Superconductivity and Hole Doping in $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ Thin Films

David P. Norton, D. H. Lowndes, B. C. Sales, J. D. Budai, B. C. Chakoumakos, and H. R. Kerchner
Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6056

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We have grown superconducting $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin films that exhibit a superconducting onset temperature of 43 K with $T_c(R=0)=34.9$ K. This is the first time, to our knowledge, that 1:2:3-phase superconductivity has been achieved by substituting Ca for Pr, without the presence in the alloy of Y or any other rare-earth element R for which $RBa_2Cu_3O_{7-\delta}$ is superconducting. This result supports the view that hole localization/filling contributes substantially to the suppression of superconductivity by Pr in $PrBa_2Cu_3O_{7-\delta}$, and clearly demonstrates that this suppression can be compensated by appropriate hole doping with Ca.

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Early in the history of high-temperature superconductors, it was found that the superconducting properties of the materials $RBa_2Cu_3O_{7-\delta}$ were nearly independent of the rare-earth element R.[1,2] This was surprising as many of the lanthanide elements possess magnetic moments, normally a condition detrimental to superconductivity, and indicated that the CuO_2 planes and the rare-earth ions are electronically isolated. The exceptions to this behavior are Ce, Tb, and Pr, which do not form superconductors, with only Pr forming a single-phase "1:2:3" structure. $PrBa_2Cu_3O_{7-\delta}$ is a semiconductor,[3-5] but is quite similar to the superconducting "1:2:3" compounds in structure and oxygen chemistry, undergoing the orthorhombic-to-tetragonal transition at values of temperature and oxygen content close to those for $YBa_2Cu_3O_{7-\delta}$.[6] However, substitution of Pr for Y in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ suppresses T_c, with superconductivity disappearing at $x\sim0.5$.[3-5,7-10]

Most of the discussion of the suppression of 1:2:3-phase superconductivity by Pr centers around its valence. Magnetic-susceptibility measurements indicate that the Pr valence is nearly +4.[5,11] A recent neutron-diffraction investigation of the separation of the CuO_2 planes in $PrBa_2Cu_3O_{7-\delta}$ concludes that Pr has a mixed valence of $\sim+3.3$.[12] X-ray-absorption spectroscopy studies comparing Pr, Gd, and Ho in 1:2:3-phase compounds revealed features attributable to both Pr^{+3} and Pr^{+4}, again suggesting a mixed-valence system.[13] A valence greater than +3 for Pr in $PrBa_2Cu_3O_{7-\delta}$ would explain both the lack of superconductivity and the semiconducting behavior, since Pr could contribute electrons to the CuO_2 planes, filling the mobile holes responsible for conduction.[14] However, resonant valence-band photoemission studies suggest that Pr is trivalent in $PrBa_2Cu_3O_{7-\delta}$.[15] Some x-ray-absorption and structural studies indicate a valence of +3 as well.[16] Obviously, there is debate over the valence of Pr in $PrBa_2Cu_3O_{7-\delta}$.

Two mechanisms have been proposed for the suppression of T_c by Pr in the 1:2:3 phase. The first involves superconducting pair breaking by local moments, due to spin-dependent exchange scattering of the holes in the CuO_2 planes, with hybridization between the Pr $4f$ states and the CuO_2 valence-band states contributing as well.[7,8,17] The main evidence for magnetic pair breaking is that the reduction of T_c with increasing x in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ appears to follow the Abrikosov-Gorkov pair-breaking model. However, other rare-earth elements, such as Gd, possess a much larger spin magnetic moment with no apparent effect on T_c. This apparent discrepancy has been explained by the larger radial extent of the Pr ion, leading to significant hybridization of the Pr $4f$ electrons with the CuO_2 valence band and magnetic pair breaking.[8,9,17] The second mechanism involves the filling and/or localization of holes available for conduction in the CuO_2 planes. If the valence of Pr is nearly +4, the additional electron contributed by the Pr ion is expected to fill mobile holes in the CuO_2 planes, effectively leaving the holes localized on the Pr, reducing conduction and eliminating superconductivity. This view may be too simplistic, as recent evidence from electron-energy-loss spectroscopy has been interpreted to mean that the *total* hole concentration is unaffected by Pr content in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[18] An alternative view is that strong hybridization of the Pr $4f$ with O $2p$ states leads to localization of the holes without requiring a Pr formal valence greater than +3 or significant changes in the *total* hole (mobile and trapped) concentration, although the mobile hole concentration can decrease as indicated by Hall[19] and muon-spin relaxation measurements.[6,18,20] Henceforth, we use the term "hole localization/filling" to refer to the two closely related effects that can occur for a strongly hybridized mixed-valence element such as Pr, for which it is necessary to distinguish carefully between valency and ionicity.[21] The most convincing evidence that Pr produces hole localization/filling and suppresses superconductivity has been presented by Neumeier *et al.* in a study of the superconducting behavior of $Y_{1-x-y}Ca_yPr_xBa_2Cu_3O_{7-\delta}$ alloys.[22] In this alloy system, the substitution of Ca for Y should add holes to the CuO_2 planes. If Pr reduces the *mobile* hole concentration available for conduction in the CuO_2 planes, then the addition of holes by Ca should compensate the effect of Pr in suppressing T_c. This behavior has indeed been observed. However, the presence of Y in all of the samples they considered $(0 \le x \le 0.2, 0 \le y \le 0.2)$ somewhat complicates the interpretation of their results, because of the possibility that phase separation yields Y-rich regions.[23] These superconducting Y-rich regions could form a percolative path resulting in the observed superconducting behavior. Infante *et al.* suggested that such a percolation model can be used to quantitatively describe the dependence of T_c on the Pr concentration in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[23] In order to eliminate this possibility, one would like to investigate hole doping by Ca in the absence of Y or any other element R for which $RBa_2Cu_3O_{7-\delta}$ is superconducting.

