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Variation in T_c and carrier concentration in Tl-based superconductors

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T_c variations observed in some Tl-based superconductors were investigated. Clear correlations were found between T_c, carrier concentration, and c-axis length. In particular, for $Tl_2Ba_2CuO_6$, a decrease in oxygen content of about 0.1 per formula unit, which corresponded to a decrease in hole concentration of 0.2, increased T_c up to about 80 K, and elongated the c axis by about 0.4%. The carrier concentration in that system could also be decreased by substitution of La for Ba, which resulted in an increased T_c value. T_c variations caused by a change in oxygen content were also observed in $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$. It was demonstrated that superconductivity appears in a certain appropriate range of carrier concentration.

Numerous investigations have been made to elucidate the mechanism of high-T_c superconductivity. In particular, as to relations between superconductivity and other parameters, many studies have been done, and some clear correlations between T_c, crystal structures, and carrier concentration have been found so far. For example, in the Bi or Tl systems, there exist fruitful variations in crystal structures which include several CuO_2 sheets between Bi-O or Tl-O layers.[1,2] They tend to show higher-T_c values as the number of CuO_2 sheets increases up to three, suggesting the relation between T_c and crystal structures. In particular, some systematic changes have been observed in the series of $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ ($n=1$, 2, and 3) by detailed structural analysis. It was revealed that as the number of CuO_2 sheets increased, the lattice parameter a and the Cu—O bond length along c axis, which corresponded to the distance between Cu and apical oxygen in Cu-O octahedrons or pyramids, became shorter.[3] This suggests that T_c's would reflect detailed structural parameters. On the other hand, as for carrier concentration, clear correlations with T_c values were observed as well. In the La system with K_2NiF_4-type structure, it was revealed that carrier concentration controlled by substitution of Sr^{2+} for La^{3+} had a vital importance for the occurrence of superconductivity, and that its change caused a change in material behavior from an antiferromagnetic insulator to a metallic conductor via a superconductor.[4,5] In the Y system, carrier concentration is controlled by the oxygen content and it is also responsible for its superconductivity.[6,7] As mentioned above, both structure and carrier concentration are very important factors for the superconductivity.

In the Tl-based superconductors, it has been a tempting subject to reveal the relations among superconductivity, detailed structures, and carrier concentration, because some of them showed large variations in T_c, although their crystal structures were almost the same.[3,8–14] In our previous paper,[15] it was first pointed out that a wide range of T_c values in $Tl_2Ba_2CuO_6$ showed a clear correlation with its c-axis length. It was also revealed that this change in T_c was caused by a small change in the oxygen content, suggesting the relation between T_c and carrier concentration. In the present study, we further investigate the large T_c variation and carrier concentration caused by a change in the oxygen content in $Tl_2Ba_2CuO_6$ (2:2:0:1), and discuss their correlations quantitatively. We also control the carrier concentration of the system by the substitution of La^{3+} for Ba^{2+}, and investigate its superconductivity. In addition, relations between T_c and oxygen content in other Tl-based superconductors with different crystal structures such as $Tl_2Ba_2CaCu_2O_8$ (2:2:1:2), $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2:2:2:3), and $TlBaLaCuO_5$ (1:2:0:1-type) (Ref. 16) are studied. The two former ones have different numbers of CuO_2 sheets between Tl-O double layers, and the latter one has a Tl-O monolayer. The effect of carrier concentration on T_c in different crystal structures are then discussed.

Synthesized samples were $Tl_2Ba_2CuO_6$, $Tl_2(Ba_{1.8}La_{0.2})CuO_6$, $Tl_2Ba_2CaCu_2O_8$, $Tl_2Ba_2Ca_2Cu_3O_{10}$, and $TlBaLaCuO_5$. They were prepared by solid-state reactions. Mixtures of Tl_2O_3, BaO, CaO, CuO, and La_2O_3 powders with designed compositions were pressed into pellets. The pellets were wrapped in Au foil, and sintered at 860 °C for 5–10 h in oxygen atmosphere. After grinding, they were sintered again at 880–890 °C for 5–10 h in oxygen atmosphere. Structural identification was carried out by powder x-ray diffraction and all samples were confirmed to be single phase. Electrical properties were examined by dc resistivity using a conventional four-probe method. Superconducting properties were also examined by ac susceptibility using a self-inductance method. Regardless of their T_c values, all samples which showed superconductivity gave large diamagnetic signals, suggesting the superconductivity was of a bulk nature.

Oxygen content was controlled by changing the annealing condition, and the change in oxygen content was determined by weight measurement. Samples sintered in oxygen atmosphere were then reduced by annealing in argon atmosphere at 350–600 °C for 3–5 h, resulting in T_c change and loss of weight. Successive annealing in the oxygen atmosphere at 350 °C recovered both T_c and the sample weight. The complete reversibility in both T_c and the sample weight throughout this annealing process assured us that the change in T_c was caused by the change in oxygen content.

