

Transport and structural properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown by pulsed-laser deposition

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We have studied the transport and structural properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown by pulsed-laser deposition, focusing on Ca substitution levels $x \geq 0.3$ for which the bulk material is metastable. Films with $0.4 \leq x \leq 0.5$ exhibit a superconducting transition due to divalent cation doping on the rare-earth site. $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films exhibit a superconducting onset temperature as high as 47 K with $T_c(R=0) = 35$ K. X-ray-diffraction and electrical-transport data suggest that Ca doping levels greater than $x = 0.5$ are possible, although disorder is introduced as the divalent to trivalent cation ratio becomes large. This work demonstrates that 1:2:3-phase superconductivity can be achieved by substituting Ca for Pr, without the presence in the alloy of Y or any other rare-earth element, R, for which $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is superconducting. This result supports the view that hole localization, due to hybridization of the Pr 4*f* electronic levels with the O 2*p* orbitals, contributes substantially to the suppression of superconductivity by Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and demonstrates that this suppression can be partially compensated by appropriate hole doping with Ca.

I. INTRODUCTION

The superconducting properties of the materials $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are nearly independent of the rare-earth element R.^{1,2} This is surprising as many of the lanthanide elements possess magnetic moments, normally a condition detrimental to superconductivity, and indicates 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. $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a semiconductor,³⁻⁵ but it 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁶ However, substitution of Pr on the rare-earth site, R, in $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ suppresses T_c with superconductivity disappearing at $x > 0.5$.³⁻¹⁶

Much of the discussion concerning the suppression of 1:2:3-phase superconductivity by Pr has centered around its valence. Magnetic susceptibility measurements indicate that the Pr valence is nearly +4.^{5,17} Neutron-diffraction investigations of the separation of the CuO_2 planes in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ lead to the conclusion that Pr has a mixed valence greater than 3.^{18,19} 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.²⁰ A formal valence greater than +3 for Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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.²¹ However, some resonant valence-band photoemission, x-ray absorption, and structural studies suggest that Pr is trivalent in

$\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.^{22,23} Obviously, there is some confusion over the valence of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Lopez-Morales *et al.* suggest that the value obtained for the valence of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ depends on whether an experiment measures properties associated with the Pr—O bond (that would yield Pr^{+4}) or the charge near the Pr site (that would indicate Pr^{+3}).⁶ They consider the formal valence of Pr to be +3, but with significant hybridization of the Pr 4*f* states with the CuO_2 valence bands leading to mixed-valence character as well.^{6,24-26} A large body of experimental evidence and band-structure calculations suggest that significant hybridization of the Pr 4*f* states with the CuO_2 valence bands occurs due to the larger radial extent of the Pr ion.^{9,24,27-30} Within this model, most, if not all, of the experimental data on $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can be interpreted consistently.

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.^{7,8,24} The reduction of T_c with increasing x in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ appears to follow the Abrikosov-Gorkov pair-breaking model. However, the Abrikosov-Gorkov model does not predict the occurrence of a metal-to-insulator transition to accompany this suppression of superconductivity, although this is observed experimentally as x is increased. In addition, other rare-earth elements, such as Gd, possess a much larger spin magnetic moment, with no apparent effect on T_c . However, hybridization of the Pr 4*f* electrons with the CuO_2 valence band could lead to magnetic pair breaking.^{8,9,24} The second mechanism for suppression of T_c by Pr 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 (relative to Y) 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 appears to be too simplistic as recent evidence from electron energy loss and soft-x-ray-absorption spectroscopy suggest that the *total* hole concentration is unaffected by Pr content in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.^{31,32} An alternative view is that strong hybridization of the Pr 4*f* with O 2*p* 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 does decrease as indicated by Hall,^{33,34} Cu NMR,³⁵ mid-ir ellipsometric,³⁶ and muon-spin relaxation measurement.^{6,31,37} As with magnetic pair breaking, the mechanism for hole localization is intimately related to the strongly hybridized mixed valency of the Pr.³⁸

Some rather convincing evidence that Pr produces hole localization that suppresses superconductivity has been presented in studies of the superconducting behavior of $\text{Y}_{1-x-y}\text{Ca}_y\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ alloys.³⁹⁻⁴¹ 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 the samples considered ($0 \leq x \leq 0.2, 0 \leq y \leq 0.2$) somewhat complicates the interpretation of their results because of the possibility that phase separation yields Y-rich regions, which could form a percolative path.⁴² Ideally, one would like to investigate hole doping by Ca in the absence of Y or any other element *R* for which $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is superconducting. Previously, we reported that metastable $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films, which are fully superconducting with $T_c(R=0) \sim 35$ K, can be grown by pulsed-laser deposition.⁴³ 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 supports the view that hole localization is at least partially responsible for the suppression of superconductivity by Pr in 1:2:3-phase compounds.

