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T^* phase $(Bi_{0.5}Sr_{1.5})(Y_{2-x}Ce_x)Cu_2O_{8-\delta}$ superconductors: The effect of ionic radius on structure

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We have successfully synthesized the superconductor $(Sr_{1.5}Bi_{0.5})(Y_{2-x}Ce_x)Cu_2O_{8-\delta}$, the crystal structure of which is similar to that of T^*-phase $(Nd,Sr,Ce)_2CuO_4$. This structure is also believed to be without the double Bi-O layer as in $Bi_2Sr_2(L,Ce)_2Cu_2O_y$, and the coupling between layers in $(Sr,Bi)_2(Y,Ce)_2Cu_2O_{8-\delta}$ is stronger than in $Bi_2Sr_2(L,Ce)_2Cu_2O_y$. The transition temperature is actually increased by about 8 K. This result seems to be different from that in Tl-based superconductors. It is also found that the ionic radius of the A site in the Cu perovskite unit $ACuO_{3-\delta}$ is critical to the formation of the T, T', T^* phases.

Since the discovery of superconductivity in La-Ba-Cu-O systems,[1] many layered superconducting copper oxide compounds with various structures have been synthesized. All these compounds are combinations of several different types of structural blocks, such as perovskite, rocksalt, and fluorite blocks.[2,3] However, previously only T^*-phase $(Nd_{1.18}Sr_{0.82})(Nd_{1.46}Ce_{0.54})Cu_2O_8$ (Ref. 4) and T'-phase $(Nd_{1.85}Ce_{0.15})CuO_4$, in which the carriers are electrons,[3] have been synthesized.

We now discuss on what carrier type depends. There exist two viewpoints on carrier type. One view is that the CuO_2 sheets under compression in the $T/0$ structure are readily doped p type, but not n type; CuO_2 sheets under tension are readily doped n type, but not p type (such as in the T' phase). The other is that the stability of a higher formal valence on copper increases with its anion coordination, and the Cu in the p type T structure is sixfold coordinated, whereas in the n-type T' structure it is only fourfold coordinated. Synthesis of materials with only fourfold coordination of Cu is very important for the understanding carrier type. The T^* phase is closely related to the T' phase. When the ionic radius of an A site decreases in the Cu perovskite unit $ACuO_{3-\delta}$, the T^* phase transforms into the T' phase. Here we report the discovery of a family of superconducting copper oxides with T^* phase in which the rocksalt block (Nd,Sr)O in $(Nd_{1.18}Sr_{0.82})(Nd_{1.46}Ce_{0.54})Cu_2O_8$ is replaced by (Bi,Sr)O. The highest transition temperature observed is 34 K at a composition of $x=0.85$ and is higher than 28 K for $(Nd,Ce,Sr)_2CuO_4$. This structure is also believed to be without Bi-O bilayers, as in $Bi_2Sr_2(Nd,Ce)_2Cu_2O_y$.[5]

The starting materials for the synthesis were Bi_2O_3, $SrCO_3$, Y_2O_3, CeO_2, and CuO. After mixing according to the formula $(Bi_{0.5}Sr_{1.5})(Y_{2-x}Ce_x)Cu_2O_{8-\delta}$ $(0.4 \leq x \leq 1.0)$, the mixed powder was slowly heated to 950 °C in oxygen flow for several overnight cycles of calcining and mechanical grinding. After pressing into pellets, they were reacted at 980 °C in flowing oxygen for 36 h, then cooled to 500 °C at the rate of 0.25 °C/min held for 10 h, and finally cooled to room temperature by a furnace. The x-ray powder-diffraction patterns indicate that the materials were single phase for Ce concentrations (x) ranging from 0.6 to 0.9.

