Relationship between Oxygen Nonstoichiometry and Structural Changes in Bi-2212 Superconductors

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The X-ray diffraction patterns for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ sintered in air or Ar indicated that the reduction in the number of excess oxygen ions induced a structural change from orthorhombic to pseudotetragonal. To explain the oxygen nonstoichiometry effect in this system, we presented the model that there were two different locations for excess oxygen in the $Bi_2Sr_2CaCu_2O_{8-y}$ structure, i.e., in the Bi–O layer and in the vicinity of the Cu–O sheets. Compared with the $Bi_2Sr_{2-x}La_xCaCu_2O_{8+y}$ system, it was considered that substituting Y for Ca in this model resulted in coulomb interaction between the excess oxygen ion (O_i^{2-}) in the vacant sites around Ca^{2+} ions and the Y^{3-} ion in the Ca^{2-} site (Y_{Ca}^+). The association between O_i^{2-} and Y_{Ca}^+ was thought to explain the reduction of the orthorhombicity. When the valency of Bi decreased, the period of modulation in $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$ increased from $4.2b$ to $4.4b$. This result suggested that the modulation period was correlated with the excess oxygen in the Bi–O layer. These results supported this model for the origin of the excess oxygen in the Bi-2212 structure. © 1992 Academic Press, Inc.

1. Introduction

Since the discovery of 105 K Bi superconductors (*1*), a number of studies on $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$) have been made (*1, 2*). Superconducting transition temperatures (T_c) of 5–20 K (*2, 3*), 84 K (*1*), and 105 K (*1*) have been reported for $n = 1(2201$ phase), 2(2212 phase), and 3(2223 phase), respectively. The superconducting transi-

tion temperatures of 84 K for the 2212 phase and 105 K for the 2223 phase were achieved by partial substitution of Ca for Sr. The partial substitution (i.e., $x < 0.6$) of Ln($= Y$, Nd, Eu, Gd, or Lu) for Ca in superconducting $Bi_2Sr_2Ca_{1-x}Ln_xCu_2O_{8+y}$ resulted in an antiferromagnetic insulator (*4–7*). A structural change from tetragonal to orthorhombic was observed around $x = 0.5$. Also, a partial substitution of La for Sr in superconducting $Bi_2Sr_{2-x}La_xCaCu_2O_{8+y}$ (*7*) resulted in an antiferromagnetic insulator at $x > 0.6$, but the structure remained tetragonal. It was found that a substitution of Y for Ca caused

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a structural change from tetragonal to ortho-rhombic while the substitution of La for Sr did not induce any structural changes. This has not been clearly explained.

The structure of the superconducting $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$) has been characterized by an incommensurate modulation (8–11). In $Bi_2Sr_2CaCu_2O_{8+y}$, the modulation was typically one-dimensional along the b axis (12). Also, from the results of X-ray diffraction ($13, 14$–16), it was found that there were Ca^{2+} ions between the adjacent Cu–O sheets and Sr ions between the Cu–O and Bi–O sheets. The modulated structure in Y-doped $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ was also investigated ($6, 17$). In this system, the modulation period decreased linearly from $4.8b$ at $x = 0.0$ to a commensurate one of $4.0b$ at $x = 1.0$, where b was the average lattice parameter along the b axis (6). A characteristic domain structure in the modulated structure was also found in this system for $0.8 < x < 1.0$ (17). Several models have been proposed for the origin of the structural modulation in this system. Yamamoto et al. (18) pointed out that the existence of excess oxygen in the Bi–O layer was the major cause for such modulations on the basis of their Rietveld analysis using powder neutron diffraction data. Therefore, it was thought that the orthorhombicity was due to the detailed structure of the BiO planes as shown in Refs. (10) and (18), where oxygen moved along one of the otherwise equivalent a, b axes toward a pair of bismuth atoms, to satisfy the normal Bi–O distances. Wu et al. (19) obtained large-area scanning tunneling microscope images of the Bi(Pb)–O layers in $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+y}$. The atomic-resolution images indicated that excess oxygen atoms were present in the Bi(Pb)–O layers. Therefore, additional oxygen ions in the BiO layers is thought to oxidize the CuO layers sufficiently to produce superconductivity, and it also produces a structural modulation whose period is not commensurable with the lattice and which depends on the number of extra oxygens.

