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Characterization of Bi-Doped High-*Tc* Superconductor $SmBa_2Cu_3O_y$ by X-Ray Diffraction

(Bi-doped Sm-Ba-Cu-O system/high-T_c supercoductor/X-ray diffraction)

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Bismuth has been successfully introduced into the Sm-Ba-Cu-O system. X-ray powder diffraction patterns show that $Sm_{1-x}Bi_xBa_2Cu_3O_y$ samples with $x = 0.1$, 0.2, which were prepared by sintering, consist of two phases: the main phase has the orthorhombic perovskite-like structure reported for the high-*Tc* superconductor $YBa_2Cu_3O_{7-\delta}$ and the impurity phase is identified with $BaCuO_2$. It is found that the x-dependences of the lattice parameters are very similar to those for $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ or $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. These results indicate that the Ba sites in the main phase are partly occupied by Bi^{3+} or Sm^{3+} ions.

INTRODUCTION

Since the discoveries of 30-K superconductivity in the La-Ba-Cu-O system[1,2] and 90-K superconductivity in the Y-Ba-Cu-O system,[3] extensive studies have been carried out on systems modified by atomic substitutions to understand the fundamental mechanism of high-T_c superconductivity and to search new high-T_c materials.

Substitutions of Y by other elements in the lanthanide series do not substantially change T_c as well as the crystal structure.[4-7] In contrast, the replacement of Cu by M (=Fe, Co, Ni, Zn...) brings about a great decrease of T_c and a transition from orthorombic to tetragonal phase with increasing amount of M.[6,8,9]

The introduction of Bi is susceptible to modify the superconducting properties of the oxides since the Bi^{3+} ion is characterized by the presence of the lone pair s^2 which sometimes is stereochemically active.[10] Moreover, the valence state of Bi^{5+} is also possible. Subustituting Bi for Y in $YBa_2Cu_3O_{7-\delta}$ was tried by Jung et al.[11] However, no change in lattice parameters was observed, which suggests that there is no solubility range of Bi in the Y-based lattice.

We report a successful introduction of Bi into the Sm-Ba-Cu-O

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system. The Sm-Ba-Cu-O system was chosen from the point of view that the ionic radius of Bi^{3+}, 1.11 Å, is comparable to that for Sm^{3+}, 1.09Å. It is to be noted that the Y^{3+} ion has the size of 1.015 Å which is smaller than the Sm^{3+} ion. In this paper, samples of $Sm_{1-x}Bi_xBa_2Cu_3O_y$ are prepared by sintering under various conditions and are characterized by X-ray diffraction studies.

EXPERIMENTAL

The samples were synthesized by the solid-state reaction[3] of powders (Sm_2O_3, $BaCO_3$, Bi_2O_3 and CuO). Table I summarizes the condition of the sample preparation. For samples ♯8223-1, ♯8216-1 and ♯8223-2, the mixtures were heated in air at 900 ℃ for 6 h. Then, they were ground and cold pressed with 3-4 kbar/cm² to form pellets of 1-cm diameter and about 0.2-cm thickness. The pellets were sintered in flowing oxygen gas at 950 ℃ for 10 h and cooled to room temperature in the furnace at a rate of 0.7 ℃/min. For other samples, the mixtures were first heated in air at 820 ℃ for 8 h. The pellets were sintered in air at 860 ℃ for 10 h for samples ♯8512-1, ♯852-1 and ♯852-2. For samples ♯8512-3, ♯852-3 and ♯852-4, the pellets were sintered in flowing oxygen gas at 845 ℃ for 10 h. The color of all the products was black.

