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## LETTER TO THE EDITOR

# Revival of superconductivity in $Y_{0.4}Pr_{0.6}Ba_2Cu_3O_{7-\delta}$ by the isovalent substitution of Sr

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**Abstract.** Polycrystalline samples of  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  have been prepared and characterized by *x*-ray powder diffraction, differential thermal analysis, and temperature dependence of resistivity and AC susceptibility. We observed that both superconductivity and metallic conductivity were revived at  $x \geq 0.75$ , accompanied by an orthorhombic-to-tetragonal transition. The superconducting transition temperature could be further enhanced by increasing the Sr content, suggesting that there is an ion-size effect on  $T_c$  at the Ba site. The results were discussed in terms of the Pr-O covalent bonding effect.

The  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  system has attracted much attention [1] since it shed light on the mechanism of superconductivity in cuprates. With increasing *x*,  $T_c$  decreased monotonically and superconductivity was completely quenched at  $x = 0.6$ . In the  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  series (*R* = rare earth elements except Ce or Pm), it was found [2] that the variation of  $T_c$  was related to the size of the *R* ion. At fixed Pr concentration,  $T_c$  decreased with increasing radius of the *R* ion. For smaller radius of *R* ion, the critical Pr concentration  $x_{cr}$  for the quenching of superconductivity is higher. These results were therefore referred to as the ion-size effect [2], which took place at the *R* site. Is there a similar effect at the Ba site? This question would be of great interest to understand the cause of the ion-size effect and other related problems in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ . Very recently, we reported [3] the structural properties and superconductivity in the  $Y_{1-x}Pr_xBaSrCu_3O_{7-\delta}$  system. We found that the  $x_{cr}$  is substantially higher than that in the Sr-free system. In order to understand the effect of substituting Sr for Ba, we investigated the  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  system. It was found that both superconductivity and metallic conductivity could be revived by the isovalent substitution, suggesting there is an ion-size effect at the Ba site in the  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  system.

Polycrystalline samples of  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  ( $x = 0, 0.5, 0.75, 1.0$  and  $1.25$ ) were prepared by a solid-state reaction method. Stoichiometrical dry powders of 4N  $Y_2O_3$ , 3N  $Pr_6O_{11}$ , 3N  $BaCO_3$ , 3N  $SrCO_3$  and 3N  $CuO$  were well mixed in an agate mortar. The

mixed powder was fired in air at 1203–1223 K for 24 h. This stage was repeated at least twice to improve the homogeneity. Then the reground powder was pressed into pellets at a pressure of 4000 kg cm<sup>-2</sup>. The pellets were sintered at about 1243 K for 24 h in flowing oxygen, followed by an additional annealing at 773 K for another 24 h. The cooling rate was controlled at 1 K min<sup>-1</sup>.

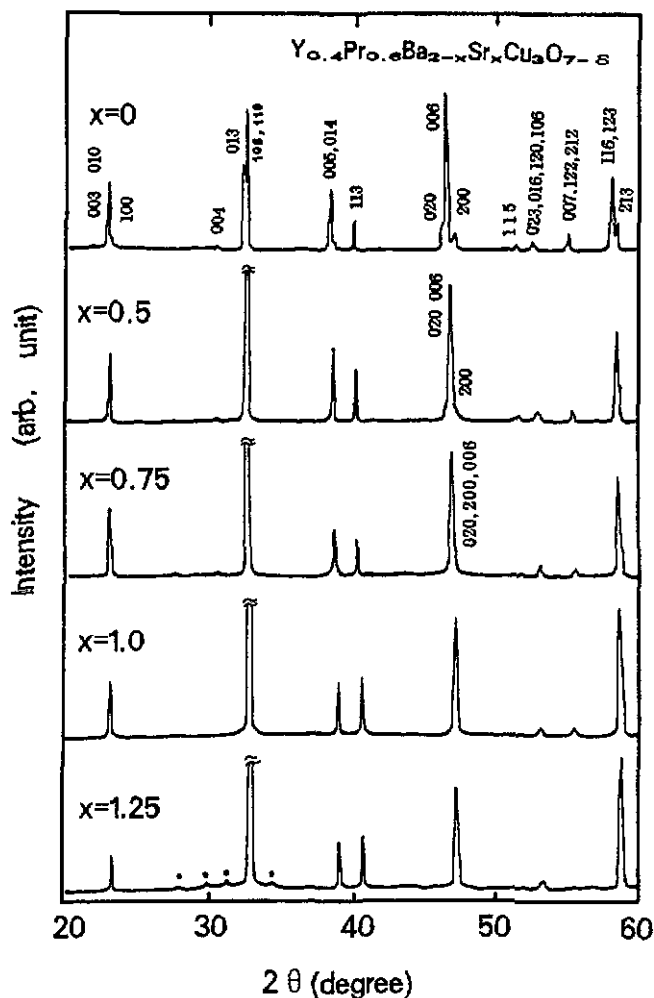


Figure 1. XRD patterns with Cu K $\alpha$  radiation for  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  pellets. The small dots refer to Sr–Cu–O impurities.