Materials prepared in 1 atm of oxygen can show superconducting transition temperatures as high as about 30 K. Thermogravimetric analysis indicates that the oxygen content of an as-prepared single phase of $x=0.85$ was deficient, $\delta \simeq 0.1$. In order to investigate the effect of the oxygen content on superconductivity, the as-prepared samples were sealed in thick-walled quartz tubes containing enough oxygen, which was released by $KMnO_4$, to result in oxygen pressures of 5, 10, and 20 atm at 500 °C. Annealing times were 24 h at 500 °C with subsequent gradual cooling to room temperature. The x-ray powder-diffraction patterns show that the T^* phase remains unchanged after annealing in 5 atm of oxygen, but the samples decompose into CuO, CeO_2, and other phases after annealing in 10 and 20 atm of oxygen. Annealing in 5 atm of oxygen increases both the superconducting volume fraction and T_c ($T_c=34$ K for $x=0.85$). It was found that superconductivity takes place in a small range of oxygen content and the thermodynamic stability is closely related to the oxygen deficiency δ.

The crystallography of $(Bi_{0.5}Sr_{1.5})(Y_{2-x}Ce_x)Cu_2O_{8-\delta}$ $(0.6 \leq x \leq 0.9)$ was determined with x-ray powder diffraction. The x-ray powder-diffraction pattern (see Fig. 1) indicates that $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_8$ is tetragonal with $a=3.822$ Å and $c=12.659$ Å, and has a crystal structure similar to that of $(Nd,Ce,Sr)_2CuO_{4-\delta}$ (T^* phase) with $a=3.855$ Å and 12.49 Å. The x-ray powder-diffraction and electron microprobe analyses show $(Bi_{0.5}Sr_{1.5})(Y,Ce)_2Cu_2O_8$ as the predominant phase (>95%) and a slight less amount of CeO_2 and no other phase. It is worth pointing out that Bi is critical to the formation of the T^* phase.

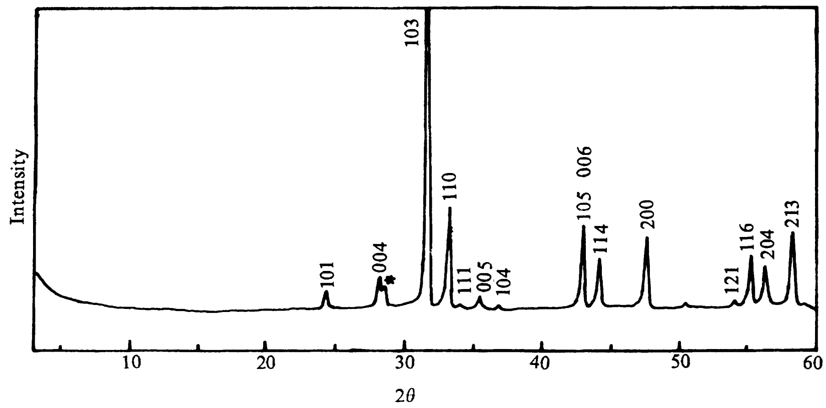


FIG. 1. X-ray powder-diffraction pattern of the sample $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_{8-\delta}$.

Figure 2 shows the temperature dependence of the resistivity between 4.2 and 300 K measured on a bar-shaped sample of $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_8$. The resistivity decreases with decreasing temperature; the sample demonstrates semiconducting behavior between 100 K and the onset of superconductivity of about 40 K. The resistivity reaches zero at 30 K. Figure 3 shows the magnetic ac susceptibility versus temperature plots for the sample of $x=0.85$, measured by the mutual-inductance method. The resistivity and Meissner data are in good agreement with each other. These data suggest that the sample $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_8$ shows bulk superconductivity. Since there exists only the T^* phase $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_8$ and CeO_2, we believe that the T^* phase is responsible for the superconductivity. Its superconducting transition temperature is higher by 5 K than that of $(Nd,Ce,Sr)_2CuO_4$.

