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The effect of Ca doping on the superconductivity of $(R_{0.4}Pr_{0.6})Ba_2Cu_3O_{7-\delta}$ compounds prepared at high pressure (R = La, Pr, Nd, Sm, Eu, Gd and Y)

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Abstract

The nearly single phase $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ (R = La, Pr, Nd, Sm, Eu, Gd and Y) superconducting compounds should be prepared at high temperature and high pressure. The critical temperature of these compounds is over 100 K which is much higher than that of the traditional R-123 superconductors which do not have Ca doping on the rare-earth site. Our results shows that Pr behaves in the same way as other rare-earths in the 123-phase compounds due to the doping with Ca ions.

1. Introduction

Materials of the (rare-earth) $Ba_2Cu_3O_{7-\delta}$ class superconduct at a critical temperature of about 90 K not only for Y but also for La, Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb and Lu on the rare-earth site [1, 2]. The exceptions to this behaviour are Ce, Tb and Pr, which do not form superconductors; of these only Pr can form a single-phase 123 structure of the $YBa_2Cu_3O_{7-\delta}$ type. The lack of superconductivity and semiconducting behaviour in $PrBa_2Cu_3O_{7-\delta}$ has attracted much attention.

The possible reasons for the anomalous behaviour of $PrBa_2Cu_3O_{7-\delta}$ can be classified into four kinds of model:

- (1) Hole filling: in this model in contrast with most of the rare-earths in the trivalent state that lead to superconductivity, Pr was thought to be in the quadrivalent state or in a mixed state larger than +3 valence in Pr-123 compounds. The extra Pr electron fills a hole in an adjacent cuprate plane, which is assumed to be the origin of superconductivity.
- (2) Direct magnetic pair breaking: a superconducting pair is broken by local moments of Pr.
- (3) Hybridization: the significant hybridization of the Pr 4f states with the O 2p electron in the CuO_2 plane leads to localization of the carrier.

- (4) Defect: Pr occupies the wrong Ba-site instead of its own rare-earth site.

However, none of these models can explain all of the experiments.

The suppression of T_c by the substitution of Pr on the rare-earth site was discovered first [4–6], and the T_c of these compounds monotonically decreases with increasing Pr concentration (x) in the region $x < x_{cr}$ (where x_{cr} is the critical concentration beyond which the superconductivity completely vanishes). However, the critical concentration of Pr in the $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds is different, for the various rare-earth ions the larger the ionic radius the less the critical concentration of Pr, in other words at a given concentration of Pr, T_c decreases with increasing the radius of the rare-earth ion. This is called the ionic size effect of T_c in $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

Doping with bivalent Ca ions for Pr was a simple way to introduce holes to partially compensate for the decrease of charge carriers due to hole localization or hole filling. However, it is very difficult to prepare the single phase of $Pr_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ with x larger than 0.3 under ambient conditions. Recently we successfully prepared the single phase of Pr-123 bulk materials for x beyond 0.3 under high temperature and high pressure, the T_c is beyond 97 K [8, 9] and reaches 117 K [10], much higher than that for any pure R-123 materials that usually have T_c around 92 K. Therefore, it is worth studying this material in detail. In fact the suppression of T_c by Pr in the 123 phase compounds is still one of the issues in the search for the mechanism of high- T_c superconductivity, even though superconductivity has been found in a single crystal sample grown by the travelling-solvent floating-zone method [11]. In this paper we report on the preparation of Ca-doped ($R_{1-x}Pr_x$)-123 compounds ($R = La, Pr, Nd, Sm, Eu$ and Y) under high temperature and high pressure, and their physical properties, as well as the effect of pressure on T_c .

2. Experimental details

The precursor of $(R_{1-x}Pr_x)_{0.5}Ca_{0.5}Ba_2Cu_3O_y$ ($R = La, Pr, Nd, Sm, Eu, \text{ and } Y$) was first prepared by a solid state reaction method for high-pressure synthesis. Stoichiometric amounts of predried R_2O_3 , $CaCO_3$, $BaCO_3$, and CuO powders of high purity were mixed, ground and then calcined under a reduction atmosphere of Ar (or N_2) flow at temperatures from 800 to 835 °C for 40 h, before cooling to room temperature.

