Superconductivity in \((Y_{1-z}M_z)Ba_2Cu_3O_{7-\delta}\) (M = Cd and Zn) Systems

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We have investigated the superconductivity in the pseudoquaternary systems \((Y_{1-z}M_z)Ba_2Cu_3O_{7-\delta}\) with M = 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 \((Y_{1-z}Z_{nz})Ba_2Cu_3O_{7-\delta}\) system.

I. Introduction

The discovery of superconductivity in the \(La - Ba - Cu - O\) system has attracted tremendous mount of research interest in the copper oxide systems. Superconductor with transition temperature \(T_c \approx 90\) K was subsequently discovered in \(Y - Ba - Cu - O\) by Wu et. al \cite{1}, and later identified as \(YBa_2Cu_3O_{7-\delta}\) oxygen-deficient perovskite structure \cite{2,3,4}. 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 weak \cite{5,6,7}.

Among the three rare earth ions (Ce, Pr and Tb) that doesn’t exhibit superconductivity when substituted for Y, \((Y_{1-z}Pr_z)Ba_2Cu_3O_{7-\delta}\) produces monotonic decreasing of \(T_c\) as Pr concentration \(x\) increases and finally destroys the superconductivity as \(x > 0.59\) \cite{8,9,10,11}, which indicates that \(R^{3+}\) (R = 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 \((Y_{1-z}M_z)Ba_2Cu_3O_{7-\delta}\) also causes \(T_c\) to decrease monotonically with increasing doping concentration \(x\) and destroys the superconductivity for \(x\) greater than certain values \cite{12,13,14}. 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 \cite{15,16,17}.

In order to study the chemical substitution effect on \(YBa_2Cu_3O_{7-\delta}\), we have investigated the superconductivity in the \((Y_{1-z}M_z)Ba_2Cu_3O_{7-\delta}\) systems with M = Cd and Zn. Cd was chosen to substitute Y because its ionic radius \((Cd^{2+} = 0.97\) Å) 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 \((Zn^{2+} = 0.74\) Å), 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°C for 1 day and furnace cooled. Reacted powder were then ground and pressed into pellets, followed by annealing between 850°C and 930°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 Philips 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 \(\Delta T_c\) 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 \(2\theta \approx 29.2°\) 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 \(R(T)/R(300\ K)\) 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 \(YBa_2Cu_3O_7\), 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 \(\Delta T_c\)
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 $\Delta T_c$ were also observed. The transition temperature $T_c$ together with the transition width $\Delta T_c$ 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 Å, 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 stoichiometry, to balance the valence of the metal ions, $Cu^{3+}$ ions are converted to $Cu^{2+}$. This produces gradual change of $R(T)/R(300K)$ 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 $\delta$ 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 conditions $^{18}$.

Shown in Fig.4(a) are the normalized resistance $R(T)/R(300K)$ 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 $\Delta T_c$. A continuous transition from metallic to semiconducting behavior was also observed. A $T_c$ (solid circles) and $\Delta T_c$ (vertical
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 Å, which is closest to the ionic radius of Cu$^{2+}$ (0.72 Å), 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 $(Y_{1-x}Zn_x)Ba_2Cu_3O_7-\delta$ 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 $YBa_2Cu_3O_{1-x}$. Since a simple charge-counting shows that substituting Na$^+$ for Y$^{3+}$ should 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 $x \equiv 0.3$ for Na doping and up to $x \equiv 0.6$ 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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References


