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Superconductive transition at 98.5 K in monoclinic $(Bi,Pb)_2Sr_2CaCu_2O_y$

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By annealing the $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ superconductor (2:2:1:2 phase) with $x=0.2$ in the absence of oxygen, a high-T_c value of 98.5 K was observed. The lattice of this superconductor was revealed to be monoclinic. The formation of this superconductor with an unexpectedly high T_c value for the 2:2:1:2 phase is difficult to explain simply by consideration of the optimum carrier concentration, and it is likely correlated with the structural transformation of the superconductor.

It has been revealed that T_c's of cuprate superconductors are very sensitive to their carrier concentration.[1,2] A maximum T_c of around 80–85 K has been obtained for $Bi_2Sr_2CaCu_2O_y$ (2:2:1:2 phase) through changing the hole concentration of the samples by cation substitution in air.[1,3–5] Further, we found that the optimum hole concentration per unit cell with the highest T_c value in $Bi_2Sr_2Ca_2Cu_3O_y$ (2:2:2:3 phase) is larger than that in the 2:2:1:2 phase.[3,4] Fukushima *et al.*[6] reported that Pb substitution in the 2:2:1:2 phase, followed by annealing in N_2, removes oxygen from the system, causing the T_c value to rise to the 90-K class. Even without Pb substitution, a T_c of above 95 K has been reported.[7,8] In order to clarify the variation of T_c, especially in the case of a N_2- or Ar-annealed phase in the Pb-substituted 2:2:1:2 phase, we have studied the changes in structure and T_c for different Pb content, before and after annealing in N_2 or Ar.

We found a maximum T_c of 98.5 K is attainable for the 2:2:1:2 phase of the Pb-substituted system, after annealing in N_2 or Ar, which is 20 K higher than that prepared in ambient oxygen. While it was reported that Pb substitution promoted a structural change of superconductors from pseudotetragonal to orthorhombic,[6] we found here that annealing Pb-substituted Bi-Sr-Ca-Cu-O samples in N_2, Ar, or very low O_2 pressure of $\frac{1}{18}$-atm results in a structural change from orthorhombic to monoclinic. We believe that such a remarkable improvement of T_c is difficult to explain simply by considering the change of hole concentration alone, and must be closely correlated with the crystal structures. Such effects as the shape of the crystal lattice, or the position of each of the elements including oxygen in a unit cell must be considered.

Starting powders were prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, and $Ca(NO_3)_2 \cdot 4H_2O$ in water, drying by evaporation, and calcining in air at 800 °C for 2 h. These powders were ground, pressed into pellets, sintered in $\frac{1}{18}-\frac{1}{5}$ atm of O_2 for 40–60 h at 800–830 °C. Some of the pellets were annealed in N_2 or Ar at 500–780 °C for 8 h, after they were prepared in air at 830 °C for 40 h. Four kinds of samples, $x=0$, 0.05, 0.20, and 0.30 in $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ were prepared. The concentrations of Bi, Pb, Sr, Ca, and Cu were determined by induction-coupled plasma atomic emission spectroscopy (ICP-AES) (ICPS-50A, Shimadzu Co.). The atomic ratios in the samples were $(Bi,Pb)_{1.99-2.12}Sr_{1.98-2.14}Ca_{1.01-1.10}Cu_2O_y$, which were consistent with the nominal ones, to within 10%. There was no difference in the cationic concentrations before and after annealing in N_2. The superconductive properties were determined by measuring the temperature dependence of ac magnetic susceptibility, by the field-cooling method (Meissner effect). Each sample was reground and pelletized prior to the ac susceptibility measurement. The cell parameters were determined by powder x-ray diffraction (XRD) using Cu $K\alpha$ (RAD-IIIB, Rigaku denki). The peaks were assigned according to those indexed by Onoda *et al.*[9] Hole concentration was estimated from the formal charge of Cu. The formal charge of Cu was determined by ordinary idometric titration methods.[5] The formal charge of Bi and Pb are assumed to be trivalent and divalent, respectively.[10]

Temperature dependences of magnetic susceptibility for the $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ samples annealed in N_2 at 750 °C are shown in Fig. 1. The T_c of all N_2 annealed samples is definitely above 93.0 K. The highest T_c of 98.5 K is observed at $x=0.2$. A single superconductive transition is observed in all samples, indicating that no 2:2:2:3 phase is formed, consistent with the x-ray diffraction measurement which showed no diffraction peaks due to the 2:2:2:3 phase. For comparison, ac magnetic susceptibility