Table I. Condition of sample preparation for $Sm_{1-x}Bi_xBa_2Cu_3O_y$

Sample	x	Sintering	Cooling rate (℃/min)
♯8223-1	0.0	(O_2), 950 ℃, 10h	0.7
♯8512-1	0.0	air, 860 ℃, 10h	0.7
♯8512-3	0.0	O_2, 845 ℃, 10h	1.5
♯8216-1	<0.1	O_2, 950 ℃, 10h	0.7
♯852-1	0.1	air, 860 ℃, 10h	0.7
♯852-3	0.1	O_2, 845 ℃, 10h	1.5
♯8223-2	<0.2	(O_2), 950 ℃, 10h	0.7
♯834-3	<0.2	O_2, 850 ℃, 8h	0.5
♯852-2	0.2	air, 860 ℃, 10h	0.7
♯852-4	0.2	O_2, 845 ℃, 10h	1.5

The samples were studied by X-ray powder diffraction measurents at room temperature using Cu-K_α or Co-K_α radiation. The X-ray data were taken at Agne Gijutsu Center, Tokyo.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows a typical X-ray diffraction pattern for a $Sm_{1-x}Bi_xBa_2Cu_3O_y$ sample with $x=0.1$ which was prepared by sintering in flowing oxygen gas at 950 ℃. Most of the peaks can be indexed on the basis of a primitive orthorhombic cell, which is analogous to that for $YBa_2Cu_3O_{7-\delta}$,[12] with $a=3.853$ Å, $b=3.909$ Å and $c=11.712$ Å. We also find extra weak lines which indicate the presence of an impurity phase. The second phase is identified with $BaCuO_2$. The highest-intensity line is a doublet composed of the (*hkl*) = (103), (110), and (013) lines. The splitting is caused by the orthorhombic distortion of tetragonal cell. The splitting between the (020) and (200) lines is also due to this distortion. An X-ray diffraction pattern was also obtained by the use of Co-K_α radiation for the sample with $x=0.1$. (see Fig.4(a)) In this pattern, we notice that the (0 2 0) and (0 0 6) lines are nearly overlapping, which makes the peak profile non-symmetric.

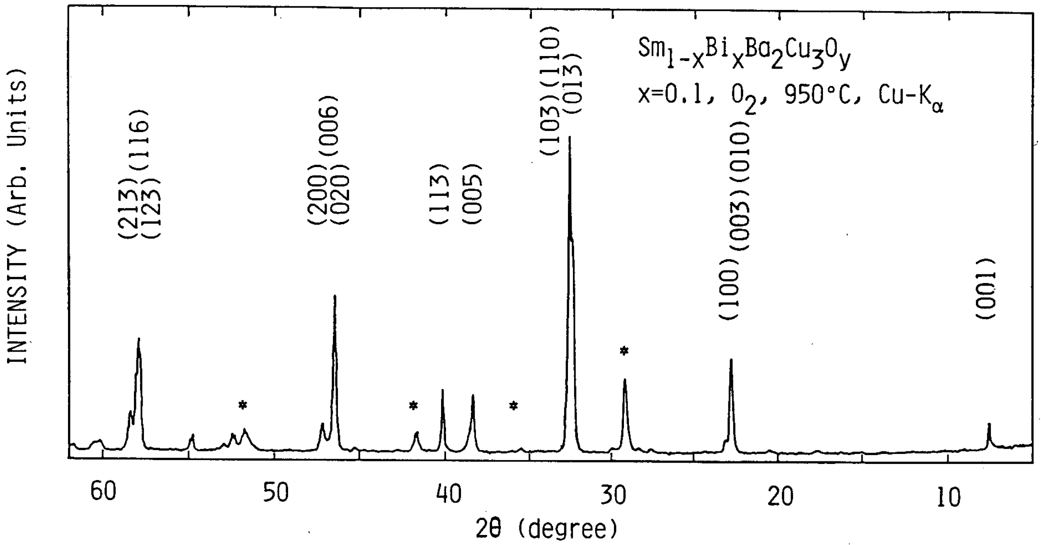

Fig.1. X-ray powder diffraction pattern for $Sm_{1-x}Bi_xBa_2Cu_3O_y$ with $x=0.1$. The sample was sintered in flowing oxygen gas at 950℃. The asterisk indicates the impurity phase.