X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max- $\gamma$ A rotating target x-ray diffractometer with monochromatic Cu K $\alpha$  radiation at room temperature. Lattice parameters were calculated by a least-squares-refinement programme. The differential thermal analysis (DTA) was performed in air up to 1100 °C on a thermal analyser manufactured by the Shanghai Balance Instrument Factory. The temperature dependence of the resistivity ( $R$ – $T$ ) was measured by a standard four-probe method in the range 13–300 K. The temperature was determined by a newly calibrated Rh–Fe thermocouple. AC

susceptibility was measured by a mutual inductance method. The inductance bridge had a sensitivity better than  $0.1 \mu\text{H}$ . Oxygen content was determined by iodometric titration with the precision of  $\delta$  better than 0.02 [3]. It was shown that the oxygen content was in the range of 6.90–6.95, and the sample with higher Sr concentration had a slightly lower oxygen content.

XRD patterns for the as-prepared pellets of  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  (figure 1) showed that the samples were essentially monophasic in the range of  $0 \leq x \leq 1.0$ . When  $x$  was increased to 1.25, small amounts of Sr–Cu–O impurities formed, indicating that the Sr solid solubility was close to 1.25 under ambient conditions. Figure 1 shows that there is crystal preferential orientation parallel to the (001) plane in the samples since the (00 $l$ ) reflections are quite strong. This makes it easier to index (006), (020) and (200) peaks in the XRD patterns. With increasing  $x$ , (020) and (200) reflections overlap more and more with (006) diffraction, indicating an orthorhombic-to-tetragonal transition. Lattice parameter calculation makes it clearer. Figure 2 shows the lattice parameters versus Sr content  $x$ . With increasing  $x$ ,  $a$  and  $b$  become closer until they are almost equal at about  $x = 0.75$ . Note that the oxygen content was always near 7.0; the structural transition may originate from the change of oxygen atomic position within the Cu(1)O layer, probably induced by the entrance of Sr. It is also noted that the lines on figure 2 are basically in accordance with Vegard's law, implying Sr has been incorporated. It is expected that Sr occupies the Ba site since they are isoalent and both have a large size.

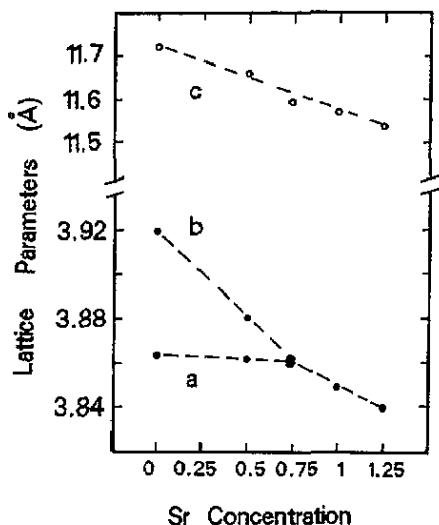


Figure 2. Lattice parameters versus Sr content  $x$  in  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ .

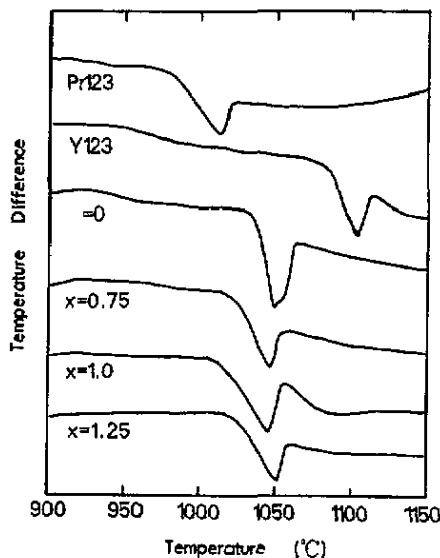


Figure 3. DTA curves for  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  powders.

