Oxygen and the Formation of New Ordered Perovskite-Based Structures in the Bi–Sr–O System

BOKHIMI*

Institute of Physics, National University of Mexico (UNAM), a.p. 20-364, 01000 México D. F., Mexico

AND M. PORTILLA

Department of Chemistry, National University of Mexico (UNAM), a.p. 70-197, 01000 México D. F., Mexico

We have found one amorphous and three crystalline phases in the Bi–Sr–O system for Sr : Bi molar ratios between 1.0 and 3.0. A first approximation for the structure of two of the crystalline phases was obtained. They are based on the perovskite structure. One of the phases has the composition $Sr_{10}Bi_6O_{24-y}$, which is cubic with space group $Fm3m$ and cell parameter $a = 8.476(2)$ Å. It is obtained only if the sample is slow cooled from temperatures above 600°C in an oxygen-containing atmosphere. The second phase has the composition $Sr_6Bi_2O_{12-y}$, which is tetragonal with space group $I4/mmm$, cell parameters $a = 6.0058(3)$ and $c = 8.3718(5)$ Å. This phase is obtained only if the sample is prepared in an oxygen-containing amtosphere. We observe that oxidation of part of the bismuth atoms is necessary to obtain the above-described phases. © 1993 Academic Press, Inc.

1. Introduction

Oxygen deficiency plays an important role in the superconducting properties of the High-T_c superconductors (1–4). In the YBCO system the dependence of the system properties on oxygen deficiency is very well known (5), and the results of all authors are consistent. That is not the case for the BSCCO system, where different results are reported for a given superconducting phase (2). In that system, it is not clear why the effect of the oxygen deficiency in each superconducting phase is different. In this case the atoms that can change their valence are bismuth and copper. Reports on the 2201 and 2212 phases of the BSCCO system show that the average valence of

bismuth atoms is larger than 3.0 (6–8) and that the transition temperature to the superconducting state and the valence of copper atoms increase as this valence decreases. This suggests that the oxygen concentration in the BSCCO system changes in the local Bi–Sr–O environment. It is well known that in order to obtain superconductivity in the BSCCO 10 K phase, strontium atoms must be partially substituted by bismuth atoms (9). These facts induced us to investigate in detail the Bi–Sr–O system with emphasis on the role of the oxygen deficiency in its crystalline structural properties. The phase diagram for this system has been studied (10). However, in the interpretation of the results it was assumed that all bismuth atoms have a valence of 3+, which is not correct for all cation molar ratios, as will be evident from the present work.

* To whom correspondence should be addressed.

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2. Experimental

High-purity powders of Bi_2O_3 and $SrCO_3$ with the Sr : Bi molar ratios between 1.0 and 3.0 were well mixed in a mortar, calcined in air at 800°C and sintered at 830°C for 24 hr in a desired atmosphere of air, oxygen, or argon. Some samples were quenched from the sintering temperature into liquid nitrogen.

X-ray powder diffraction of the samples was obtained in a Siemens D-5000 diffractometer with $CuK\alpha$ radiation and a secondary beam monochromator. The structure of the phases present in the samples were determined by similarity of their X-ray diffractograms with those found in the Ba_8 $Y_{3-z}Cu_zW_4O_{24-y}$ system (11), and refined by the Rietveld method with the WYRIET version 2 (12) and DBWS-9006PC (13) programs.
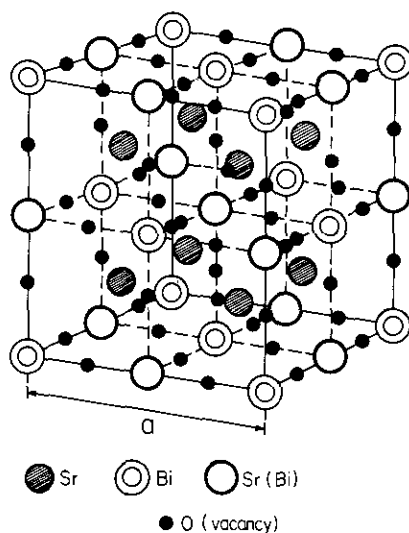