Figure 2 shows an X-ray diffraction pattern for a sampie with $x=0.2$ which was sintered in air at 860 ℃, and Fig.3 shows a diffraction pattern for a sampie with $x=0.2$ which was sintered in flowing oxygen gas at 845 ℃. These figures indicate that samples with $x=0.2$ consist of two phases: an orthorhombic perovskite-type structure and $BaCuO_2$. The intensities of peaks related with the impurity phase are enhanced compared with the case of $x=0.1$. It is surprising that there is no prominent difference between the sample sintered in air and the sample sintered in oxygen gas as can be seen in Figs. 2 and 3.

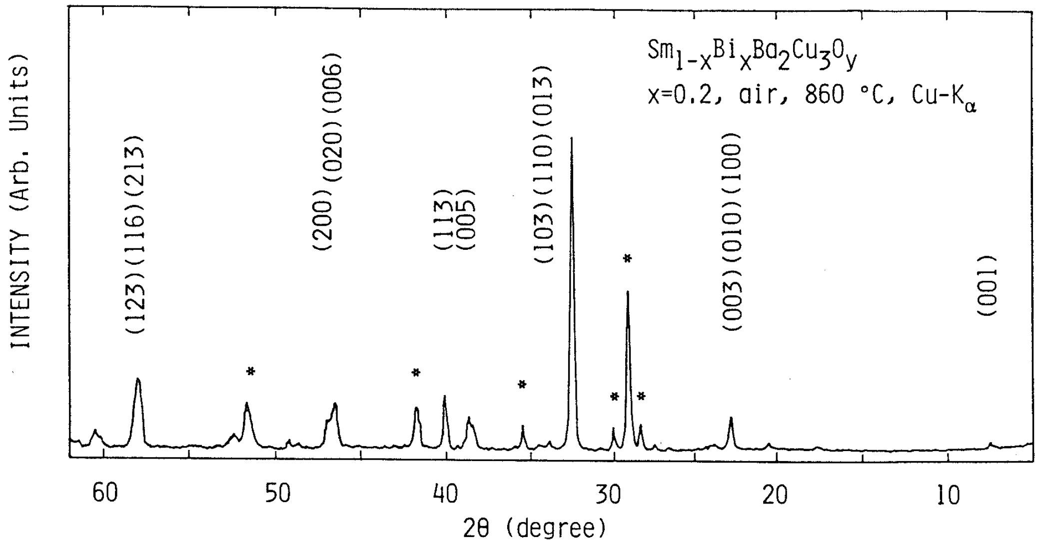

Fig.2. X-ray powder diffraction pattern for $Sm_{1-x}Bi_xBa_2Cu_3O_y$ with $x=0.2$. The sample was sintered in air at 860 ℃. The asterisk indicates the impurity phase.