Pressure synthesis was carried out in a cubic-anvil apparatus. In order to make an appropriate oxygen atmosphere 5 wt% KCO_4 powder was added to these precursor pellets. The pellets were wrapped in gold foil. These precursor pellets were quenched to room temperature in the pressure cell after the synthesis under a high pressure of 6 GPa and high temperature of 900 °C for 0.5 h. The temperature was measured by the calibration curve of temperature and electrical power, and pressure was calibrated by the phase transition point of elemental Bi and Ba.

The effect of pressure on the superconducting transition temperature was determined by a measurement of resistance in a Be–Cu pressure chamber, petroleum being used as the pressure medium.

Electrical resistance and the dc magnetic susceptibility were measured using the standard four-probe method and by a superconducting quantum interference device (SQUID) magnetometer under zero field cooling (ZFC) model, respectively. X-ray powder diffraction was carried out using a 18 kW self-rotational anode x-ray diffractometer (MXP-18A-HF type).

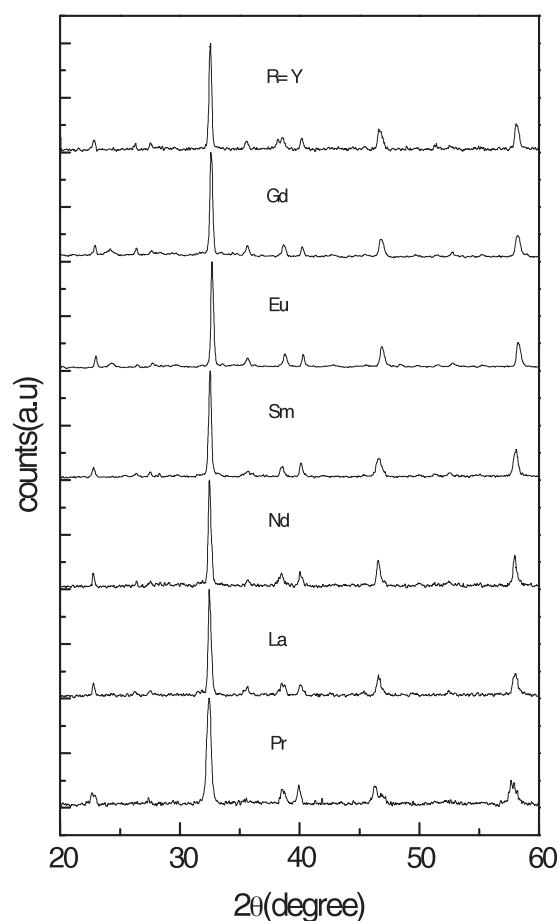


Figure 1. X-ray diffraction patterns of $(R_{0.4}Pr_{0.6})Ba_2Cu_3O_{7-d}$ prepared at high pressure ($R = La, Pr, Nd, Sm, Eu, Gd$ and Y).

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns of $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds ($R = La, Pr, Nd, Sm, Eu, Gd$ and Y) prepared under high pressure. The x-ray diffraction patterns show that all these compounds crystallize in the tetragonal Y-123 structure even though they contain a Ca concentration of 0.5. Our results indicate that high pressure favours the incorporation of Ca ions into the rare-earth site and the pressure makes the bulk compounds of $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ as stable as the thin film [12]. In fact, there is a high stress in the thin film grown on the low-temperature substrate.