Figure 4(a) shows the structure of $(Bi_{0.5}Sr_{1.5})(Y,Ce)_2Cu_2O_8$. The difference between the two T^* phases $(Bi_{0.5}Sr_{1.5})(Y,Ce)_2Cu_2O_8$ and $(Nd_{1.2}Sr_{0.8})(Nd,Ce)_2Cu_2O_8$ is that $(Nd_{0.6}Sr_{0.4})O$ in the rocksalt is replaced by $(Bi_{0.25}Sr_{0.75})O$. Bismuth is necessary to form the T^* phase. $(Bi_{0.5}Sr_{1.5})(Y,Ce)_2Cu_2O_8$ has no double Bi-O layers as in $Bi_2Sr_2(Nd,Ce)_2Cu_2O_y$ [see Fig. 4(b)]. From the point of view of the coupling between layers, the coupling between layers in $(Bi_{0.5}Sr_{1.5})(Y,Ce)_2Cu_2O_8$ should be stronger than that in $Bi_2Sr_2(Nd,Ce)_2Cu_2O_y$. However, the transition temperature is actually increased by about 8 K, without the Bi-O bilayers as in $Bi_2Sr_2(Nd,Ce)_2Cu_2O_y$. This suggests that the coupling between successive Cu perovskite units becomes stronger and the reduced spatial separation of the Cu-O slabs in the new structure [by 5.2 Å in $(Bi,Sr)_2(L,Ce)_2,Cu_2O_y$ compared to the $Bi_2Sr_2(L,Ce)_2Cu_2O_y$ structure] leads to an enhanced superconducting transition temperature. This result seems to be different from that in Tl-based superconductors, in which the transition temperature is reduced by 15 and 30 K, when the Tl-O bilayer is replaced by a Tl-O monolayer for double and triple CuO_2 layer compounds.[6] Parkin *et al.* have suggested that the coupling between layers depends on the degree of hybridization of the Tl-O and Cu-O bands.

It is found that the T, T', and T^* phases depend strongly on the ionic radius of the A site in the Cu perovskite unit $ACuO_{3-\delta}$. When $A=La$, the structure is T phase with sixfold coordination of Cu, while when $A=Pr$, Nd, or Sm the structure is T' phase with only fourfold coordination of Cu in which the carriers are electrons. When La is partially replaced by the smaller ions Sm, Eu, Gd, and Dy, and T phase is transformed into the T^* phase with fivefold coordination of Cu,[7] and the T^* phase is also formed after the ions (Pr,Nd,Sm) in the T' phase are replaced by the larger Sr ions.[4] This suggests that the structure transforms from the T phase into the T' phase with decreasing ionic radius of the A

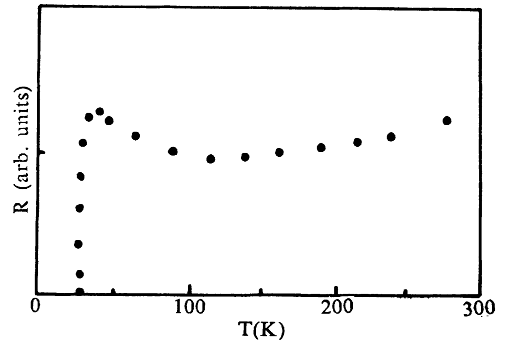


FIG. 2. Temperature dependence of the resistivity for the sample $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_{8-\delta}$.