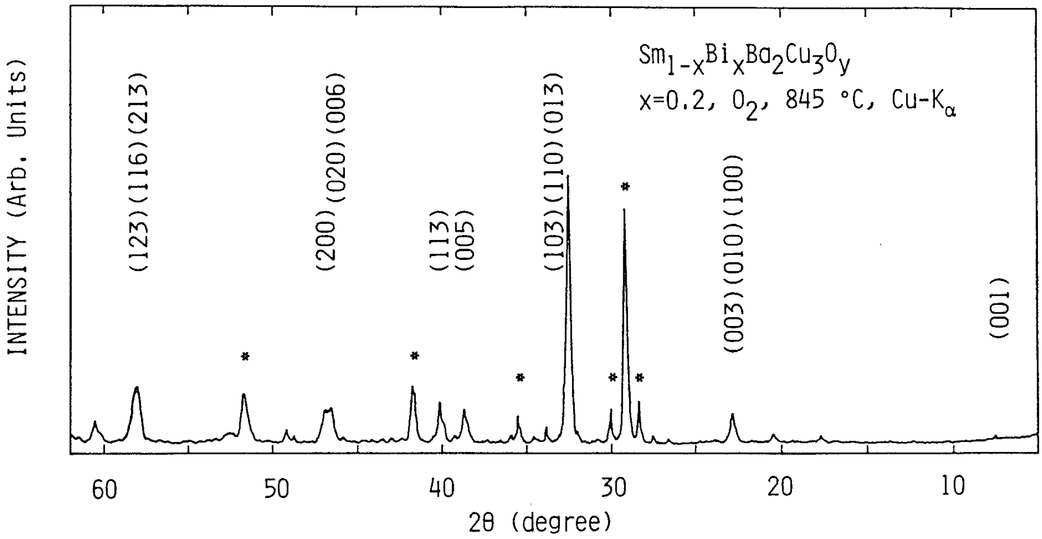

Fig.3. X-ray powder diffraction pattern for $Sm_{1-x}Bi_xBa_2Cu_3O_y$ with $x=0.2$. The sample was sintered in flowing oxygen gas at 845 ℃. The asterisk indicates the impurity phase.

The determined lattice parameters ara $a=3.858$ Å, $b=3.897$ Å and $c=11.673$ Å for the sample sintered in air and $a=3.862$ Å, $b=3.893$ Å $c=11.678$ Å for the sample sintered in flowing oxygen gas. Remarkable findings are the disappearance of the splitting between the (103), (110) lines and the (013) line within the experimental resolution and the decrease of the intensity of the (020) peak together with the decrease of the separation between the (200) and (020) lines. These results reveal that the orthorhombic distortion is decreased with increasing amount of Bi. The feature is more clearly shown in Fig. 4(a), (b) and (c), where the data were collected by employing

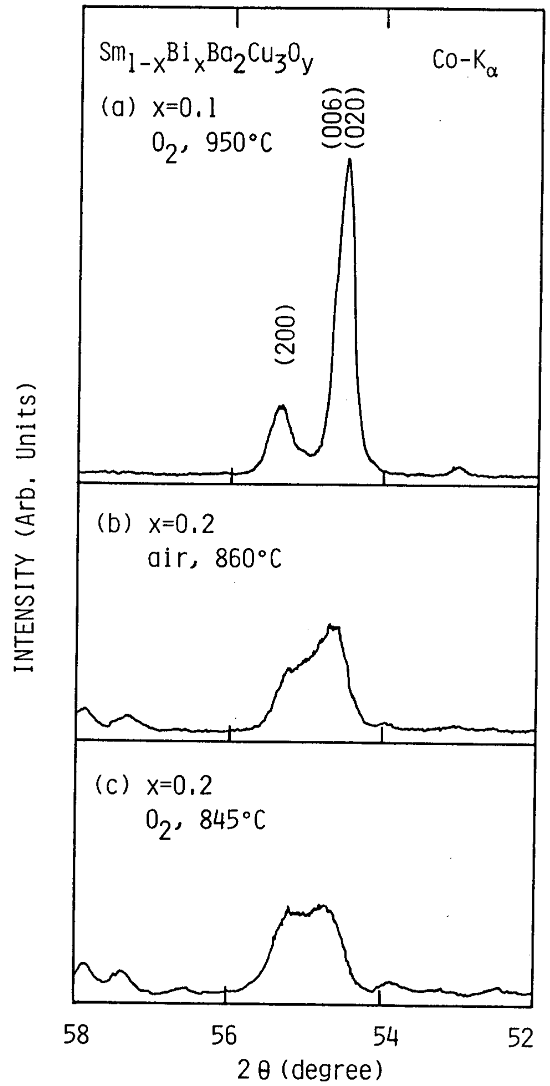

Fig.4. X-ray powder diffraction patterns obtained by the use of Co-K$_\alpha$ radiation for $Sm_{1-x}Bi_xBa_2Cu_3O_y$: (a) $x = 0.1$, the same sample as in Fig.1, (b) $x = 0.2$, the same sample as in Fig. 2, and (c) $x = 0.2$, the same sample as in Fig.3.