In this paper, we report on the transport and structural properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown by pulsed-laser deposition, focusing on Ca substitution levels $x \geq 0.3$ for which the bulk material is metastable. Films with $0.4 \leq x \leq 0.5$ exhibit a superconducting transition due to divalent cation doping on the rare-earth site. Although superconductivity is induced due to the addition of holes through Ca substitution, x-ray-diffraction data suggest that disorder also is introduced, particularly for $x > 0.5$. $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films exhibit a superconducting onset temperature as high as 47 K, with $T_c(R=0) = 35$ K. Critical current densities as high as 10^5 A/cm² at 4.2 K have been measured as well. Apparently, 1:2:3-phase superconductivity can be achieved by substituting Ca for Pr, without the presence of the alloy of Y or any other rare-earth element *R* for which $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is superconducting. This result is con-

sistent with the view that hole localization, due to hybridization of the Pr 4*f* electronic levels with the O 2*p* orbitals, contributes substantially to the suppression of superconductivity by Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and demonstrates that this suppression can be partially compensated by appropriate hole doping with Ca.

II. RESULTS AND DISCUSSION

$\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films were grown by pulsed-laser ablation as has been described elsewhere.⁴⁴ Pressed and fired ceramic targets of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ 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 targets were composed of material with the tetragonal 1:2:3 structure along with a small amount of BaCuO_2 . (001) SrTiO_3 substrates were utilized for most of these experiments, although LaAlO_3 , MgO , yttria-stabilized zirconia and KTaO_3 substrates sometimes were 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. Throughout this paper, the growth temperature refers to the heater temperature as measured by an attached thermocouple. The film composition was assumed to be the same as the target composition which is typically the case for pulsed-laser deposition.

Figure 1(a) shows the resistivity for three thin-film

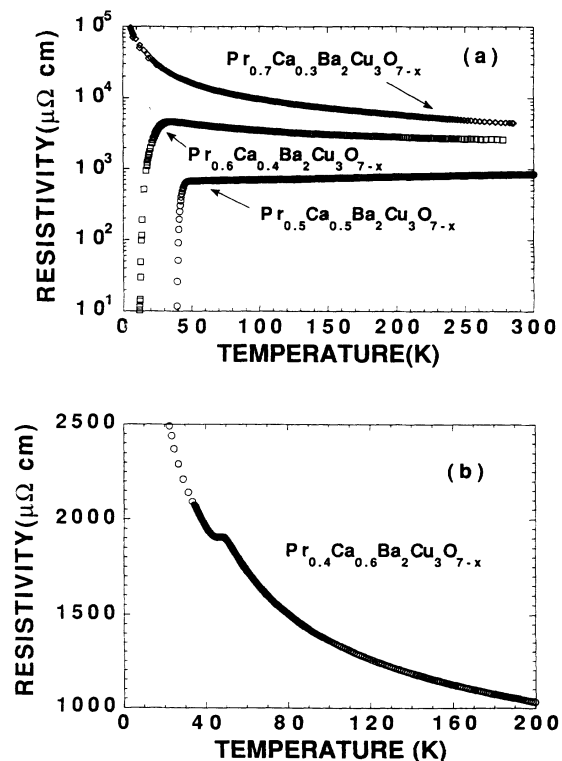


FIG. 1. Resistivity as a function of temperature for $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films with (a) $x = 0.3, 0.4, 0.5$ and (b) $x = 0.6$. Films were grown at 680°C on (100) SrTiO_3 .