FIG. 2. Unit cell of the $Sr_{10}Bi_6O_{24-y}$ cubic phase with space group $Fm3m$. It is constructed of ordered perovskites with corner-shared BiO_6 and SrO_6 octahedra in a proportion of three to one.
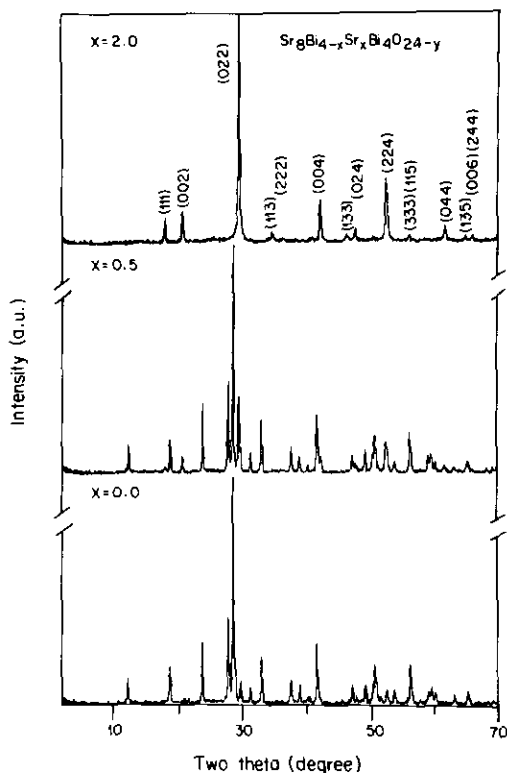
Thermogravimetric analysis of the samples was done in air and in argon from room temperature to 1000°C and from there to room temperature, with heating and cooling rates of 10 degrees per minute.

Electrical resistivity of all samples was measured at room temperature by the four-probe technique.

3. Results and Discussion

Figure 1 shows X-ray diffractograms of samples of the $Sr_8Bi_{4-x}Sr_xBi_4O_{24-y}$ system sintered at 830°C and slowly cooled in air, with $0 \le x \le 2$. For $x = 0$ the samples have only the orthorhombic $Bi_2Sr_2O_5$ phase (14); as x is increased the samples have a mixture of two phases, the $Bi_2Sr_2O_5$ phase and a new phase, which is obtained pure when $x = 2.0$, that corresponds to the stoichiometry $Sr_{10}Bi_6O_{24-y}$. In a first approximation the crystalline structure of this new phase is cubic with space group $Fm3m$. It is based on the perovskite structure with corner-shared BiO_6 and SrO_6 octahedra ordered along the $\langle 100 \rangle$ directions (Fig. 2), with a proportion of three BiO_6 to one SrO_6 octa-
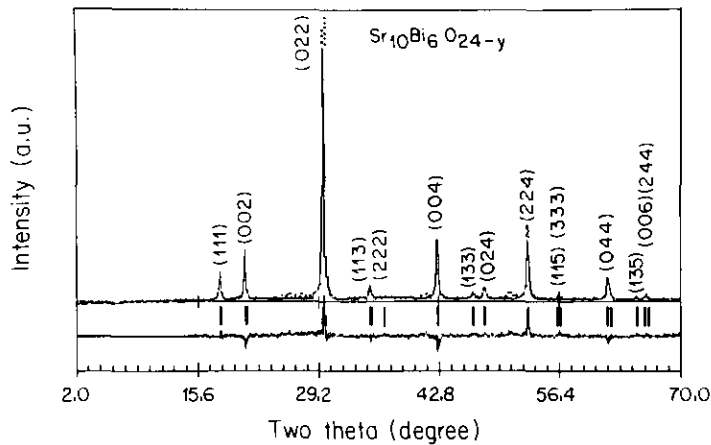
FIG. 3. Rietveld refinement plot of the $Sr_{10}Bi_6O_{24-y}$ cubic phase, $R_F = 0.098$. Dots represent the experimental X-ray diffractogram; continuous line represents the corresponding calculated data.

hedra. Figure 3 shows the corresponding Rietveld refinement plot. We have obtained an R_F value of only 0.098, which is indicative that the proposed structure is only a first approximation. Table I shows the corresponding refined parameter. It was not possible to refine the isotropic thermal displacements; their values were fixed at 0.0. The refined cell parameter is 8.476(2) Å.