In $Tl_2Ba_2CuO_6$, samples sintered in the oxygen atmosphere showed no superconductivity or at most a superconductivity with T_c of ~10 K, and by argon annealing they showed superconductivities up to 87 K as the highest-T_c value. In Fig. 1, T_c values and c-axis lengths are plotted against the relative changes in the oxygen content. In this figure, the relation between c-axis length and oxygen content is derived from our previous data in Ref. 15, using the master curve of the relation between T_c and oxygen content determined by the present experiment. It is demonstrated that the change in oxygen content caused the change in both T_c and c-axis length. A very small decrease in oxygen content, about 0.1 per formula unit, increased the T_c value up to about 80 K, and elongated the c axis of about 0.4%. Samples whose oxygen desorption exceeded beyond 0.15 per formula unit could not be prepared, because the sample tended to be decomposed. This c-axis elongation is rather large in comparison with that in $YBa_2Cu_3O_{7-\delta}$. In the Y system, oxygen desorption of about 0.5 per formula unit elongates the c axis of about 0.7%,[17] which is about one third of that in $Tl_2Ba_2CuO_6$. It is amazing that such a small decrease in oxygen content increases T_c up to 87 K. Supposing that the change in oxygen content causes the change in carrier concentration, the oxygen decrease of 0.1 per formula unit corresponds to the decrease of hole concentration by 0.2.

It was suggested that the nonsuperconductivity in $Tl_2Ba_2CuO_6$ was in an excessive hole concentration state and that decrease in hole concentration improved the superconductivity. This idea was also supported by resistivity measurements. Figure 2 shows temperature dependences of resistivity for samples with various T_c values. As the T_c becomes higher, the normal-state resistivity increases, which indicates that a sample with a higher-T_c value has a lower-carrier concentration. In addition, preliminary Hall measurements confirmed the decreased hole concentration state in higher-T_c samples. However, the estimated decrease in carrier concentration (Hall number) corresponding to the T_c variation from 0 to 80 K was about 0.5, which was much larger than the value (0.2) estimated from the oxygen content. Such discrepancy indicates that the Hall number no longer reflects the chemical doping in such a high-carrier concentration range.[18] All these features are very similar to those observed in La-Sr-Cu oxides.[5,19] It is concluded that superconductivity appears only in a certain appropriate range of carrier concentration, and disappears in an excessive hole concentration region. As to the Hall measurements, detailed results and discussion are forthcoming.

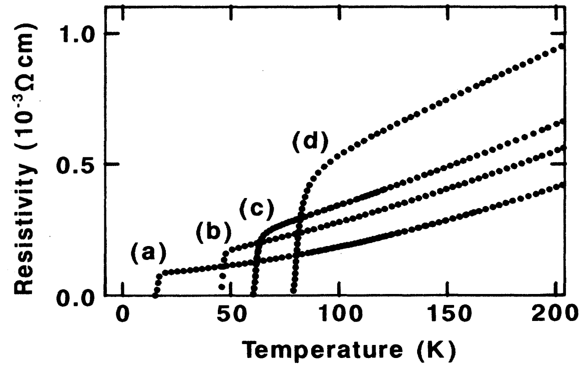

FIG. 2. Temperature dependences of resistivity for $Tl_2Ba_2CuO_6$. (a) As-sintered in the oxygen atmosphere. (b)–(d) Annealed in argon atmosphere at 425, 500, and 585 °C for 5 h, respectively.

The carrier concentration in the 2:2:0:1 structure was expected to be controlled by substituting La^{3+} for Ba^{2+}, as well. A substitution sample of $Tl_2(Ba_{1.8}La_{0.2})CuO_6$ was successfully synthesized. It was notable that it showed superconductivity with a T_c of about 40 K even after oxygen annealing at 350 °C for over 10 h, suggesting that La substitution decreased the hole concentration and gave rise to superconductivity. Further annealing in argon atmosphere still increased the T_c up to 70 K. However, the T_c value did not exceed 70 K even when the oxygen content was reduced by about 0.1 per formula unit. It should be noted that the maximum T_c value for the La substituted sample was smaller than that for $Tl_2Ba_2CuO_6$. This may indicate that the effect of doping on T_c could be substantially different in between both cases of doping, i.e., by oxygen or by ion substitution.