samples with Ca contents of $x = 0.3, 0.4, 0.5$. Resistivity was measured using a standard four-point method with the current density less than 10 A/cm^2 . As seen in the figure, the resistivity decreases as the Ca concentration increases, consistent with the view that substituting a divalent into a rare-earth site hole dopes the material. A superconducting transition was observed for both the $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [$T_c(\text{onset}) \sim 25 \text{ K}$, $T_c(R=0) \sim 10 \text{ K}$] and the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [$T_c(\text{onset}) \sim 47 \text{ K}$, $T_c(R=0) \sim 35 \text{ K}$] samples, with no transition observed for the $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film. ac magnetic susceptibility measurements on the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films also indicated a superconducting transition. For $\text{Pr}_{0.4}\text{Ca}_{0.6}\text{Ba}_3\text{Cu}_3\text{O}_{7-\delta}$ thin films, no $R=0$ superconducting state was observed, although the resistivity demonstrated a reentrant behavior, as seen in Fig. 1(b). This reentrant behavior suggests that a small volume fraction of superconducting material with $T_c(\text{onset}) \sim 47 \text{ K}$, is present in the material. Although this behavior is reminiscent of a mixed-phase material, this does not appear to be the case here as no impurity peaks were observed in the x-ray-diffraction pattern for this film. However, significant broadening of the 1:2:3 x-ray-diffraction peaks was evident. In addition, the (00 l) peaks for the $\text{Pr}_{0.4}\text{Ca}_{0.6}\text{Ba}_3\text{Cu}_3\text{O}_{7-\delta}$ film are not located at exactly integral d -spacing positions, which indicates significant disorder in the material. Note that a Ca content $x > 0.5$ creates a 1:2:3-alloy material in which the majority of the rare earth sites contain a divalent, instead of trivalent, cation in addition to the totally divalent cation occupation of the Ba site. This substitution should prove to be quite disruptive to the electronic properties of the CuO_2 planes, leading to a material with characteristics of both the 1:2:3 structure, with trivalent and divalent cation site ordering, and of the so-called "infinite layer" tetragonal structure, which contains equivalent divalent sites between all the copper oxide layers.⁴⁵⁻⁴⁷ Note, however, that the ideal infinite layer structure contains no copper oxide chains and no oxygen atoms in the plane of the divalent cations.

It is interesting to compare the properties of Ca-doped $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films with films that are doped with other cations. Figure 2 shows the resistivity for three films of nominal composition $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. All of these films were grown at 680°C . The $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film has a resistivity that is slightly metallic, and a superconducting transition with $T_c(\text{onset}) = 47 \text{ K}$ and $T_c(R=0) = 35 \text{ K}$. We also have studied the magnetic field dependence of the superconducting transition, and find that $T_c(\text{mid})$ decreases by approximately 4 K in a magnetic field of 8 T . The room temperature resistivity is approximately $1 \text{ m}\Omega \text{ cm}$. The $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film, in which trivalent Y is substituted for Pr, is initially semiconducting with a room temperature resistivity of $2.5 \text{ m}\Omega \text{ cm}$. A superconducting onset is observed at $\sim 22 \text{ K}$, although no $R=0$ state is achieved. Thus, we see that Ca doping of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, for $x \leq 0.5$, leads to films with a lower resistivity and a higher value of T_c than for Y-doped $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$

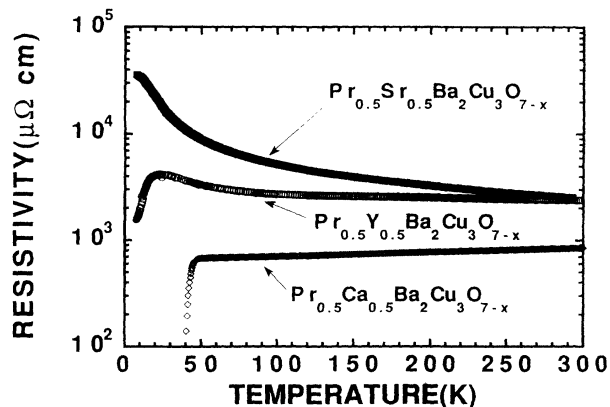


FIG. 2. Resistivity as a function of temperature for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown on (100) SrTiO_3 at 680°C .