In this paper, we report on the growth and superconducting properties of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin films and show that hole localization/filling contributes substantially to the suppression of T_c in $PrBa_2Cu_3O_{7-\delta}$. We find that $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ films are fully superconducting with $T_c(R=0) \sim 35$ K. The superconducting transition obviously cannot be the result of phase segregation of a stable superconducting phase as there are no such phases known involving only Pr or Ca. This result presents some of the clearest evidence to date that the suppression of superconductivity by Pr in 1:2:3-phase compounds involves hole localization/filling.

$Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin films were grown by pulsed-laser ablation as has been described elsewhere.[24] Pressed and fired ceramic targets of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ were prepared from stoichiometric quantities of high-purity Pr_6O_{11}, $CaCO_3$, $BaCO_3$, and CuO in a manner similar to that used to produce superconducting R-1:2:3 pellets. Powder x-ray diffraction indicated that the resulting ceramic target was composed of material with the tetragonal 1:2:3 structure along with a small amount of $BaCuO_2$. $SrTiO_3$ (001) substrates were utilized for most of these experiments, although $LaAlO_3$, MgO, yttria-stabilized zirconia, and $KTaO_3$ substrates were sometimes included. Film growth was carried out in an oxygen pressure of 200 mTorr. After deposition, the films were cooled in 400 Torr of oxygen at 10 °C/min.

Figure 1 shows the superconducting transition for a $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin film. The superconducting transition is fairly sharp with $T_c(90\%) = 43$ K, $T_c(50\%) = 40.2$ K, $T_c(10\%) = 38.3$ K, and $T_c(R=0) = 34.9$ K. The contrast in electrical properties with a $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ film (also shown) is remarkable: The $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ film is semiconducting with divergent low-temperature resistance, while the $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ film is metallic and superconducting. ac magnetic-susceptibility measurements on our $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ films confirm that a superconducting transition occurs with weak critical currents induced. Figure 2 shows resistance versus temperature for several $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ thin films grown on $SrTiO_3$ at various substrate temperatures. These measurements used a standard four-point method with a current less than 10 A/cm^2. As is evident, the superconducting properties of the $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ thin films depend quite strongly on growth conditions (substrate temperature). The film with the highest T_c was grown at 640 °C. In contrast, a film grown at 730 °C exhibits an onset temperature of ~ 12 K with $T_c(R=0)$ less than 4.2 K. The reason for this dependence on substrate temperature becomes evident from the x-ray-diffraction data discussed below.

We have not yet been able to detect a superconducting transition in the bulk $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ targets, even though x-ray diffraction shows some of the targets to be

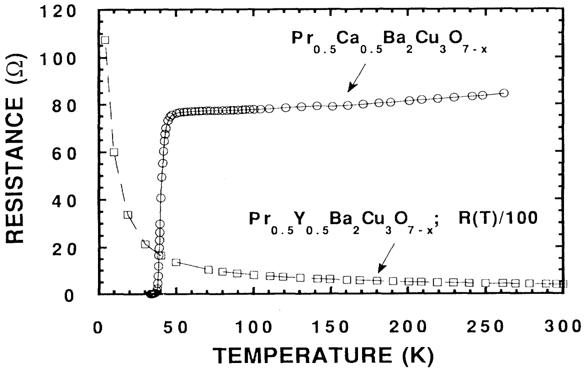

FIG. 1. Resistance vs temperature for a $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin film grown at 640 °C on (001) $SrTiO_3$; film thickness is approximately 300 nm. Also shown is the resistance behavior for a $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ thin film grown under the same conditions; film thickness is approximately 120 nm.