Figure 4 shows a thermogravimetric analysis curve of this phase. It shows that the sample loses oxygen above 600°C, which becomes stronger above 730°C. During the cooling, the sample absorbs oxygen at 600°C. The distance between the maximum in the warming curve (around 600°C) and the minimum in the cooling curve (around 700°C) corresponds to a weight loss of 1.9%. Assuming that the stoichiometry at the maximum is $Sr_{10}Bi_6O_{24}$, with five bismuth atoms with valence 5+ and one with valence 3+, which corresponds to the maximum allowed oxygen concentration in the ordered perovskite structure, this weight loss is equivalent to the loss of three oxygen atoms per formula. If the sample is quenched from a temperature above 830°C, after it has lost oxygen, it shows also only
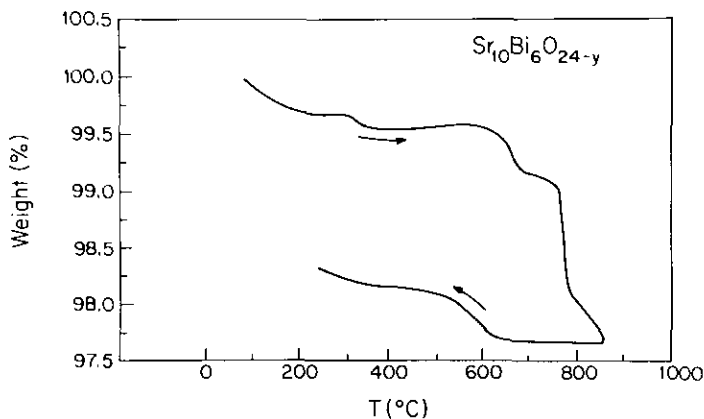

FIG. 4. Thermogravimetric analysis curve in air of the $Sr_{10}Bi_6O_{24-y}$ cubic phase. The sample was heated and cooled at a rate of 10 degree per minute.

TABLE I

$Sr_{10}Bi_6O_{24-y}$ Phase: Atomic Fractional
Coordinates and Occupation Numbers

Atom	Site	x	y	z	n
Bi(1)	$4a$	0.00	0.00	0.00	1.00
Bi(2)	$4b$	0.50	0.50	0.50	0.50
Sr(1)	$8c$	0.25	0.25	0.25	1.00
Sr(2)	$4b$	0.50	0.50	0.50	0.50
O	$24e$	0.176(4)	0.00	0.00	1.00

one phase, but the crystalline structure of this phase is no more cubic, it has a lower symmetry. We have not determined its structure. Figure 5B shows the corresponding X-ray diffractogram. The same result is obtained if the sample is prepared in an argon atmosphere. The cubic phase is obtained only if the sample is cooled slowly in an oxygen-containing atmosphere; according to the thermogravimetric analysis, under these conditions the sample absorbs oxygen. From the above analysis we deduce that in the cubic phase, five of the bismuth
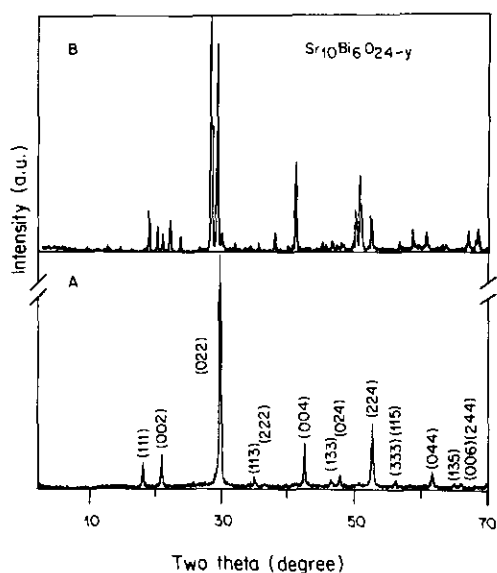

FIG. 6. X-ray diffractograms of the Sr_8Bi_{4-x} $Sr_xBi_4O_{24-y}$ system for $2 \leq x \leq 4$.

atoms are oxidized to a valence of $5+$. This oxidation allows more oxygen atoms to be incorporated into the crystalline structure.

Figure 6 shows the X-ray diffractograms as the strontium concentration is increased. For $2 < x < 4$ the samples are a mixture of two phases, the cubic phase discussed above and a new phase, which is related to the cubic phase but with tetragonal symmetry. For $x = 4.0$ the samples have only this tetragonal phase, it has the stoichiometry $Sr_6Bi_2O_{12-y}$. Results related to this phase have been reported (15). The crystalline structure for the tetragonal phase was modeled with an atom distribution with symmetry given by the space group $I4/mmm$ with the unit cell given in Fig. 7, which is derived from the unit cell shown in Fig. 2. In this tetragonal phase there is also an ordering of corner-shared BiO_6 and SrO_6 octahedra along the $\langle 100 \rangle$ directions but the pro-