Recently, we investigated the effects of oxygen nonstoichiometry on resistivity and superconducting transition temperature and the relationship between the structural modulation and the superconducting properties of $Bi_2Ca_{2.5}Nd_{0.5}Cu_2O_{8+y}$ and $Bi_2Ca_{2.5}La_{0.25}Pr_{0.25}Cu_2O_{8+y}$ (20). It was observed that the modulations in both compounds was near commensurate with a period equal to $9b$, and the superconducting properties of $Bi_2Ca_{2.5}Nd_{0.5}Cu_2O_{8+y}$ and $Bi_2Ca_{2.5}La_{0.25}Cu_2O_{8+y}$ were dependent on oxygen partial pressure during sintering, but the modulation period remained unchanged. If the extra oxygen ions in the Bi–O layer were the main reason for the modulated structure in these compounds, the modulation period should have been affected by the oxygen content. However, this mechanism did not seem to work for any one of the Sr-free samples. Recently, Wu et al. (21) utilized a scanning tunneling microscopic (STM) technique to characterize the local electronic and structural effects of oxygen doping in $Bi_2Sr_2CaCu_2O_{8+y}$. Oxygen was removed from as-grown superconducting single crystals ($T_c = 85$ K) by vacuum annealing ($P = 10^{-3}$ Torr) at 673 K. The samples became nonsuperconducting after annealing for 30 hr in vacuum at 673 K. The STM images of superconducting and nonsuperconducting samples exhibit the one-dimensional super-structure characteristic of $Bi_2Sr_2CaCu_2O_{8+y}$ superconductors, and similar atomic structure. They considered that the annihilation of superconductivity in $Bi_2Sr_2CaCu_2O_{8+y}$, when the oxygen content, $8 + y$, was reduced, might be due to the loss of oxygen not from the Bi–O sheets but from somewhere in the vicinity of the Cu–O sheets.

In this paper, we report that the reduction in excess oxygen enhances the structural change from orthorhombic to pseudotetragonal, and on the effects of oxygen nonstoichiometry on structural transformation and modulation period in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$.

2. Experimental

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ and $Bi_2Sr_{2-x}La_x$ $CaCu_2O_{8+y}$ compounds were prepared by a conventional solid state reaction method. Powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, La_2O_3, and CuO were mixed and calcined at 1123 K for 10 hr in air. The mixed powders were ground and pressed into parallelepiped bars of $3 \times 3 \times 20$ mm^3. The bar samples of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ compound were sintered under two different conditions. One was sintering in the temperature range of 1133 to 1203 in air and cooling to room temperature at a rate of 200 K/hr. Another was sintering at 1093 and 1113 K in Ar and cooling to room temperature at a rate of 500 K/hr in the same atmosphere. All the samples were found to be single phase. The lattice parameters were determined by X-ray powder diffraction (XRD) using $CuK\alpha$. The peaks were found to be in good agreement with those indexed by Onoda et al. (13). The structural modulation was observed through electron diffraction. The specimens for the electron diffraction were flakes prepared by crushing sample bars. The average valencies of both Bi and Cu ions were determined by a coulometric titration technique (22). This technique involves two steps of titration. The oxygen content of the 2212 samples was determined by the sum of the amounts of Bi^{5+} and Cu^{3+} ions and charge balance.

3. Results

The X-ray diffraction patterns for Bi_2Sr_2 $Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$ sintered in air and Ar are shown in Figs. 1a'–1c'. The diffraction pattern depends strongly on both the sintering temperature and the atmosphere. In a reducing condition, i.e., in Ar, the (2000) and (0200) peaks are seen to merge into a single peak, as shown in Figs. 1b' and 1c'. This means that the symmetry has changed from orthorhombic to pseudotetragonal. The lat-
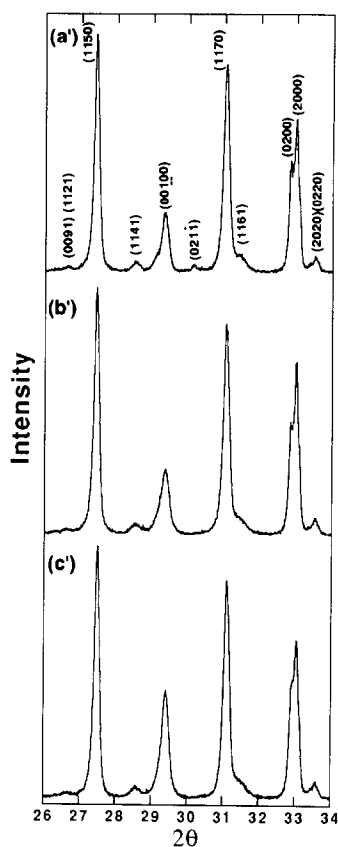

FIG. 1. X-ray diffraction patterns of Bi_2Sr_2 $Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$: (a') sintered in air at 1183 K, (b') sintered in Ar at 1093 K, and (c') sintered in Ar at 1113 K. a', b', and c' show the details of the (2000, 0200) peaks.