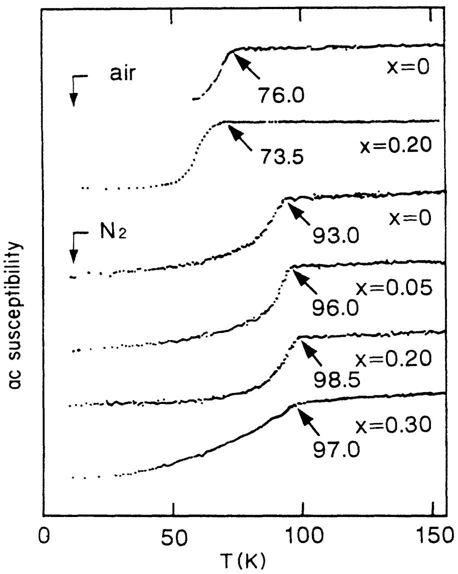

FIG. 1. ac magnetic susceptibility vs temperature in $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ in ambient O_2 or N_2. T_c rises dramatically following annealing in N_2, where the highest T_c of 98.5 K is observed in $x = 0.2$.

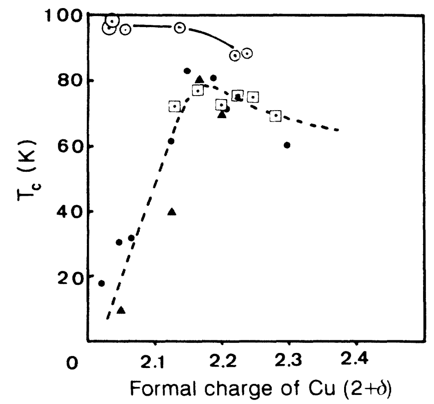

FIG. 2. T_c dependence of the Pb substituted 2:2:1:2 phase on the Cu formal charge. The 2:2:1:2 phase annealed in N_2 (○) and those without annealing (□) are shown. The T_c vs formal charge of Cu, presented in Refs. 1 and 7, is shown by ▲ and ●, respectively. The trend of T_c dependence for the samples prepared in N_2 annealing (——) is clearly different from that of the samples prepared in ambient oxygen (····).

plots of samples with $x = 0$ and 0.2 prepared in air are also shown in Fig. 1. It is clear that the 20-K improvement of T_c is produced by N_2 annealing. Ar annealing also raised the T_c to 91.0–97.0 K. When the annealing temperature was increased to 780 °C, the highly substituted sample of $x = 0.3$ decomposed to $Bi_2Sr_2CaO_6$ and Cu_2O.[11] In most cases annealing just below the decomposition temperatures gives the highest T_c value.

The T_c dependence on hole concentration in the 2:2:1:2 phase has been studied by several groups.[1,3,5,12,13] In order to establish whether the present T_c of above 93.0 K is explained simply by the change of hole concentration, the T_c of a 2:2:1:2 phase with a different formal charge of Cu is measured using $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ samples. The hole concentration is varied by controlling the partial pressure of O_2 during sintering, and by changing the Pb substitution ratio. In Fig. 2, the T_c values of 2:2:1:2 phase are plotted against the formal charge of Cu. For samples prepared in ambient oxygen (represented by □), the plot is approximately consistent with the results reported by Tamegai *et al.*[1] and Maeda *et al.*[5] (shown by ▲ and ●, respectively). Furthermore, the optimum value of the Cu formal charge which gave the highest T_c, of around 85 K for the 2:2:1:2 phase, ranges between 2.10 and 2.15. The formal charge of Cu for the standard $Bi_2Sr_2Ca_1Cu_2O_y$ sample prepared in air is located around 2.20,[12] so that by substitution of Y for Ca, the highest T_c of around 85 K is obtained for a smaller formal charge.

In contrast to these results, the T_c values of the 2:2:1:2 phase obtained following N_2 treatment are clearly different (as represented by ○) and the plots show anomalous features. The excess formal charge of Cu, δ, is varied from 0.03 to 0.25 by controlling the annealing temperature. As the formal charges of Bi and Pb are fixed to 3+ and 2+, the Cu formal charge shown in Fig. 2 is the maximum estimation. If Bi^{5+} or Pb^{4+} exist in the system, then the Cu formal charge should be smaller than that shown in Fig. 2. The highest T_c was obtained for smaller charge values of the samples annealed in N_2 or Ar at 750 °C. This is in contrast to the Y-substituted samples, where the decrease in the Cu formal charge ($\delta < 0.10$) resulted in a decrease in the T_c value (see Fig. 2).[1] The value of T_c should not be treated only as a function of the carrier concentration. Annealing in higher temperature causes smaller formal charge value and the samples decompose eventually above 780 °C. From ICP-AES measurements, there are slight changes in the cationic concentrations caused by annealing in ambient N_2 or Ar below 750 °C. Therefore, the excess oxygen contents are directly compared to each other by the formal charge values. For $x = 0.2$, the N_2 annealing at 750 °C caused the slight change of the cationic composition from $Bi_{1.71}Pb_{0.40}Sr_{2.14}Ca_{1.10}Cu_{2.00y}$ to $Bi_{1.70}Pb_{0.42}Sr_{2.12}Ca_{1.08}Cu_{2.00}O_y$, and caused the dramatic decrease of oxygen content from 8.14 to 7.83 in $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$. It should be noted that oxygen content (7.83) after N_2 annealing is smaller than that of the ideal structure (8.0). This result indicates that there is an oxygen deficiency after N_2 annealing.