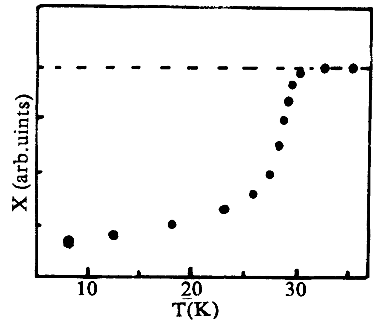
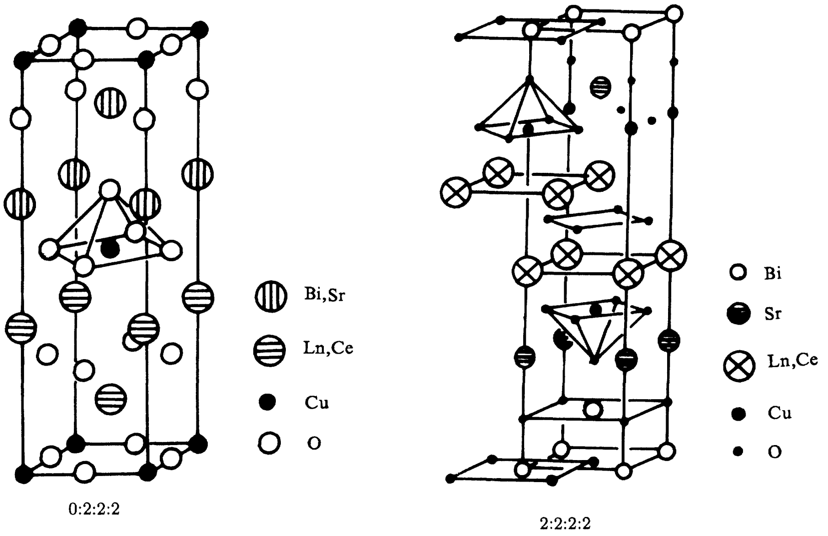


FIG. 3. Magnetic ac susceptibility vs temperature plots for the sample of $x=0.85$.



0:2:2:2

2:2:2:2

FIG. 4. Crystal structure of $(Bi,Sr)_2(Y,Ce)_2Cu_2O_{8-\delta}$ (0:2:2:2 phase, left) and $Bi_2Sr_2(Nd,Ce)_2Cu_2O_y$ (2:2:2:2 phase, right).

site in the Cu perovskite unit ACuO$_{3-\delta}$. The T^* phase appears for ionic radii of the A site in ACuO$_{3-\delta}$ between La^{3+} and Nd^{3+}. It is interesting that the ionic radius of the A site in the new T^* phase $(Sr_{1.5}Bi_{0.5}))(Y,Ce)_2Cu_2O_y$ nearly equals that in T^* phase $(Nd,Sr,Ce)_2CuO_4$. This suggests that the ionic radius of A site is very critical to synthesis of the T^* and T' phases. Bi is absolutely essential to the formation of the T^* phase $(Bi,Sr)_2(Y,Ce)_2Cu_2O_{8-\delta}$. This may be due to the smaller ionic radius of Bi than that of Sr^{2+}, and Bi^{3+} replacing partially the Sr^{2+} results in a decrease of the ionic radius of the A site. But the ionic radius of the A site in $Sr_2(Y,Ce)_2CuFeO_y$ with the T^* phase nearly equals (and is even larger than) the radius of La^{3+}. This may be related to the fact that the Fe partially occupies the Cu site.[8]

If a hole concentration of 0.15 per Cu atom is considered as optimal for superconductivity, our preliminary determination of the optimal Ce content for $(Bi_{0.5}Sr_{1.5})(Y_{1.15}Ce_{0.85})Cu_2O_8$ results in Bi$^{3.7+}$. This suggests that Bi^{3+} and Bi^{5+} exist in the sample. It is known that the T^* phase of $(Nd,Ce,Sr)_2CuO_4$ is formed by doping Sr in the T' phase of $(Nd,Ce)_2CuO_4$ with electrons as the charge carriers. On the other hand, the T' phase transforms into the T^* phase when the ionic radius of the A site increases in the perovskite with oxygen-deficient ACuO$_2$. Thus it may be possible that the superconductor with the T' phase related to $(Bi,Sr)_2(Y,Ce)_2Cu_2O_8$ with a T^* phase may be synthesized. Related experiments are in progress to test this possibility and understand the carrier-type dependence.

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