a_{per}\sqrt{2} \approx 5.79$ Å, $c = 2a_{per} \approx 8.18$ Å

[001]* and [110]* directions correspond with the 4-fold axes of a perovskite subcell. Obvious differences between these patterns reflect that the $[100]_{per}$, $[010]_{per}$, and $[001]_{per}$ directions are no longer symmetrically equivalent as should be expected for a cubic system. In most cases, however, a square array of spots corresponding to an 8.18 Å × 8.18 Å unit cell is observed on ED patterns along these directions (Fig. 3). The fact that the intensity of the weaker reflections significantly varies when displacing the selective diaphragm strongly suggests the presence of overlapping orientation domains in the material. This pattern in Fig. 3 can be interpreted as the overlap of domains in [001]* and [110]* orientations where two [110]* domains are rotated by 90° along the zone axis with respect to each other. The ED pattern of Fig. 3 similarly is a superposition of two single-crystal patterns of [100]* and [010]* oriented domains. It was also verified by EDX that the different variants do not have a different content of Sc and Bi. A homogeneous cation distribution was found with Sr:Sc:Bi = 2.02(4):0.98(4):1.00(4) atomic ratio which is in good agreement with the Sr_2ScBiO_6 composition. The analysis of a number of diffraction patterns and Fourier transforms taken from single-domain high-resolution images reveals the extinction conditions $h0l$, $h + l = 2n$ and
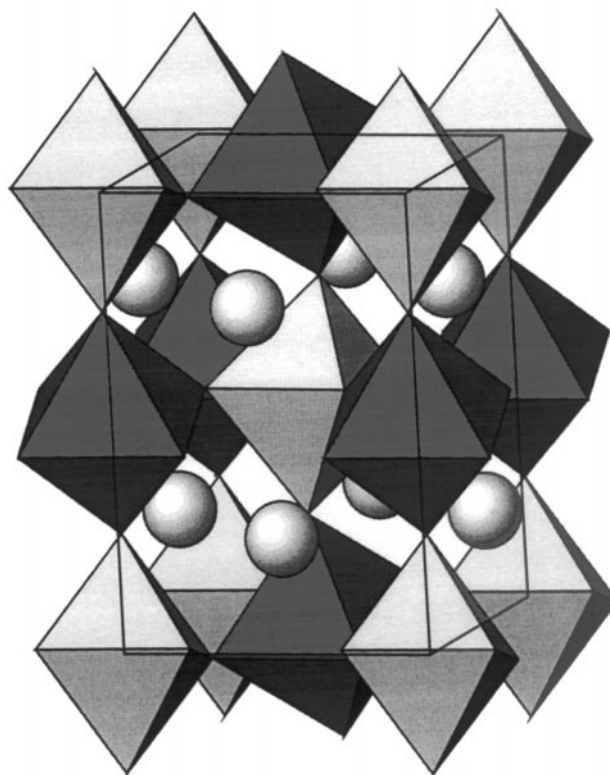

FIG. 4. Structure model of Sr_2ScBiO_6. Sc and Bi are located at the center of the octahedra; Sr atoms are shown as spheres.
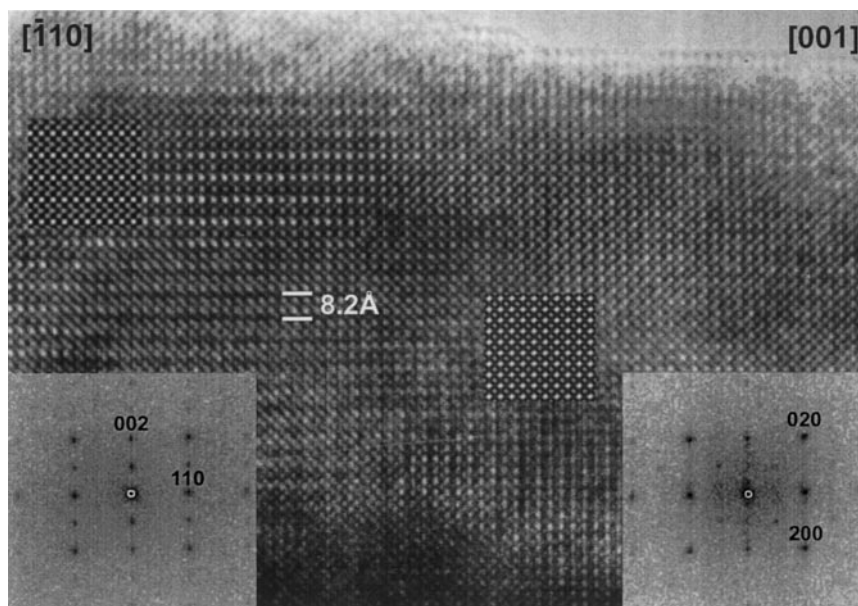
FIG. 5. HREM image of Sr_2ScBiO_6 showing $[\bar{1}10]$ (left side) and $[001]$ (right side) oriented domains. The corresponding Fourier transforms are shown as insets. The simulated theoretical $[\bar{1}10]$ and $[001]$ images were calculated at $f = -700$ Å, $t = 30$ Å.