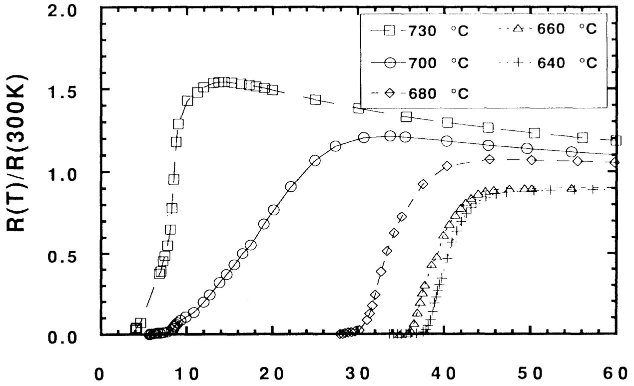

FIG. 2. Normalized resistance vs temperature for $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin films grown on (001) $SrTiO_3$ at various substrate temperatures; film thicknesses are approximately 300 nm.

nearly phase-pure 1:2:3 material. This inability to make the target material superconducting may be related to differences in the ability to properly incorporate large amounts of Ca into the bulk compound and into epitaxial films grown under laser-ablation conditions. Difficulties in obtaining the proper oxygen stoichiometry in bulk samples also cannot be ruled out. Since this superconducting compound was successfully grown as an epitaxial thin film while not forming (to date) in bulk samples, the implication is that other difficult chemical substitutions may be possible using epitaxial films and/or laser ablation.

Four-circle x-ray diffraction was utilized to observe the epitaxial relationship of the film and substrate as well as to search for any impurity phases in the films. Figure 3 illustrates that no significant impurity peaks were observed in a θ-2θ scan along the surface normal. Inam *et al.* have shown that $PrBa_2Cu_3O_{7-\delta}$ epitaxial thin films tend to grow with the *a* axis instead of the *c* axis perpendicular to the substrate at reduced substrate temperatures.[25,26] We find this to be the case for $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ as well. X-ray-diffraction data show a greater percentage of material growing with the *a* axis perpendicular to the substrate as the substrate temperature is reduced from 730 to 640 °C. From the superconducting transport measurements (Fig. 2) and x-ray-diffraction results, there is a clear correlation between T_c and the amount of *a*-axis perpendicular material present. The film with the highest T_c, grown at 640 °C, consists almost totally ($>90\%$) of *a*-axis perpendicular grains. The most significant difference between the *a*-axis and *c*-axis perpendicular material is that their lattice parameters and structures are not the same. The *c*-axis perpendicular material is nearly tetragonal with $a \sim b \sim 3.87$ Å and $c = 11.686$ Å. θ-2θ scans through the $(205)c\perp$ and $(0.25)c\perp$ reflections show a single broad peak, indicating tetragonal material with possible short-range orthorhombic order. φ scans through the $(205)c\perp$ and $(225)c\perp$ peaks show in-plane alignment of the substrate and film $\langle 110 \rangle$ directions, as has been reported for *c*-axis perpendicular $YBa_2Cu_3O_{7-\delta}$.[27] On the other hand, the *a*-axis perpendicular grains are orthorhombic with $a = 3.834$ Å, $b = 3.90$ Å, and $c = 11.75$ Å. The origin of this difference in lattice parameters for *a*-axis and *c*-axis perpendicular grains is puzzling as the *c*-axis lattice parameter for orthorhombic $YBa_2Cu_3O_{7-\delta}$ is smaller than that for the tetragonal phase.[28] Possible explanations include differences in the substitution of Ca into *a*-axis and *c*-axis perpendicular material. One must also consider the fact that the *a-b* plane and *c*-axis thermal expansion coefficients will differ in this anisotropic material, leading to orientation-dependent strain for an epitaxial film on a substrate with a somewhat different thermal-expansion coefficient. Similar results were obtained for thin films grown on (001)-oriented MgO, yttria-stabilized zirconia, $LaAlO_3$, and $KTaO_3$ with slightly lower T_c.