The sample homogeneity was also examined by the DTA experiment. In fact, DTA is one of the best methods of detecting whether there is phase segregation, especially on a small scale (which makes it difficult to observe by XRD). Figure 3 shows the DTA curves for the samples. It can be seen that there is basically one endothermic peak at about 1000–1060 °C for each sample, suggesting that the sample has good homogeneity.

The temperature dependence of electrical resistivity for  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  samples is shown in figure 4. The end member sample of  $x = 0$  exhibits semiconducting

behaviour with no superconducting transition, which is in accordance with the previous reports [1]. With increasing Sr content to 0.5, the temperature coefficient becomes positive in the range of 120–300 K. When  $x = 0.75$ , the sign of superconductivity can be seen with  $T_{c(\text{onset})} = 17$  K. For  $x = 1.0$ , it is observed that  $T_{c(\text{zero})} = 18$  K, and the metallization is realized. With increasing  $x$  to 1.25,  $T_c$  can be further raised to 23 K. Therefore, Sr substitution for Ba can lead to the revival and enhancement of superconductivity in the  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  system. In this respect, we suggest that the ion-size effect on  $T_c$  also exists at the Ba site.

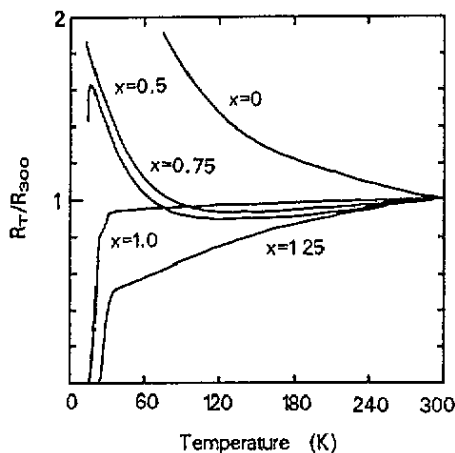


Figure 4. Temperature dependence of normalized resistivity for  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  samples.

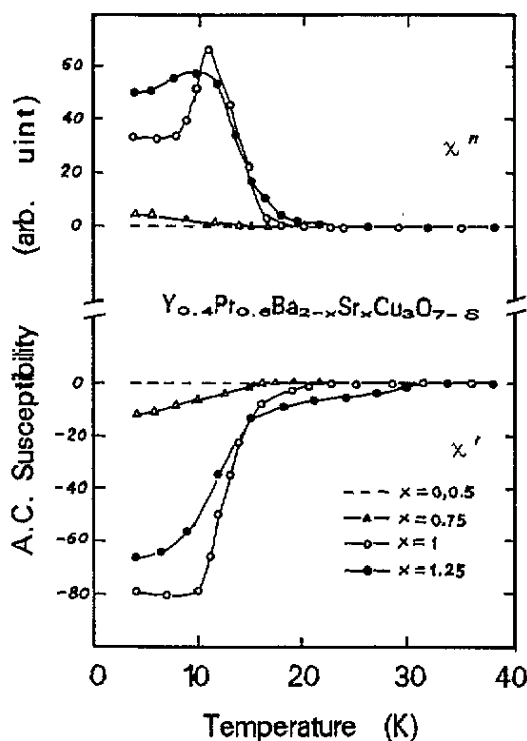


Figure 5. AC susceptibility versus temperature for  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ .

The above result was confirmed by magnetic measurement. Figure 5 shows the AC susceptibility versus temperature for the samples. It was found that the  $T_c$  from the magnetic measurement is about the same as the  $T_{c(\text{mid})}$  (at which the resistivity drops to half of its extrapolated normal-state value) from the electrical measurement. We used a standard  $YBa_2Cu_3O_7$  sample to estimate the superconducting volume percentage roughly, and it was observed that the diamagnetic signal of the  $x = 1.0$  sample was comparable to that of  $YBa_2Cu_3O_7$ . So, the revived superconductivity is really a bulk effect.

With regard to the cause for the ion-size effect, there has been no satisfactory proposal up to now. Previous interpretation [2] was based on the assumption that the hybridization between the local state of the Pr ion and the valence band of the  $CuO_2$  plane is larger in  $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  with larger R ionic radius, which seems unreasonable [4]. Muroi and Street [4] proposed a 2D percolation model. However, the model has difficulty accounting for

the variation of electrical and/or magnetic properties when Pr concentration is constant. For example, Sr substitution for Ba in  $\text{Tl}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{PrCu}_2\text{O}_7$  [5] and  $\text{Pr}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_2\text{NbO}_{8-y}$  [6] results in a decrease of  $T_N$ ; in this work, Sr substitution for Ba led to the revival of superconductivity.

