Superconductivity in $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ ($M = \text{Cd}$ and Zn) Systems

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We have investigated the superconductivity in the pseudoquaternary systems $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ with $M = \text{Cd}$ and Zn . Ac electrical resistance $R(T)$ measurements indicate that increasing Cd concentration x gradually changes the sample from metallic behavior to semiconducting behavior and finally destroys the superconductivity. However, for $x \leq 0.6$, substitution of Y with Cd produces no appreciable change in the superconducting transition temperature T_c . As $x \geq 0.7$, T_c was observed to decrease rapidly with increasing Cd concentration x . In contrast, monotonic decreasing in T_c with Zn doping concentration x for $0 \leq x \leq 0.3$ was observed in the $(Y_{1-x}Zn_x)Ba_2Cu_3O_{7-\delta}$ system.

I. Introduction

The discovery of superconductivity in the $La - Ba - Cu - O$ system has attracted tremendous amount of research interest in the copper oxide systems. Superconductor with transition temperature $T_c \cong 90$ K was subsequently discovered in $Y - Ba - Cu - O$ by Wu et. al², and later identified as $YBa_2Cu_3O_{7-\delta}$ oxygen-deficient perovskite structure³⁻⁵. Replacing Y with most of the rare-earth ions including Nd, Sm, Eu, Er, Dy, Tm and Lu produces no effect on the superconducting transition temperature T_c , indicating that interactions between the rare earth ions and the copper oxide planes are very weak⁶⁻⁸.

Among the three rare earth ions (Ce, Pr and Tb) that doesn't exhibit superconductivity when substituted for Y, $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ produces monotonic decreasing of T_c as Pr concentration x increases and finally destroys the superconductivity as $x > 0.5$ ⁹⁻¹³, which indicates that R^{3+} ($R = \text{rare earth ions}$) and consequently the copper valence are important for the occurrence of the superconductivity. Replacing Y by 3+

ions such as Al, Ga and Bi in $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ also causes T_c to decrease monotonically with increasing doping concentration x and destroys the superconductivity for x greater than certain values^{14,15}. These results and intensive studies of the oxygen deficiency on the effect of T_c in $YBa_2Cu_3O_{7-\delta}$ reveal the importance of the crystal structure and oxygen content to the superconductivity^{16,17}.

In order to study the chemical substitution effect on $YBa_2Cu_3O_{7-\delta}$, we have investigated the superconductivity in the $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ systems with $M = \text{Cd}$ and Zn . Cd was chosen to substitute Y because its ionic radius ($Cd^{2+} = 0.97 \text{ \AA}$) is quite close to that of Y^{3+} and some rare earth ions (eg., Eu and Nd). Besides, Cd ($4d^{10}5s^2$) has completely filled 4d levels and has definite 2+ valence. Substitution of Y (3+) with Cd (2+) might only produce the effect on the Cu valence without affecting the crystal structure and avoiding the complication of the magnetic moment effects. Zn ($3d^{10}4s^2$), with completely filled 3d levels and definite 2+ valence, but smaller ionic radius ($Zn^{2+} = 0.74 \text{ \AA}$), was also studied for comparison.

2. Experimental Details

The $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ ($M = Cd$ and Zn) samples were prepared by solid state reaction. Appropriate amount of high purity powder of Y_2O_3 , $BaCO_3$, CuO , ZnO and CdO were mixed together first, heated in air at $900^\circ C$ for 1 day and furnace cooled. Reacted powder were then ground and pressed into pellets, followed by annealing between $850^\circ C$ and $930^\circ C$ in flowing O_2 atmosphere for 24 hr and cooled down slowly in O_2 flow to room temperature. Ac electrical resistance measurements were made by the conventional four-wire technique using a Linear Research Model LR 400 ac resistance bridge operating at a frequency of 16 Hz. Platinum and germanium thermometers were used as the temperature sensors. The X-ray diffraction data were obtained on a Phillips XRD PW 1729 powder diffractometer utilizing $Cu K_\alpha$ radiation. The superconducting transition temperature T_c (50%) is defined as the temperature in which the resistance drops to 50% of its extrapolated normal state value and the transition width ΔT_c is defined as the temperature difference between T_c (90%) and T_c (10%).

3. Results and Discussion

Shown in Fig.(1) are the X-ray diffraction patterns for different x values of $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ samples. A careful inspection of the diffraction spectra reveals that all the major peaks of oxygen deficiency perovskite structure appear for Cd concentration $x < 0.6$ and no other extra noticeable peak was found within this x range. The main change observed was the decreasing in the splitting between the X-ray doublets as x increases. Since the ionic radius of Cd^{2+} is close to that of Y^{3+} , it is possible that within this Cd concentration, the major effect of Cd doping is on the replacement of the Y sites which produces gradual changes on the lattice parameters without destructing the crystal structure. For $x = 0.6$, the peak intensity at $2\theta \approx 29.2^\circ$ becomes appreciable, indicating that some $BaCuO_2$ phase starts to form in the sample. As $x \geq 0.7$, this peak starts to dominate and the samples are multiple phased.

The normalized ac electrical resistance $R(T)/R(300$

Fig.1. X-ray powder diagram for $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ with Cd concentration x between 0 and 1.0.