tice parameters of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2$ O_{8+y} samples are shown in Fig. 2. It is seen that the length of the b axis decreases as the degree of reduction increases. (Note that the degree of reduction in the present experiment increases in the following order: (a) air at 1183 K, (b) Ar at 1093 K, and (c) Ar at 1113 K.) This result suggests that the reduction in excess oxygen reduced the orthorhombicity. The oxygen contents of two samples, i.e., those sintered in air at 1183 K and in Ar at 1093 K, were determined by a coulometric titration technique, as given in Table I. Actually, the oxygen contents are
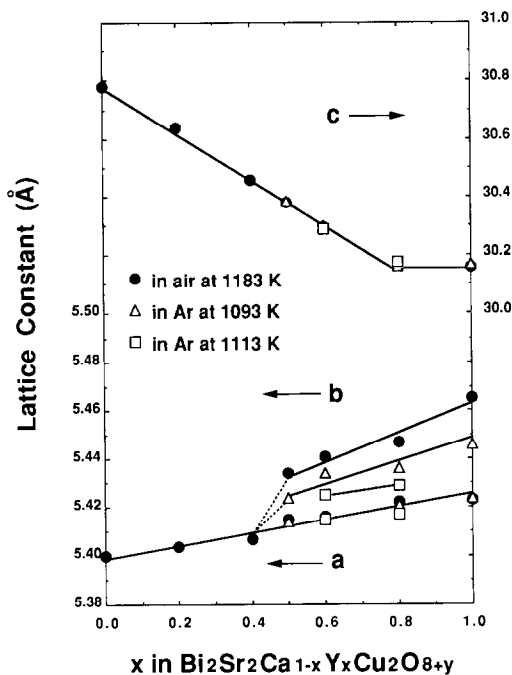
FIG. 2. Lattice parameters a, b, and c with x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ at the differential sintering condition.

FIG. 3. Electron diffraction patterns for $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8-y}$ sintered in (a) air and (b) Ar.

smaller in the sample sintered in Ar at 1093 K than those in air. Thus, the Bi valency is smaller in the sample sintered in Ar than that in air.

Assuming that the structural modulation is caused by excess oxygen ions in the Bi–O layers, it follows that the Bi valency should decrease with increasing modulation period.

TABLE 1

THE SINTERING CONDITION, THE VALENCIES OF Bi AND Cu, AND THE OXYGEN CONTENT OF $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$

Sintering condition	Bi valency	Cu valency	Oxygen content
a. Air (at 1183 K)	3.03	2.11	8.44
b. Ar (at 1093 K)	2.99	2.06	8.35

Figure 3 shows electron-diffraction patterns for two samples of $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$, one sintered in air at 1183 K and the other in Ar at 1093 K. The incident beam was always parallel to the c axis. Note that fundamental spots are indexed for the 2212 structure, ignoring modulations. In addition to the fundamental spots, superlattice spots which indicate the existence of modulation are observed along the b axis. The period of modulation, m, is defined to be an inverse of the distance between the first-order superlattice spot and the 100 spot. When the excess oxygen decreases, m increases from a value of $4.2b$ to $4.4b$. This result is consistent with the change in the Bi valency and indicates excess oxygen ions located in the Bi–O layers. Therefore, the oxygen nonstoichiometry is crucially related with the structural transformation in $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$.

Figure 4 shows oxygen contents of the samples in the $Bi_2Sr_{2-x}La_xCaCu_2O_{8+y}$ system and the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system. The oxygen content in both systems monotonically increases as x increases. It is concluded that the substitution of Y for Ca in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ system and the substitution of La for Sr in the $Bi_2Sr_{2-x}La_x CaCu_2O_{8+y}$ system result in a parallel effect
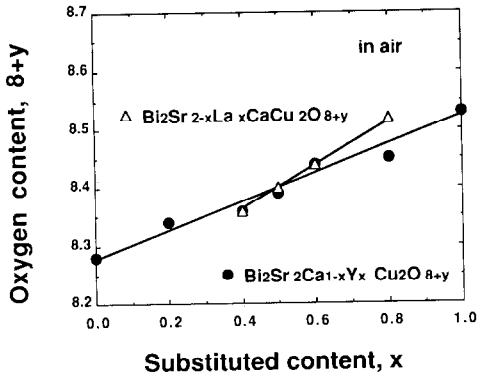
FIG. 4. The oxygen content is plotted against the composition, x in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ and $Bi_2Sr_{2-x}La_xCaCu_2O_{8-y}$.

for the introduction of excess oxygen into the lattice. Next we reconfirmed Koike *et al*'s result (7) that the structure of Bi_2Sr_2Ca Cu_2O_{8+y} remained tetragonal even when La was substituted for Sr.