Co-K$_\alpha$ radiation.

The presence of the impurity phase in the samples with $x = 0.1$ and $x = 0.2$ suggests that the Sm^{3+} ions are not directly replaced by Bi^{3+} ions. The formation of $BaCuO_2$ phase produces an excess amount of trivalent ions, Sm^{3+} or Bi^{3+}, and the deficiency of Ba^{2+} ions. This induces the occupation of Ba sites by Sm^{3+} or Bi^{3+} ions. Therefore, it becomes evident that the main phase is analogous to $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ or $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. It is reported that, in such a Sm- or Eu-rich system, excess Sm or Eu atoms are located at the Ba sites.$^{13)}$ The lattice parameters for the main phase in the $Sm_{1-x}Bi_xBa_2Cu_3O_y$ samples are plotted in Fig.5 as a function of x. Figure 5 shows that, with increasing x, the a parameter increases and the b

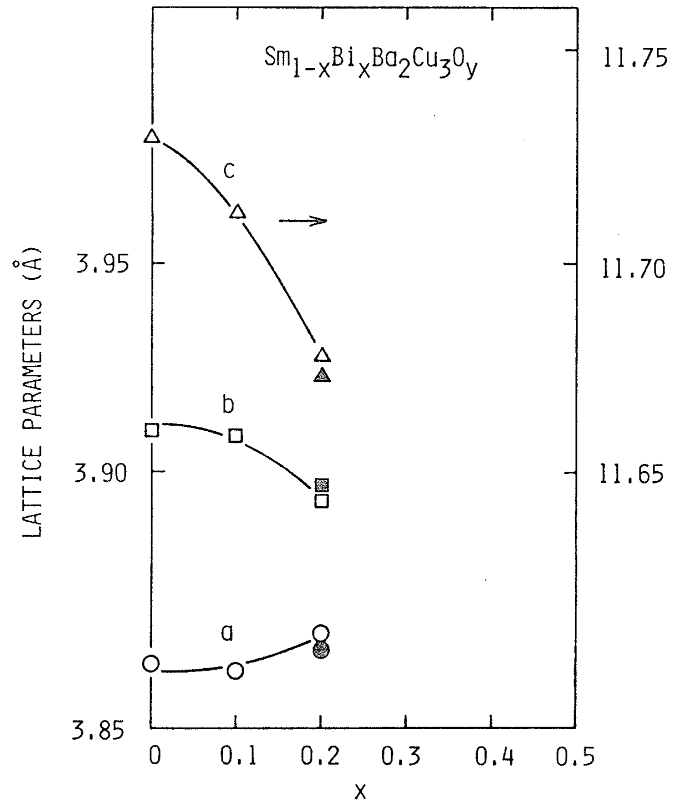

Fig.5. Lattice parameters for $Sm_{1-x}Bi_xBa_2Cu_3O_y$ as a function of x. The open symbols represent the data for the samples sintered in flowing oxygen gas, and the solid symbols represent the data for the sample sintered in air. The data for $x=0$ are taken from ref.14.

and c parameters are decreased. The shortening of the c parameter is correlated with the replacements of the Ba sites by smaller Sm^{3+} or Bi^{3+} ions. These trends in the lattice parameters are the same as those observed in $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ or $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$.[13]

From the above arguments based on the experimental observations, we conclude that, in the Bi-doped Sm-Ba-Cu-O system, the Ba sites are partly replaced by smaller Sm or Bi ions as in the $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ or $Eu_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ system. Electrical properties have been measured on the Bi-doped $Sm_{1-x}Bi_xBa_2Cu_3O_y$ samples and a different behavior of the superconducting transition has been observed between the samples sintered in air and the samples in oxygen gas. The results will be reported elsewhere.

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