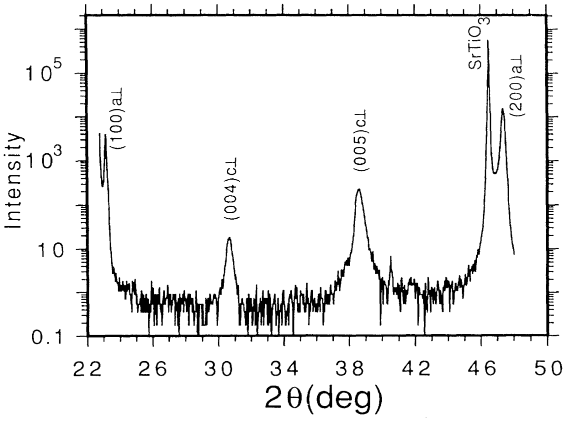

FIG. 3. θ-2θ x-ray-diffraction scan along the $(00l)$ axis for an epitaxial $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ thin film, indicating the presence of both *a*-axis and *c*-axis perpendicular grains. This film was grown at 660 °C with $T_c(R=0) = 34.9$ K.

These experiments strongly support the idea that Pr suppresses T_c in $PrBa_2Cu_3O_{7-\delta}$ by reducing the mobile hole concentration. The fact that replacing Y by Pr in $YBa_2Cu_3O_{7-\delta}$ transforms a metal into a semiconductor suggests this argument. The demonstration in this work that $PrBa_2Cu_3O_{7-\delta}$ can be made superconducting by Ca substitution on the Pr site strongly supports this view. The primary result of Ca doping is to introduce additional holes into the CuO_2 planes to compensate the hole localization/filling by Pr. If magnetic pair breaking was the primary cause of the suppression of T_c, it would be difficult to explain how Ca doping could compensate for it. In fact, Ca doping produces superconductivity in $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ with T_c higher than for $Pr_{0.5}Y_{0.5}Ba_2Cu_3O_{7-\delta}$ ($T_c \sim 0$), so hole localization/filling must be the primary cause of the suppression of T_c.

As was pointed out earlier, Neumeier *et al.* reported similar results for the $Y_{1-x-y}Ca_yPr_xBa_2Cu_3O_{7-\delta}$ system.[22] Based upon their results for $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.2$, they derived an empirical expression for the dependence of T_c on the Y, Pr, and Ca content,

$$T_c(x,y) = 97\ \mathrm{K} - (425\ \mathrm{K})(0.1 - 0.95x + y)^2 - (96.5\ \mathrm{K})x\,. \tag{1}$$

Although the last term in this expression was originally attributed to magnetic pair breaking, the same authors have since dismissed this interpretation and find no evidence for magnetic pair breaking.[20] This equation predicts $T_c = 42.2$ K for $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$, which is remarkably close to the 43-K superconducting onset temperature that we find. Based upon this equation, however, this value for T_c is very near the maximum possible by substituting Ca for Pr in $PrBa_2Cu_3O_{7-\delta}$. As Ca doping apparently cannot fully compensate the suppression of T_c by Pr, a mechanism in addition to simply hole localization/filling also must be involved. As was pointed out earlier, strong hybridization of Pr $4f$ electrons with the CuO_2 valence band appears to occur. Changes in the band structure related to this hybridization could be involved in this additional decrease in T_c.

With the x-ray-diffraction data revealing no impurity peaks, it appears that nearly all of the Ca is incorporated substitutionally at the Pr site into the $PrBa_2Cu_3O_{7-\delta}$ structure. However, recent studies indicating that Pr can occupy the Ba site complicate this interpretation. In the $PrCaBaCu_3O_{7-\delta}$ system, for instance, x-ray-diffraction intensity studies indicate a scrambling of the Pr and Ca between the Y and Ba sites.[23] This same study also found that $PrBa_{2-x}Ca_xCu_3O_{7-\delta}$ samples were single phase with $x \leq 0.8$. Obviously, it is difficult to say with certainty precisely how the Ca is incorporated into the $PrBa_2Cu_3O_{7-\delta}$ matrix. This uncertainty in the amount of Ca substituting for Pr does not change the impact of the major result of this work: hole doping through Ca substitution compensates for the suppression of superconductivity by Pr.

In conclusion, we have grown superconducting $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-\delta}$ epitaxial thin films. This is the first time that this material has been formed. The main significance of superconductivity in this material is in showing that hole doping by Ca substitution compensates the suppression of superconductivity by Pr, without the confusing possibility that a percolative path of $YBa_2Cu_3O_{7-\delta}$ exists to give the superconducting behavior. This result cannot be explained within the context of magnetic pair breaking, and provides convincing evidence that hole localization/filling is responsible for the suppression of superconductivity by Pr in $RBa_2Cu_3O_{7-\delta}$.

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