Considering that the ion-size effect may exist at both the R site and the Ba site, we suggest that there should be a common point connecting them. That is probably the Cu–O bond length within the  $\text{CuO}_2$  sheet as stated below.

Recently, we emphasized the Pr–O covalent bonding effect in  $\text{PrBa}_2\text{Cu}_3\text{O}_7$ , based on the minute structural anomaly related to both Pr and O(2,3) atoms [7]. It is proposed that the Pr–O covalency creates a new narrow band related to the Pr 4f electron near the Fermi level ( $E_F$ ). The itinerant holes within the  $\text{CuO}_2$  plane may be transferred to the new band and changed into a kind of small polaron, which is unfavourable for superconductivity and metallization, probably due to the band narrowing [8]. So, Pr–O covalent mixing should be responsible for the quenching of both superconductivity and metallic conductivity. So, the suppression of  $T_c$  by Pr is related to the extent of covalent mixing between Pr and O(2,3) atoms. As we know, the covalent ingredient is mainly dependent on the energy difference between the  $E_F$  (probably across the  $\pi_{xy}^*$  band) and the Pr 4f level ( $E_f$ ), i.e.,  $\Delta = E_F - E_f$ . The larger the  $\Delta$ , the weaker the Pr–O covalent bonding. It is learned that  $E_f$  is probably below  $E_F$  following the result of resonant photoemission data in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  [9], and  $E_F$  can be raised when the Cu–O(2,3) bondlength is shortened according to the tight-binding band structure calculation [10]. Sr substitution for Ba in  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  will increase the  $\Delta$  by shortening the Cu–O(2,3) bondlength (nearly half of the  $a$  and  $b$  axes, see figure 2), which is unfavourable for the Pr–O covalent mixing. Therefore, the superconductivity can be revived at a critical Pr concentration by the isovalent substitution.

In the Pr-free system of  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ , the result [11] was different. Sr substitution for Ba resulted in the slight decrease of  $T_c$ , which was thought to be due to the decrease of oxygen content. If we defined the ‘chemical pressure’ as an insolvent substitution for a larger ion by a smaller ion without changes in the crystal structure, one may conclude that the chemical pressure effect on  $T_c$  in  $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  depends on the  $y$  value. For low  $y$ , the effect is negative; for high  $y$ , the effect becomes positive, as in the  $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  system. This case is just the opposite to that of the physical (hydrostatic) pressure effect on  $T_c$  in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  [12].

One may argue that the above Pr–O covalent bonding effect would have difficulty explaining the physical pressure effect, which is contrary to the chemical pressure effect. However, it should be noticed that there are distinct differences between the physical pressure and the chemical pressure. The former has an equal effect on each atom in the crystal. Under high hydrostatic pressure, the Pr–O(2,3) and Cu–O(2,3) distances contract and the extent of contraction is rather small. The chemical pressure may have an unequal effect on each atom, and the average Cu–O(2,3) distance may be shortened distinctly (as in this work) but the Pr–O distance may even be increased. In fact, Lai *et al* [8] did observe that Sr substitution for Ba accompanied with an increase of the Pr–O bondlength in  $\text{TlBa}_2\text{PrCu}_2\text{O}_7$ . As far as the sample with high Pr concentration is concerned, the hydrostatic pressure contracts the Pr–O bondlength, and enhances the Pr–O covalent bonding, leading to the decrease of  $T_c$ . In contrast, the chemical pressure may expand the Pr–O bondlength, and weaken the Pr–O covalent mixing, thus  $T_c$  can be increased. So, the two seemingly contradictory effects originate from the difference of variation about the local structure due to the different ‘pressures’.

Incidentally, our result seems to be meaningful where the crystal structures are concerned. In the 123 compound, it is well known that the orthorhombic phase is

superconducting at about 90 K while the tetragonal phase is not superconducting or has low  $T_c$ . In  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ , however, it is the opposite: the tetragonal phase is responsible for the revived superconductivity. So, the orthorhombicity may have a less direct correlation with the superconductivity.

In conclusion, we observed that Sr substitution for Ba can revive the superconductivity and metallic conductivity in the  $Y_{0.4}Pr_{0.6}Ba_{2-x}Sr_xCu_3O_{7-\delta}$  system. The ion-size effect on  $T_c$  may also take place at the Ba site, which has been interpreted in terms of the Pr-O covalent bonding effect. It is also stated that the 'chemical pressure effect' is different from the hydrostatic pressure effect in the local structure.

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