$0k0$, $k = 2n$. The presence of $h00$, $0k0$, and $00l$, h, k, $l \neq 2n$, reflections on $[001]^*$, $[110]^*$, and $[011]^*$ patterns is caused by double diffraction as was checked by a tilt of the crystal along the row containing the forbidden reflections. According to these extinction conditions, the n glide plane passes normal to the b axis and no such plane is observed normal to the a axis, which points toward a decrease of symmetry from tetragonal to orthorhombic or monoclinic despite the identical values of a and b cell parameters. The symmetry analysis of the double $A_2BB'O_6$ perovskite with rock-salt-type ordering of B and B' cations performed by Woodward (12) reveals that there is no tilt system corresponding to an orthorhombic symmetry and compatible with $a \approx b = a_{per}\sqrt{2}$, $c = 2a_{per}$ cell dimensions and experimentally observed extinction conditions. Only one monoclinic space group ($P2_1/n$) matches well with all experimental features and it probably represents the actual space symmetry of the Sr_2ScBiO_6 compound.

The $P2_1/n$ space symmetry corresponds to the $a^+b^-b^-$ tilt system (13) and many double perovskites are known which adopt this structure. The $Sr_2Bi^{5+}M^{3+}O_6$ (M = Bi, Nd) (3,6) compounds have such a structure organization; however, they cannot be taken as a structure model for Sr_2ScBiO_6 because of the large difference in sizes of the Bi^{5+} and the M^{3+} cations. Since the ionic radii of Sc^{3+} (0.81 Å) and Bi^{5+} (0.74 Å) (9) in an octahedral environment do not differ significantly, the atomic coordinates for one such double perovskite with similar cations at the B and B' positions can be taken as a structure model of Sr_2ScBiO_6. The La_2NiRuO_6 compound (14) was chosen and the structure model was verified by comparison of the theoretical

and experimental high-resolution (HREM) images. The schematic representation of this structure is shown in Fig. 4. Figure 5 reproduces the HREM image of two domains in $[\bar{1}10]$ (the left part) and $[001]$ (the right part) orientation which correspond to the $[001]$ projection of the perovskite subcell. The Fourier transforms shown as insets in Fig. 5 allow us to determine the local orientation. The domains have a common (110) crystallographic plane, but the interface between them is ill defined. At this particular defocus and thickness the columns of cations are imaged as bright dots. The adequacy of the proposed model was confirmed by an agreement between experimental and calculated (in set, $f = -700$ Å, $t = 30$ Å) HREM images along $[\bar{1}10]$ and $[001]$ zones.

The tolerance factor for the $A_2BB'O_6$ perovskite can be estimated as $t_{per} = (r_A + r_0)/\sqrt{2}(r_B + r_{B'})/2 + r_0)$. For Sr_2NdBiO_6, Sr_2LuBiO_6, and Sr_2ScBiO_6 one obtains $t_{per} = 0.88$, 0.91, and 0.93 correspondingly. The a/b ratio increases from 0.975 for Nd (6) to 0.987 for Lu (7) and becomes practically equal to unity for Sc. As has been shown, however, the same type of crystal lattice distortion takes place in the latter case. Hence, $t_{per} \sim 0.93$ can probably be considered as a lower boundary limit for the cubic structure for these types of double perovskites.

ACKNOWLEDGMENTS

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