Figure 2 shows the temperature dependence of dc susceptibility of $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds ($R = La, Pr, Nd, Sm, Eu, Gd$ and Y). From figure 2 we note that each susceptibility curve drops rapidly at a temperature around 100 K, even though there is a kink at about 70 K in the susceptibility curve for the samples of $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ ($R = La$ and Sm), which indicates that there is a second superconducting phase in the compounds. The measurement of dc susceptibility indicates that the $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds for all measured rare-earth ions exhibit bulk superconductivity with a higher

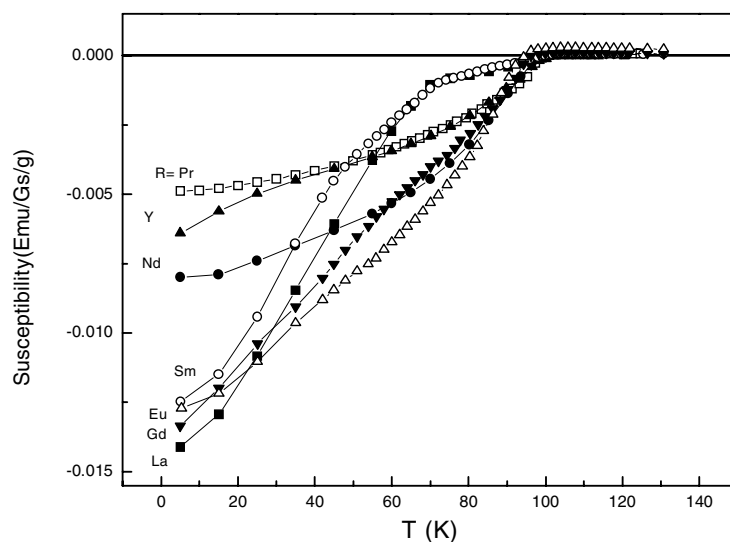


Figure 2. Temperature dependence of dc susceptibility for $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ ($R = La, Pr, Nd, Sm, Eu, Gd$ and Y).

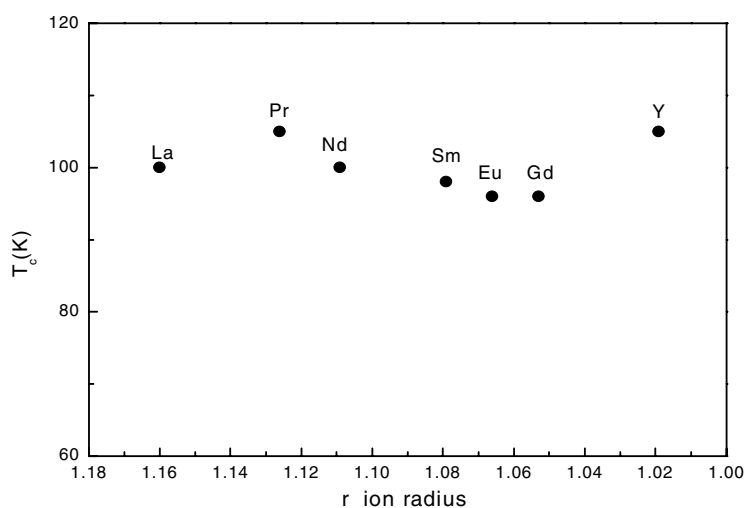


Figure 3. T_c dependence on ionic radius in $(R_{0.4}Pr_{0.6})Ba_2Cu_3O_{7-\delta}$ ($R = La, Pr, Nd, Sm, Eu, Gd$ and Y).

transition temperature around 100 K than that of any rare-earth 123 phase superconducting compound without Ca doping. All compounds are normally insulating as Pr is beyond the critical concentration of 0.6. However, T_c in the compounds increases from 92 to 100 K due to the importation of Ca ions into the rare-earth sites.

The dependence of T_c on the radius of the rare-earth ion in the $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds is shown in figure 3. Our result in figure 3 shows that the critical temperature of these compounds is nearly the same (around 100 K) even though the radius of the rare earth ion changes from 1.019 Å (for Y^{+3}) to 1.160 Å (for La^{+3}). The result is different