FIG. 5. X-ray diffractograms of the $Sr_{10}Bi_6O_{24-y}$ cubic phase, (A) after sintering at 830°C and slow cooling in air; (B) after sintering at 830°C in air and quenched from this temperature into liquid nitrogen.
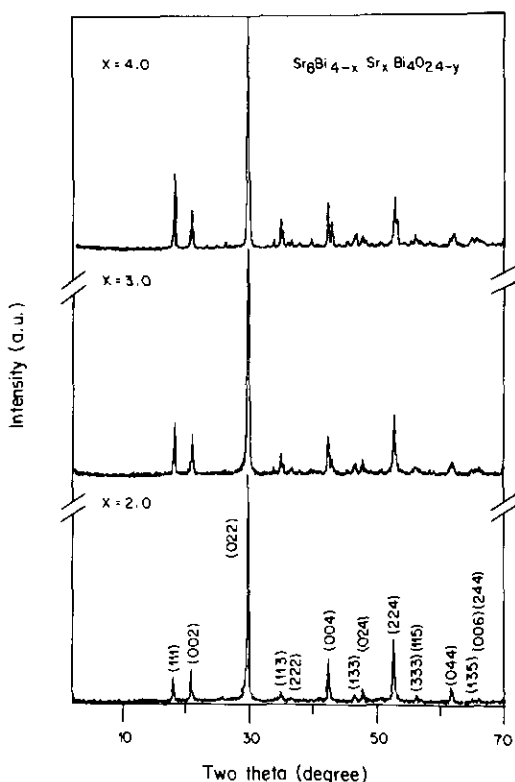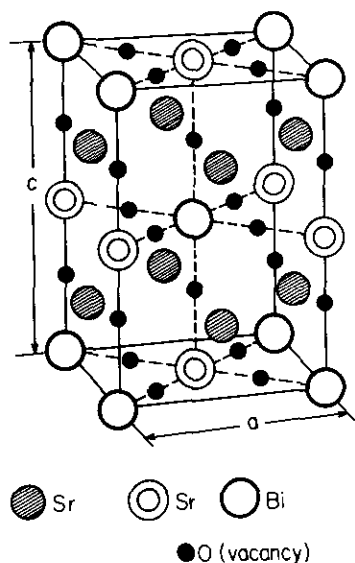
Atom	Site	x	y	z	n
Bi	2a	0.00	0.00	0.00	1.00
Sr(1)	2b	0.00	0.00	0.50	1.00
Sr(2)	4d	0.50	0.00	0.25	1.00
O(1)	4e	0.00	0.00	0.232(8)	1.00
O(2)	8h	0.227(6)	0.227(2)	0.00	0.875

FIG. 7. Unit cell of the $Sr_6Bi_2O_{12-y}$ tetragonal phase with space group $I4/mmm$. This cell is derived from the unit cell shown in Fig. 2. It corresponds to ordered perovskites with corner-shared BiO_6 and SrO_6 octahedra in a proportion one to one.

tragonal structure is only a first approximation. Table II shows the corresponding refined parameter. It was not possible to refine the isotropic thermal displacements, their values were fixed at 0.0. From the refinement we obtain the cell parameters $a = 6.0058(3)$ and $c = 8.3718(5)$ Å. It is important to note that some weak reflections (indicated with asterisks in Fig. 8) are not reproduced with our model. They are probably originated by a superstructure similar to that found in the Ba_3UO_6 system (16, 17). Because the superstructure reflections are observed in the X-ray diffractogram, and the atomic scattering factors of strontium and bismuth atoms are quite different, the superstructure is determined by
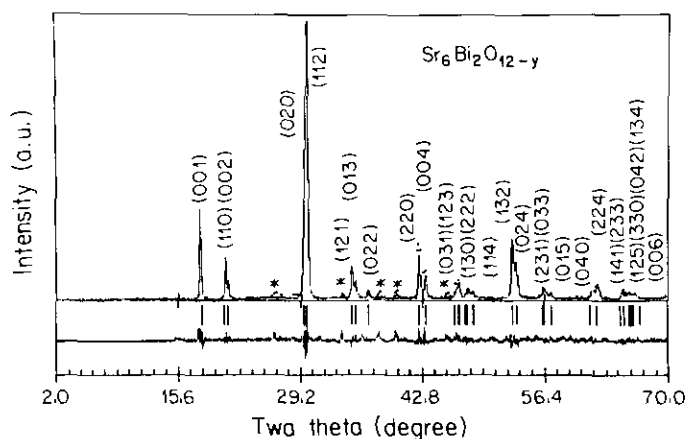
portion of the two octahedra is one to one. With this model we did a refinement of the structure by the Rietveld method, the corresponding plot is shown in Fig. 8. The R_F value is 0.069, which indicates that the te-