Next, we will discuss the relations between T_c and oxygen content in other Tl-based superconductors with different crystal structures. In $Tl_2Ba_2CaCu_2O_8$, samples sintered in oxygen atmosphere with T_c of 85 K showed higher-T_c values up to 110 K, when they were annealed in argon atmosphere at 550 °C for 5 h, showing a similar behavior to that observed in $Tl_2Ba_2CuO_6$. However, for $Tl_2Ba_2Ca_2Cu_3O_{10}$, it was observed that samples sintered in oxygen atmosphere with T_c of 116 K showed slightly lower T_c's by argon annealing. It was also confirmed that these changes in T_c were related to the changes in oxygen content, thus to the changes in carrier concentration. The relations between T_c and carrier concentration per CuO_2 sheet for the 2:2:0:1, 2:2:1:2, and 2:2:2:3 are summarized in Fig. 3. For the 2:2:0:1 and 2:2:1:2, samples sintered in oxygen atmosphere have too many hole carriers, and the decrease in oxygen content brings about an appropriate carrier concentration for the superconductivity oc-

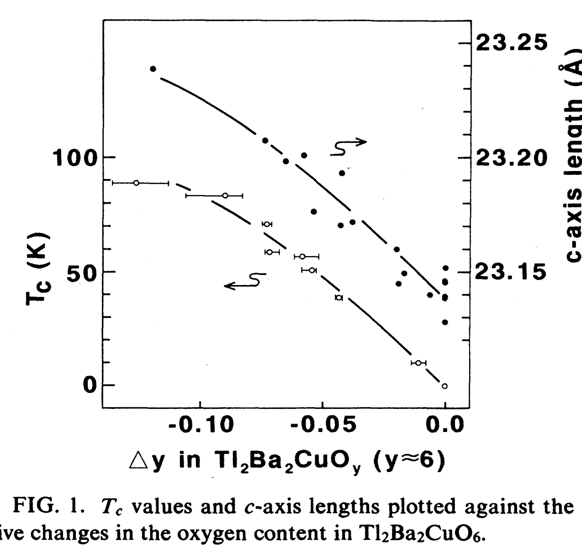

FIG. 1. T_c values and c-axis lengths plotted against the relative changes in the oxygen content in $Tl_2Ba_2CuO_6$.

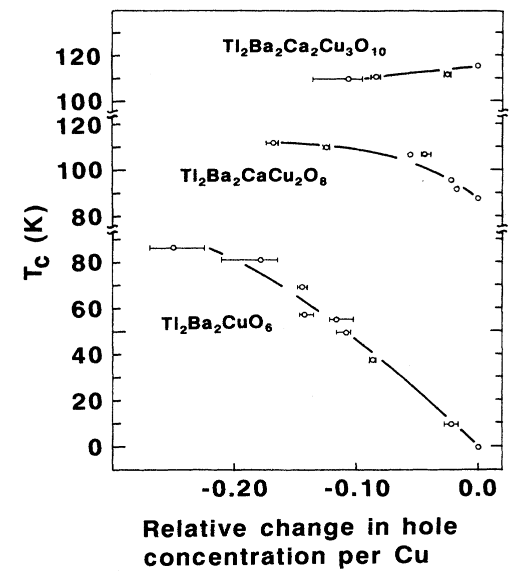

FIG. 3. Relations between T_c and carrier concentration per CuO_2 sheet for $Tl_2Ba_2CuO_6$, $Tl_2Ba_2CaCu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$.

currence. In contrast, for the 2:2:2:3, samples synthesized in 1-atm oxygen have just the appropriate carrier concentration, and the decrease in oxygen content degrades the superconductivity. The amount of change in carrier concentration per CuO_2 sheet becomes smaller as the number of CuO_2 sheets (n) per formula unit increases, which may be the reason why the range of T_c variation becomes smaller as n increases.

Finally, we will discuss where the oxygen is adsorbed and desorbed in the crystal. In the Tl-O monolayer compound, $TlBaLaCuO_5$ with 1:2:0:1 structure,[16] it was found that variation in oxygen content caused by argon annealing was quite small. Even when the as-sintered sample was annealed in argon atmosphere at 550 °C, the change in oxygen content was only about 0.01 per formula unit. This strongly suggests that oxygen desorption and adsorption take place in Tl-O double layers. In addition, the differences in oxygen content between as-sintered samples and reduced samples in argon atmosphere at 550 °C for three systems of the 2:2:0:1, 2:2:1:2, and 2:2:2:3 were almost the same and 0.1–0.15 per formula unit. Almost the same c-axis elongations of about 0.1 Å were observed for both the 2:2:0:1 and 2:2:1:2 phases. These facts also suggest that oxygen desorption and adsorption occur in the Tl-O double layers which is the common part of these structures. This speculation is consistent with the recent result of neutron diffraction; excessive oxygen atoms in $Tl_{2.0}Ba_{2.0}CuO_{6+\delta}$ are located at interstitial sites between Tl-O layers.[20]

In conclusion, clear correlations between T_c, crystal structures, and carrier concentration were found in some Tl-based superconductors. It was demonstrated that superconductivity appears in a certain appropriate range in carrier concentration.

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