of comparable doping levels. Note that a $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film, grown by single-target pulsed-laser deposition, displays somewhat different properties than an alloy film of the same composition that was grown by alternating between $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ targets, as we previously reported.⁴³ In that case, the $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film showed only semiconductorlike resistive behavior down to 4.2 K , with no evidence for a superconducting transition. Figure 2 also shows the resistivity for a $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film. In this case, the divalent Sr cation, which is somewhat larger than Ca, is substituted onto the rare earth site. X-ray-diffraction data show that these Sr-doped films have expanded lattice constants relative to the undoped or Ca-doped films, which is consistent with the assumption that the larger Sr cation substitutes onto the rare-earth site. Note that while Ca substitution on the rare-earth site leads to hole-doping and superconductivity, Sr-doping does not, even though Sr is also a divalent cation. This illustrates the importance of cation size in determining effective dopant candidates. This result is consistent with the observation that, for a given Pr concentration, T_c decreases as the rare earth-site ion size increases in $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.^{14,15,48}

It is significant that the superconducting properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films depend quite strongly on growth temperature. The $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film with the highest T_c was grown at 680°C . Figure 3 shows resistance vs temperature for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown on SrTiO_3 at various temperatures. In contrast, a film grown at 780°C exhibits an onset temperature of only $\sim 12 \text{ K}$ with $T_c(R=0)$ less than 4.2 K . The 680°C growth temperature at which we obtained $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films with the highest T_c is significantly lower than the 780°C optimum temperature for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ growth. This reflects the fact that $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x > 0.3$ is a metastable phase, which necessitates the use of lower growth temperatures.

Furthermore, we have not detected a superconducting transition in any bulk $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples. This inability to make the bulk material superconducting,

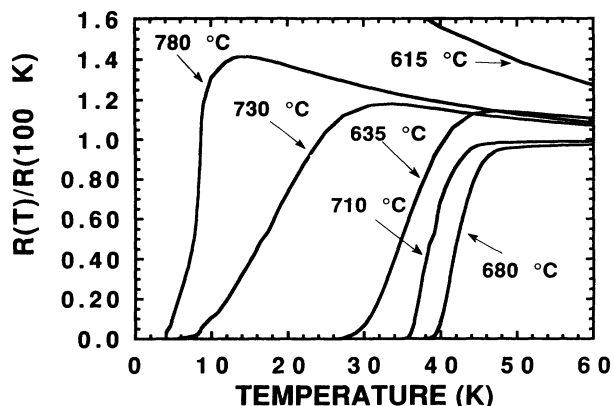


FIG. 3. Normalized resistance vs temperature for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films grown on (001) SrTiO_3 at various substrate temperatures; film thicknesses are approximately 300 nm.

while thin films are, appears to be related to an inability to properly incorporate large amounts of Ca into the bulk compound. Other examples of metastable copper oxide formation by means of epitaxial film growth include Ce substitution into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 49) and growth of the tetragonal phase of $(\text{Sr}, \text{Ca})\text{CuO}_2$ (Ref. 47).

In addition to studying the resistivity of these thin films, we also have measured their transport critical current density J_c . The J_c values were somewhat smaller than for epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films, although the values are respectable considering that the films are a mixture of a - and c -axis perpendicular grains. Figure 4

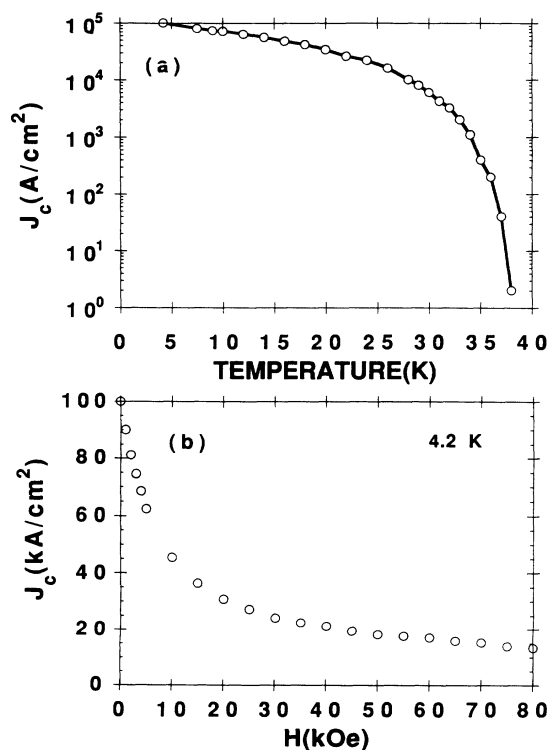


FIG. 4. Critical current density J_c for a $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film grown on (100) SrTiO_3 at 680 °C. Both (a) $J_c(H=0, T)$ and (b) $J_c(H, T=4.2 \text{ K})$ are shown.