FIG. 8. Rietveld refinement plot of the $Sr_6Bi_2O_{12-y}$ tetragonal phase, $R_F = 0.069$. Dots represent the experimental X-ray diffractogram; continuous line represents the corresponding calculated data. Asterisks indicate diffraction peaks that are not reproducible with our crystalline structure model. They correspond probably to superstructure reflections.
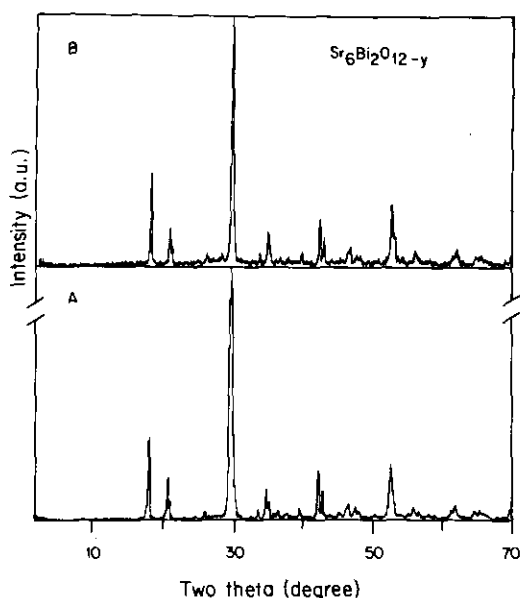
FIG. 9. X-ray diffractograms of the $Sr_6Bi_2O_{12-y}$ tetragonal phase, (A) after sintering at 830°C and slow cooling in air; (B) after sintering at 830°C in air and quenched from this temperature into liquid nitrogen.

this result, we did a thermogravimetric analysis of these samples in air. From this analysis we observe that the sample does not lose weight, in contrast to the behavior observed in the cubic phase. We have prepared samples with the Sr : Bi molar ratio 3 : 1 in an argon atmosphere. Under these conditions we do not a obtain the crystalline phase anymore, instead, we obtain an amorphous phase, as is shown in the X-ray diffractogram in Fig. 10. This result indicates that the formation of the tetragonal phase requires that the samples be prepared in an oxygen-containing atmosphere. We consider this proof that some of the bismuth atoms in the tetragonal phase are oxidized to a valence of 5+. Contrary to the behavior in the cubic phase, in the tetragonal phase, the oxygen atoms are not desorbed at high temperatures, at least at temperatures lower than 1000°C.

All samples show insulator electrical behavior.

an ordering of Sr and Bi atoms. In any case, the larger unit cell must be a composition of units similar to that shown in Fig. 7. When a sample with only this phase is sintered in air and quenched from the sintering temperature of 830°C, we do not observe any change in the crystalline structure, as is shown in Fig. 9B. In order to understand

4. Conclusions

We have shown that in the Bi–Sr–O system, for the Sr : Bi molar ratios between 1.0 and 3.0, there exist one amorphous and three crystalline phases. Two of the crystalline phases have a crystalline structure based on the perovskite, one with cubic
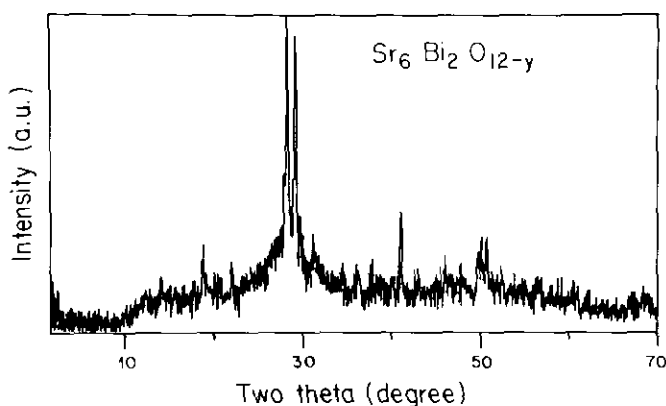

FIG. 10. X-ray diffractogram of a sample with cation composition corresponding to the $Sr_6Bi_2O_{12-y}$ tetragonal phase, calcined at 800°C and sintered at 830°C in an argon atmosphere.

symmetry and the other with tetragonal symmetry. In order to obtain these structures part of the bismuth atoms must have valence 5+, so that sufficient oxygen from the surrounding atmosphere will incorporate into the structure. Our results show how the oxygen concentration varies in the local Sr–Bi–O environment depending on the Sr : Bi ratio. These results could help in understanding the observed variation of the bismuth average valence from 3.15+ to lower values in the superconducting phases of the BSCCO system (6, 8).

Acknowledgments

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