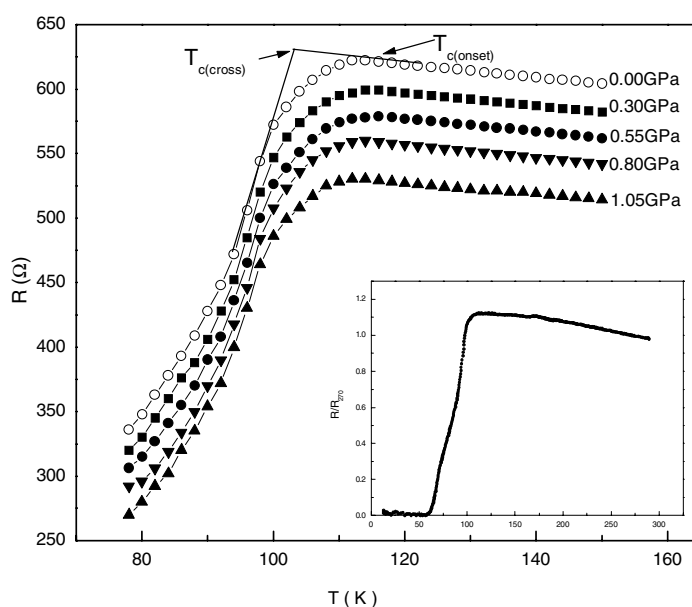


Figure 4. Temperature dependence of resistance for $(Y_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ at various hydrostatic pressures.

from the rare-earth ionic size effect of T_c in RPr-123 compounds reported by Chen *et al* [7] who pointed out that at a given Pr concentration T_c decreases linearly with increasing rare-earth ion radius. The difference indicates again that the superconducting behaviour of R-123 compounds changes completely due to the presence of Ca ions in the rare-earth sites.

Figure 4 shows the temperature dependence of resistance for the $(Y_{0.5}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compound at various pressures. The resistance measurement was carried only in the liquid N_2 region and it is sufficient to show the dependence of T_c on pressure. A complete resistance–temperature curve at ambient is inserted in figure 4. It is noted that the phase transition is broad, the resistance drops at about 100 K, but reaches zero at 60 K. Figure 5 shows the dependence of $T_{c(\text{onset})}$ and $T_{c(\text{cross})}$ on hydrostatic pressure for $(Y_{0.5}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$. The onset temperature ($T_{c(\text{onset})}$) is the temperature where the resistance deflects from the extrapolated lines of normal state resistance and the cross temperature ($T_{c(\text{cross})}$) is decided by the crossing point of the extrapolated lines of normal state resistance and the sharply dropping resistance, as shown in figure 4. A maximum in the pressure dependence of T_c (either $T_{c(\text{onset})}$ or $T_{c(\text{cross})}$) is observed. A remarkable pressure effect with dT_c/dp ($p = 0$) equal to 7.5 and 5 $K\text{ GPa}^{-1}$ is observed in the $T_{c(\text{onset})}$ and $T_{c(\text{cross})}$ curves, respectively.

4. Conclusion

We successfully prepared nearly single phase bulk $(R_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ compounds with T_c higher than 100 K by a high-temperature high-pressure method. The unusually high critical temperature and disappearance of the ionic size effect on T_c in these compounds of $(R_{0.4}Pr_{0.6})Ba_2Cu_3O_{7-\delta}$ indicate that Ca plays a very important role in the rare-earth site.

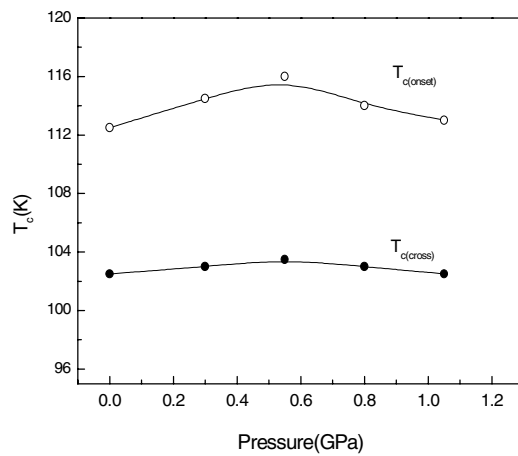


Figure 5. Pressure dependence of T_c (cross) and T_c (onset) of $(Y_{0.4}Pr_{0.6})_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$.

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