shows $J_c(T)$ in zero magnetic field for a $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin film. J_c at 4.2 K is 10^5 A/cm^2 . Also shown is the magnetic field dependence of J_c (4.2 K). This fairly high value for J_c confirms that we are observing bulk superconductivity in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, although it is lower than J_c for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films by more than an order of magnitude. This may be due to disorder, as we have evidence from x-ray diffraction that some disorder is introduced by Ca doping at these high (metastable) levels. This disorder may occur because significant Ca substitution on the Pr site essentially converts a material with well-ordered trivalent and divalent cation sites ($\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, where R is a rare-earth element) into one in which half of the rare-earth sites are occupied by divalent cations, and blurs the distinction between the rare-earth and Ba sites. Even though this high level of substitution introduces disorder, we see that Ca doping at $x \geq 0.4$ provides sufficient hole carrier density to induce bulk superconductivity.

In addition to the transport properties, we also have studied the structural properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films utilizing four-circle x-ray diffraction. Inam and co-workers have shown that $\text{Pr}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films tend to grow with the a axis instead of the c axis perpendicular to the substrate at reduced substrate temperatures.^{50,51} We find this to be even more strongly the case for $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. X-ray-diffraction data show a greater percentage of material growing with the a axis perpendicular to the substrate, as the growth temperature is reduced from 730 to 640 °C. Somewhat surprisingly, all of the $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples grown in this temperature range contain both a -axis and c -axis perpendicular material, even films grown under conditions ($T=730 \text{ °C}$) for which only c -axis perpendicular $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films are obtained.

Within each sample, an interesting difference between the a -axis and c -axis perpendicular material is observed in that both the lattice parameters and crystal structure depend on grain orientation.⁴³ The c -axis perpendicular material is nearly tetragonal for all of the $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films that we studied. $\theta-2\theta$ scans through the $(205)c\perp$ and $(025)c\perp$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁵² On the other hand, the a -axis perpendicular grains are orthorhombic. The origin of this difference in lattice parameters for a -axis and c -axis perpendicular grains remains unclear. Figure 5 shows the c -axis lattice constant for of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown on SrTiO_3 at various substrate temperatures. As has been observed for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the c -axis lattice constant expands significantly as the growth temperature is decreased. This expansion is more pronounced for the c -axis-oriented material, and may be evidence for either $(\text{Pr}, \text{Ca})/\text{Ba}$ cation or oxygen disorder. It is interesting to note that, while the c -axis lattice constant changes significantly over this growth temperature range, the a -

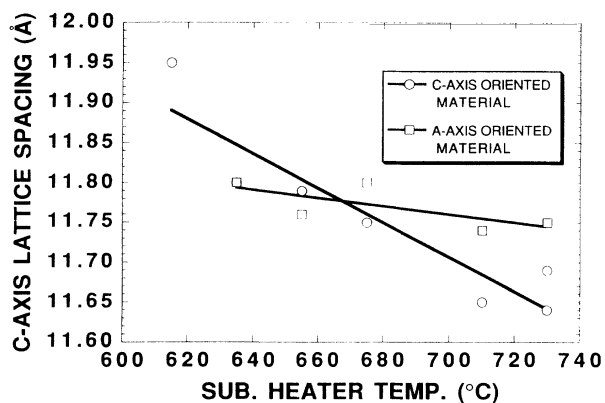


FIG. 5. c -axis lattice spacing for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown at various substrate temperatures. Note that the c -axis lattice spacings are given for both the a -axis and c -axis perpendicular material.

and b -axis lattice constants remain relatively constant with $a = b \approx 3.87 \text{ \AA}$ for the c -axis perpendicular grains and $a \approx 3.835 \text{ \AA}$, $b \approx 3.89 \text{ \AA}$ for the a -axis perpendicular material.