Another interesting point is the change of c-axis length. The lattice constant c of the present sample with T_c value over 90 K are 30.76–30.77 Å, even shorter than those before the N_2 annealing (30.78–30.89 Å). Reduction of excess oxygen in the Bi-O layer leads to an increase of c-axis length.[11] Accordingly, we consider that the reduction of the lattice constant c by N_2 or Ar annealing is not explained simply by the reduction of excess oxygen in the Bi-O layer. This suggests that annealing in N_2 leads to a structural change incorporating the Bi-O layer.

Actually, as shown in Fig. 3, the x-ray-diffraction pattern of $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_y$ depends strongly on the sintering atmosphere. With decreasing oxygen pressure from $\frac{1}{5}$ to $\frac{1}{13}$ atm, the (2000,0200) peak splits into two

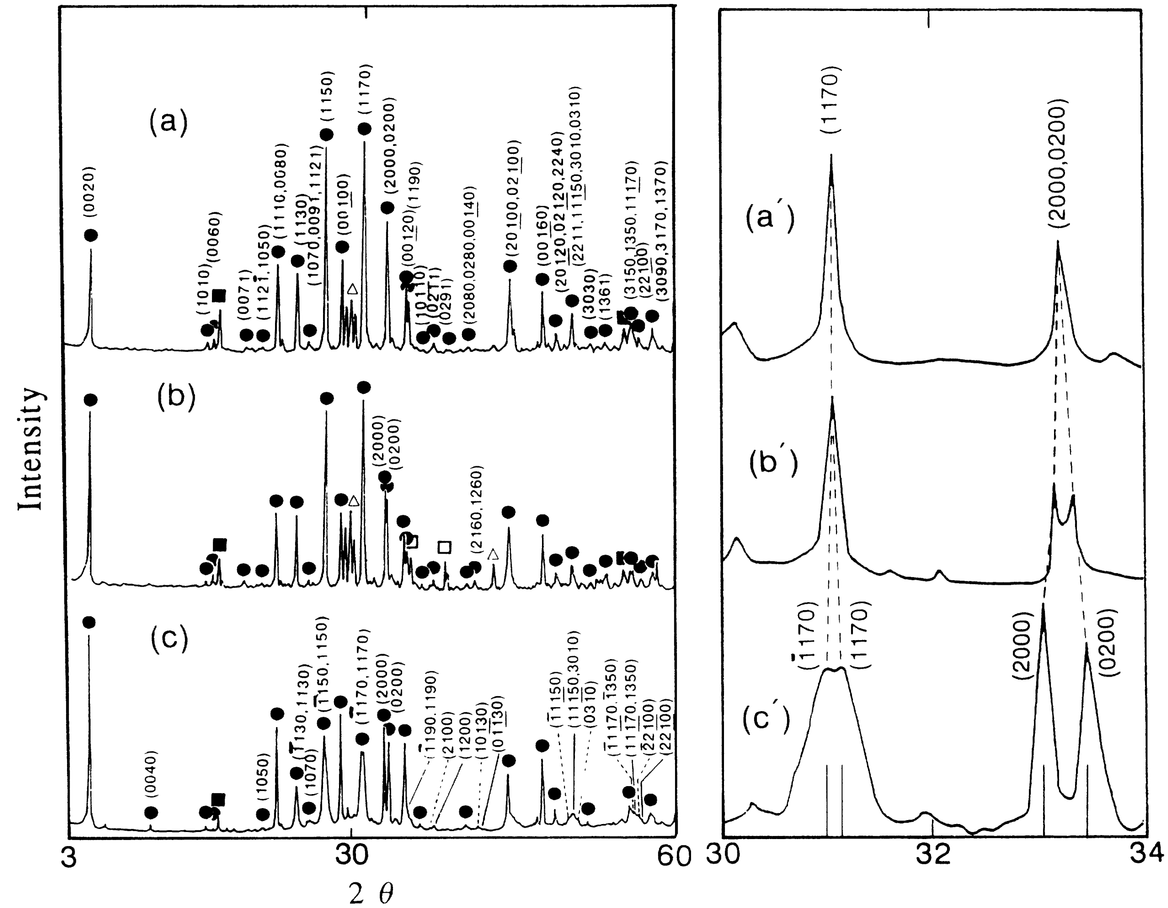

FIG. 3. XRD patterns of $Bi_{1.7}Pb_{0.4}Sr_{2.1}Ca_{1.1}Cu_{2.0}O_y$. By decreasing the O_2 pressure during annealing, the pseudotetragonal structure changed into orthorhombic and finally into monoclinic. (a) annealed in $\frac{1}{5}$ atm O_2, (b) annealed in $\frac{1}{13}$ atm O_2, and (c) annealed in N_2. (a'), (b'), and (c') show the details of the (1170) and (2000, 0200) peaks. The calculated data are shown by four lines. ●, 2:2:1:2 phase; ■, Ca_2PbO_4; □, CuO; △, unknown phase (Ref. 11).