4. Discussion

From these results of the oxygen nonstoichiometry effect in Sr-free Bi cuprates (20) and STM observation in $Bi_2Sr_2CaCu_2O_{8+y}$ (21), it seems that those are two different locations for excess oxygen in the structure, i.e., in the Bi–O layer and in the vicinity of the Cu–O sheets. To explain the oxygen nonstoichiometry in this structure, it is possible that the excess oxygen in both sites changes independently. Actually, the results in Table I and Fig. 3 may suggest that the excess oxygen of both sites is dependent on the temperature and the oxygen partial pressure.

On the basis of this picture, we now consider the difference between the substitution of Y for Ca and the substitution of La for Sr in $Bi_2Sr_2CaCu_2O_{8+y}$ to explain the different effects of substitution with structural transformation. Because of an electroneutrality condition, both the substitution of Y for Ca and the substitution of La for Sr may induce:

(a) incorporation of additional oxygen ions into the crystal and/or (b) a reduction in the Bi and/or Cu valencies (electron doping). The experimental results in Fig. 4 support effect (a). However, as explained in the following, this effect cannot cause a structural transformation as a result of oxygen nonstoichiometry. First of all, the location of excess oxygen in the crystal must be determined. Yamamoto *et al.* (18) pointed out that the cause of the excess oxygen was the existence of extra oxygen ions in the Bi dilute region of the Bi–O layer, according to the result of their Rietveld analysis. Their model supports the increase in the modulation period as the Bi valency decreases, as shown in Fig. 3, but does not explain the difference between the effects of the substitution of Y for Ca and of the substitution of La for Sr. Second, from the results of X-ray diffraction (13, 14–18), it was found that there were Ca^{2+} ions between the adjacent Cu–O sheets and Sr ions between the Cu–O and Bi–O sheets. Therefore, the ideal layer sequence on traversing the c axis of the pseudotetragnal structure may be given by

$$-Bi_2O_{2+x}-SrO-CuO_2-Ca- \\ CuO_2-SrO-Bi_2O_{2+x}-,$$
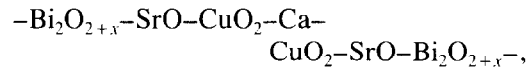
in which it is generally assumed that no oxygen is left in the Ca sheet. That is, this ideal structure suggests that the sites around Ca ions in the Ca sheet are vacant. Assuming that part of the excess oxygen settles in the vacant sites in Ca layers, we can consider that substituting Y for Ca ions directly introduces the excess oxygen into the vacant sites around Ca ions, and substituting La for Sr ions, which introduces the excess oxygen to the vacant sites, acts to intervene in the Cu–O layers. This model suggests that Y substitution results in coulomb interaction between the excess oxygen ions (O_i^{2-}) and Y^{3+} ions in Ca^{2+} sites (Y_{Ca}^+) (this substitution means the existence of an excess positive charge, $1+$, in Ca sites), but La substitution does not result in an excess positive

charge in Ca sites and introduces the excess oxygen ions at random. Thus, we can consider the model that the origin of structural transformation caused by oxygen nonstoichiometry is the association between excess oxygen ions and Y ions, e.g., $(Y_{Ca}^{+}-O_{i}^{2-}-Y_{Ca}^{+})$ and/or $(Y_{Ca}^{+}-O_{i}^{2-})$.

5. Summary

In summary, the X-ray diffraction patterns for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$ sintered in air or Ar indicated that the reduction in the number of excess oxygen ions induced a structural change from orthorhombic to pseudotetragnal. To explain the oxygen nonstoichiometry effect in this system, it was considered that there were two different locations for excess oxygen in this structure, i.e., in the Bi–O layer and in the vicinity of the Cu–O sheets. This model suggested that the excess oxygen in both sites changed independently. Compared with the $Bi_2Sr_{2-x}La_xCaCu_2O_{8+y}$ system, it was considered that substituting Y for Ca in this system resulted in coulomb interaction between the excess oxygen ions (O_i^{2-}) in the vacant sites around Ca ions and Y^{3+} ions in the Ca^{2+} site (Y_{Ca}^{+}). The association between O_i^{2-} and Y_{Ca}^{+} was thought to explain the reduction in the orthorhombicity. When the valency of Bi decreased, the period of modulation in $Bi_2Sr_2Ca_{0.4}Y_{0.6}Cu_2O_{8+y}$ increased from $4.2b$ to $4.4b$. This result suggested the location of excess oxygen ions in the Bi–O sheet and it also supported this model.

Acknowledgment

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