We also have measured the lattice parameters as a function of Ca content, as shown in Fig. 6. All of these

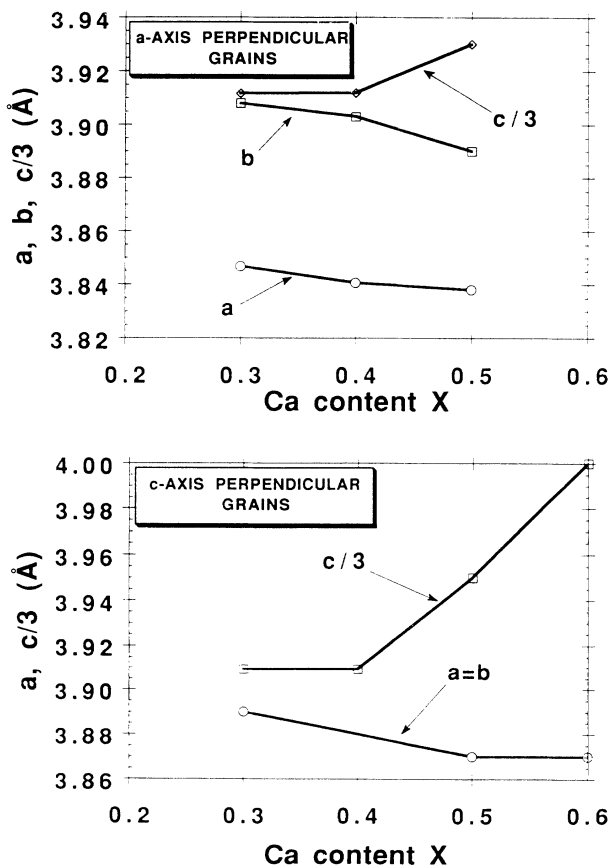


FIG. 6. Lattice parameters for $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films with various Ca contents. Films were grown at 655°C on (100) SrTiO_3 . Lattice parameters for both a -axis and c -axis perpendicular grains are shown.

films were grown at 680°C . As the Ca content is increased, the a - and b -axes decrease, while the c -axis increases. If one only considers the substitution of Ca for Pr, then significant changes in the lattice parameters are not expected, based upon the bond-length-predicting radii for eightfold coordinated Pr^{+3} (0.1126 nm) and Ca^{+2} (0.112 nm). However, disorder, as evidenced by an increase in the mosaic spread of the diffraction peaks, also increases with the Ca content. This second point is not difficult to understand, since increasing the Ca content increases the fraction of rare-earth sites that are occupied by divalent cations. This makes the chemical distinction between Ba sites and rare-earth sites (a significant fraction of which are occupied by divalent Ca) less clear, leading to disorder that possibly involves a change in coordination of either the rare-earth or Ba site. The increase in the c -axis lattice parameter as the Ca content is increased is more difficult to explain, and may involve differences in oxygen content as the Ca content is increased.

It is interesting to consider the properties of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown on substrates other than (100) SrTiO_3 . It is conceivable that the observed superconducting transition is due to a thin substrate/film interaction layer. If this were the case, then a superconducting transition would be observed for films grown on a specific substrate material, while not on others. Figure 7 shows the normalized resistance for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown at 655°C on SrTiO_3 (100), LaAlO_3 (100), MgO (100), and polycrystalline yttria-stabilized zirconia (YSZ). A superconducting transition is observed for all of these films, thus ruling out a film/substrate interaction layer as the origin of the superconducting behavior. Earlier, we pointed out that T_c increased as the growth temperature decreased (Fig. 3), and that the volume fraction of a -axis perpendicular material also increased, suggesting a correlation between T_c and the fraction of a -axis oriented material. Since a superconducting transition is observed for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown on MgO (100) (film predominantly c -axis oriented) and on polycrystalline YSZ (polycrystalline film), it does not appear that a high-

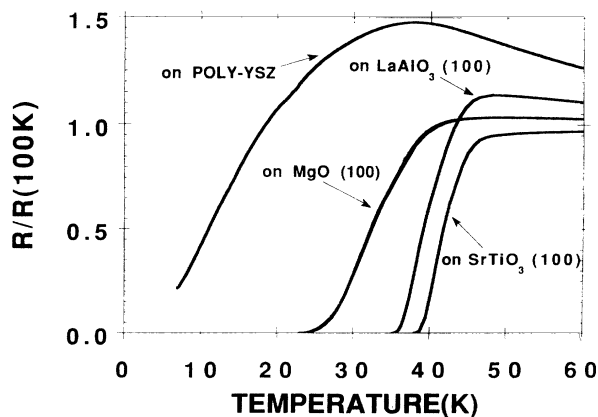


Fig. 7. Normalized resistance as a function of temperature for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films grown on various substrate materials. Films were grown at 655°C .