peaks, as magnified in (a') and (b'). This means that the symmetry has changed from pseudotetragonal to orthorhombic.[6] By annealing the sample (a) in N_2 at 750 °C for 8 h, two dramatic changes in the patterns are observed [see Fig. 3(c)]. First, the peaks from $(hkl1, hkl\bar{1})$, such as 0071, 0211, 0291, and 1361) disappear. All these peaks originate from the modulated structure,[9] implying that the modulated structure has disappeared in sample (c).[6] The disappearance of the modulated structure is also confirmed by electron-diffraction patterns incident along the c axis. Second, the peaks from 1130, 1150, 1170, 1190, and $11\underline{15}0$, $11\underline{17}0$, 1350, and 2210 are split or broadened. Even if we assume an increase of the difference between a and b lattice parameters in an orthorhombic cell, these peaks do not split or broaden. The peaks in (c) can be assigned with monoclinic structure with lattice constants of $a = 5.428$ A, $b = 5.358$ A, $c = 30.82$ A, and $\gamma = 90.5°$. By the disappearance of the modulated structure, the indices caused by the modulation are omitted.[9] As an example, the splitting of (1170) is magnified in (c'). The calculated peak positions for $(\bar{1}170)$, (1170), (2000), and (0200) are marked with vertical lines. They agree well with the observed ones. Besides the (1170) peak, each of the calculated peaks, (1130), (1150), (1190), $(11\underline{15}0)$, $(11\underline{17}0)$, (1350), and $(22\underline{10}0)$, separates into two peaks for a monoclinic cell, indicating clearly the observed splitting or broadening of the peaks in (c). This monoclinic structure allows diffraction from $(h+l)$, k, and $l = 2n+1$ planes such as $(01\underline{13}0)$, which is forbidden in the pseudotetragonal-structure of *Cccm* due to the c glide plane perpendicular to both a and b.[9] Therefore, the possible space group is either of *Pm*, *P*2, or *P*2/*m*. In the previous part, we pointed out that N_2 annealing leads to the formation of an oxygen deficiency and a structural change including the Bi-O layer. Now the structural change is found to be the disappearance of the modulation and the transformation to monoclinic, possibly caused by the oxygen deficiency in the Bi-O layer.

Crystal structure of the 2:2:1:2 phase depends on the Pb content and the partial pressure of oxygen during annealing. Increasing the Pb content changes the pseudotetragonal structure into orthorhombic or monoclinic. By annealing the $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ with $0.2 \leq x \leq 0.3$ in N_2, or in O_2, at pressures less than $\frac{1}{18}$ atm, a monoclinic structure is formed. The highest T_c of 98.5 K is observed in this particular monoclinic phase when annealed in N_2 or Ar. Thus, the change of the crystal structure in addition to the optimum hole concentration seems to play an important role in the extremely high T_c, 98.5 K, of the 2:2:1:2 phase.

In summary, we observed a structural dependence on the annealing atmosphere, which was related to the absence of oxygen for $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$. Annealing below $\frac{1}{18}$ atm of O_2 pressure leads to the formation of monoclinic $(Bi_{1-x}Pb_x)_2Sr_2CaCu_2O_y$ for $0.2 \leq x \leq 0.3$. For $x = 0.2$, the lattice parameters of a, b, c, and γ are 5.428 A, 5.358 A, 30.82 A, and 90.5°, respectively. T_c's of the samples after annealing in N_2 or Ar are all above 93.0 K, 20 K higher than those obtained before annealing. A maximum T_c of 98.5 K is observed for $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_y$ with the monoclinic structure. The origin of this high T_c cannot be explained simply in terms of the hole concentration in the 2:2:1:2 phase, as previously reported. The trend of T_c vs hole concentration known for the Y^{3+} or Nd^{3+} substituted systems do not equivocate to the present study. Changes of the CuO_2 based structure or relaxation of the incommensurate structure promoted by the N_2 or Ar annealing procedure may be crucial for the high T_c of over 93.0 K. The structural change from pseudotetragonal to monoclinic leads to a further increase of T_c to 98.5 K.

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