K) as a function of temperature T for different values of x in $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ are plotted in Fig. (2). For $x = 0$, the $R(T)/R(300 K)$ vs T behavior is similar to that had been reported for $YBa_2Cu_3O_{7-\delta}$, with $R(T)/R(300 K)$ decreases linearly with T in the normal state and an superconducting transition temperature T_c of 93 K. As Cd concentration x increases, the $R(T)/R(300 K)$ vs T decreasing rate above T_c starts to decrease. Metallic behavior retains up to $x \approx 0.6$. But the superconducting transition temperature T_c and transition width ΔT_c

Fig.2. Normalized electrical resistance, $R(T)/R(300\text{ K})$, plotted as a function of temperature T for several concentrations x of $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$. (a) $x = 0, 0.2, 0.4$, and 0.6 . (b) $x = 0.7, 0.75, 0.9$, and 1.0 .

remain almost unchanged. However, for $x \geq 0.7$, the sample changes from metallic behavior to semiconducting behavior. Finally, as $x \geq 0.8$, superconductivity was destroyed. Abrupt decreasing in T_c and broadening in ΔT_c were also observed. The transition temperature T_c together with the transition width ΔT_c as a function of Cd concentration x was plotted in Fig.(3).

This constant T_c behavior observed in the $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ system is similar to that had been reported for the $(Y_{1-x}Na_x)Ba_2Cu_3O_{7-\delta}$ system in which T_c was reported to be constant for $0 \leq x \leq 0.3$ ⁹. Both Cd^{2+} and Na^+ have ionic radii of $0.97\text{ \AA}$, and generally are nonmagnetic. The only difference between Cd^{2+} and Na^+ is their valence. The partial replacement of Y by Cd and Na produces similar effects. In both situations the smaller trivalent state of Cd^{2+} and Na^+ in the $YBa_2Cu_3O_{7-\delta}$ could result in less oxygen stoichiome-

Fig.3. The superconducting transition temperature T_c (solid circles) and transition width ΔT_c (vertical bars) plotted as a function of Cd concentration x for $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$. Constant T_c and ΔT_c are observed for $x \leq 0.6$. As $x \geq 0.6$, T_c starts to drop and ΔT_c gets broadened.

try, to balance the valence of the metal ions, Cu^{3+} ions are converted to Cu^{2+} . This produces gradual change of $R(T)/R(300\text{ K})$ vs T behavior in the normal state and decreasing of the superconducting transition temperature T_c . And T_c remains constant up to $x \approx 0.6$ for $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ instead of up to $x \approx 0.3$ for $(Y_{1-x}Na_x)Ba_2Cu_3O_{7-\delta}$. Which is reasonable since the valence of Cd is 2 instead of 1 for Na. Substitution of Y^{3+} with Cd^{2+} produces less effect (approximately one half) of trivalent state deficiency than substitution of Y^{3+} with Na^+ does. The oxygen content determined by thermogravimetry analysis (TGA) measurement show δ increases roughly as x increases and gives $0 < \delta < 0.2$ for Cd concentration $x \leq 0.6$. We noticed that recently it was reported that the superconducting transition temperature T_c of $(Y_{0.5}Na_{0.5})Ba_2Cu_3O_{7-\delta}$ is closely related to the annealing conditions¹⁸.

Shown in Fig.4(a) are the normalized resistance $R(T)/R(300\text{ K})$ vs Temperature T curves for $(Y_{1-x}Zn_x)Ba_2Cu_3O_{7-\delta}$ with $x = 0, 0.1, 0.2$, and 0.3 . Increasing Zn concentration x produces the effects of decreasing of the superconducting transition temperature T_c and the broadening of the transition width ΔT_c . A continuous transition from metallic to semiconducting behavior was also observed. A T_c (solid circles) and ΔT_c (vertical

Fig.4. (a) Normalized electrical resistance, $R(T)/R(300\text{ K})$, plotted as a function of temperature T for $(Y_{1-x}Zn_x)Ba_2Cu_3O_{7-\delta}$ with $x = 0, 0.1, 0.2$, and 0.3 . (b) The superconducting transition temperature T_c (solid circles) and transition width ΔT_c (vertical bars) plotted as a function of Zn concentration x for $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$. The dashed line shows T_c decreases linearly with x .

bars) vs Zn concentration x plot is shown in Fig.4(b). Roughly speaking, T_c decreases linearly with x . An extrapolation of this linear behavior shows that superconductivity was destroyed as $x \geq 0.4$. Since the ionic radius of Zn^{2+} is $0.74\text{ \AA}$, which is closest to the ionic radius of Cu^{2+} ($0.72\text{ \AA}$), it is possible that Zn is substituted on Cu sites instead of on Y sites. So, a comparison of the doping effect between Cd and Zn cannot be seriously made.

4. Summary

Superconductivity in the $(Y_{1-x}Cd_x)Ba_2Cu_3O_{7-\delta}$ system have been investigated by ac resistance measurement and X-ray diffraction study. The superconducting transition temperature remains almost constant up to $x = 0.6$ and decreases rapidly as $x \geq 0.7$. These results are consistent with the results that have been reported for $(Y_{1-x}Na_x)Ba_2Cu_3O_{7-\delta}$ system and reveal the importance of the trivalent state of the Y (or rare earth elements) sites for the occurrence of the superconductivity in $YBa_2Cu_3O_{1-\delta}$. Since a simple charge-counting shows that substituting Na^+ for Y^{3+} could produce the trivalent-deficiency on the Y sites twice as effective as substituting Cd^{2+} for Y^{3+} , hence T_c remains constant up to $x \cong 0.3$ for Na doping and up to $x \cong 0.6$ for Cd doping. For $(Y_{1-x}Zn_x)Ba_2Cu_3O_{7-\delta}$, T_c decreases linearly with increasing Zn concentration x and superconductivity is destroyed for $x \geq 0.4$.

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