ly a -axis-oriented film is necessary for superconductivity. However, it is clear that the superconducting properties of this material are strongly enhanced [higher $T_c(R=0)$] when a strong epitaxial relationship does exist between the film and substrate. More importantly, $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ is essentially a metastable phase, as these films exceed the bulk solubility limit of $x \leq 0.3$ that has been observed for bulk samples. The incorporation of Ca above the apparent bulk solubility limit can be attributed to the low-temperature growth conditions utilized, and to the strong epitaxial relationship between the film and substrate. This is similar to what has been observed in the growth of the tetragonal infinite layer phase of $(\text{Sr,Ca})\text{CuO}_2$.⁴⁷

These experiments strongly support the idea that Pr suppresses T_c in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in part by reducing the mobile hole concentration. The fact that replacing Y by Pr in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transforms a metal into a semiconductor suggests this argument. The demonstration in this work that $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can be made superconducting by Ca substitution on the Pr site also supports this view. The primary result of Ca doping is to introduce additional holes into the CuO_2 planes to compensate the hole localization due to the hybridization of the Pr $4f$ states with the CuO_2 valence bands. If magnetic pair-breaking were the only 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 $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $T_c(\text{onset})=25$ K, while $\text{Pr}_{0.6}\text{Y}_{0.4}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ does not superconduct, so hole localization must be a primary cause of the suppression of T_c .

As was pointed out earlier, Neumeier *et al.* reported similar results for the $(\text{Y}_{1-x-y}\text{Ca}_y)\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system.³⁹ 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,

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

This equation predicts $T_c = 42.2$ K for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, which is somewhat less than the 47-K superconducting onset temperature that we observe. However, this equation predicts that the maximum value for T_c will occur at $x \sim 0.5$, which is quite consistent with our results.

It must be noted that, as Ca doping apparently cannot fully compensate the suppression of T_c by Pr, a mechanism in addition to hole localization must be involved.

An interesting result showing that the suppression of T_c with Pr doping is not entirely due to hole localization has been presented by Takita and Oshima.⁵³ They measured the Hall coefficient for Ca-doped and Nd-doped $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ bulk samples, and showed that samples of these two alloys could be prepared with very similar values of the inverse Hall coefficient $1/R_H$ but with very different transport properties. In particular, they found that the magnitude and temperature dependence of $1/R_H$ for $(\text{Pr}_{0.1}\text{Nd}_{0.9})(\text{Ba}_{1.9}\text{Nd}_{0.1})\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ were nearly the same, with the former a superconductor with $T_c = 64$ K, and the latter an insulator, even though the Hall data suggest comparable mobile carrier densities. In addition, Iwasaki, Sugawara, and Kobayashi showed that, while T_c and conductivity systematically decrease with Pr doping in $\text{Nd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, the inverse Hall coefficient becomes almost constant for $x > 0.2$ suggesting carrier scattering and localization.⁵⁴ This suggests that another mechanism besides simply hole localization plays a role in the suppression of superconductivity in Pr-doped 1:2:3 compounds. As was pointed out earlier, strong hybridization of Pr $4f$ electrons with the CuO_2 valence band appears to occur, and could lead to both magnetic pair breaking and hole localization from the same mechanism.

In conclusion, we have studied the structural and transport properties of $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial thin films grown by pulsed laser deposition. We show that bulk superconductivity is induced in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by hole-doping with Ca substitution. The main significance of superconductivity in this material is in showing that hole doping by Ca substitution partially compensates the suppression of superconductivity by Pr, without the confusing possibility that a percolative path of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ exists to give the superconducting behavior. This result cannot be explained within the context of magnetic pair breaking alone, and provides convincing evidence that hole localization is partially responsible for the suppression of superconductivity by Pr in $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. This result also demonstrates the utility of epitaxial thin film growth in the formation of metastable materials.

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