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Structural stability of $LuBa_2Cu_3O_{7-\delta}$ and superconductivity in thin films of $Lu_{1-x}M_xBa_2Cu_3O_{7-\delta}$ ($M=$Pr, Tb, and Ce)

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We present here the results of our investigations of the structural and superconducting properties of thin films of $Lu_{1-x}M_xBa_2Cu_3O_{7-\delta}$ ($M=$Ce, Pr, and Tb), the three ambivalent rare-earth ions. Our results show that Pr and Tb ions are in the trivalent state and Ce ions are tetravalent. Structural (in)stability of the parent material $LuBa_2Cu_3O_{7-\delta}$ forms the basis of our arguments. We suggest a simple model to account for the influence of Pr ions on superconductivity in cuprates.

INTRODUCTION

Since the discovery of $YBa_2Cu_3O_{7-\delta}$, extensive and intensive investigations have been reported in the literature pertaining to substitution of Y with a trivalent rare-earth ion from the lanthanide series. $RBa_2Cu_3O_{7-\delta}$ compositions with $R=$Ce and Tb do not form in the 1-2-3- orthorhombic structure. Both cerium and terbium form, respectively, double oxides $BaCeO_3$ and $BaTbO_3$, which lead to the formation of multiphase samples.[1,2] $PrBa_2Cu_3O_{7-\delta}$ does form in 1-2-3 phase but is semiconducting and antiferromagnetic [$T_N(\mathrm{Cu})\approx 280$ K and $T_N(\mathrm{Pr})\approx 17$ K].[3,4] As praseodymium also forms double oxide $BaPrO_3$, in which it is tetravalent,[5] some authors suggest that one of the possible mechanisms for the suppression of superconducting transition temperature, T_c in $PrBa_2Cu_3O_{7-\delta}$ is that Pr ions have formal valence greater than $+3$.[4] Partial substitution of Pr in superconducting R-1:2:3 compounds depresses the T_c.[6,7] An interesting feature observed in these systems is that, the depression of T_c as a function of Pr concentration is related to the ionic radius of the host rare earth. It is lower for rare earths with smaller ionic radii.[8]

On the other hand, results relating to Lu-1:2:3 phase have been rather sketchy and/or controversial. Ku *et al.*[9] prepared 95% pure, superconducting polycrystalline Lu-1:2:3. Recently, Liu *et al.*[10] reported 90 K T_c for a single-crystal specimen. However, a number of other workers claimed that they could not stabilize the monophasic Lu-1:2:3 phase.[11–17] Hor *et al.* synthesized and examined by x-ray diffraction (XRD) most of the R-1:2:3 compounds, but could not prepare Lu-1:2:3.[11] Tarascon *et al.*[12] and Moodenbaugh *et al.*[14] could not reliably refine the Lu-1:2:3 lattice parameters and concluded that a second phase accounted for at least half the powder pattern intensity. Somasundaram *et al.*[15] and Balakrishnan, Varadaraju, and Subba Rao[16] also concluded that monophasic $LuBa_2Cu_3O_{7-\delta}$ cannot be prepared and a lower limit of the rare-earth ionic radius exists, which the 1:2:3 structure can tolerate. [Ionic radius of Lu^{+3} in eightfold coordination is 0.975 Å (Ref. 17)]. Among the nine references we have quoted (Refs. 9–17), seven references (Refs. 11–18) conclude that $LuBa_2Cu_3O_{7-\delta}$ cannot be synthesized in polycrystalline ceramic form. Recently, an extensive investigation on the phase diagram of Lu-Ba-Cu-O has been reported which claims that the Lu-1:2:3 phase cannot form in the polycrystalline form.[18] This is a complete report on this subject. Our own work, as presented in this paper, confirms the conclusion. However, the stabilization of the Lu-1:2:3 phase in single-crystal form may be due to the enhanced temperature (which is about 100–200 °C higher than the bulk sintering temperature) and the starting composition 1:23:9) which is completely off-stoichiometric. These two factors perhaps result in the formation of single crystals of metastable phases like Lu-1:2:3. Our important observation indicates that even small amount of impurities such as Pr (or any well-defined trivalent rare earth) or Sr,Ca (which are probable impurities in $BaCO_3$) would lead to stabilization of Lu-1:2:3 phase.

Here, we present the investigation of superconducting behavior of thin films of the mixed systems $Lu_{1-x}M_xBa_2Cu_3O_{7-\delta}$, $M=$Ce, Pr, and Tb. We take advantage of the fact that $LuBa_2Cu_3O_{7-\delta}$ is very close to the crystallographic stability due to the small ionic radius of Lu ions, enabling us to draw important conclusions about the valence state of these three ambivalent ions. In addition, the analysis of the data on samples of the $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, and $Lu_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$

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systems suggests a plausible mechanism for the relation between the rate of suppression of T_c and the ionic radius of the host rare earth.

EXPERIMENTAL

Thin films of $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$, $Lu_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$, and $Lu_{1-x-y}Ce_xCa_yBa_2Cu_3O_{7-\delta}$ were grown *in situ* on ⟨100⟩$LaAlO_3$, ⟨100⟩MgO, and ⟨100⟩$SrTiO_3$ substrates by pulsed laser-ablation technique. Details of target preparation, growth conditions, and the characterization are described elsewhere.[19–21]

We have also tried the nominal composition of Lu-1:2:3 material by conventional solid-state method and by repeated firing at 900–915 °C for about 24 h. Beyond this temperature range we observed a partial melting and the material gets stuck to the crucible from which removal becomes difficult. Figure 1(a) shows the XRD pattern of nominal composition of bulk Lu-1:2:3 material. The sample is multiphasic containing the lines of $BaCuO_2$, Lu_2BaCuO_5, and CuO. We also could not observe any lines corresponding to *R*-1:2:3 phase.

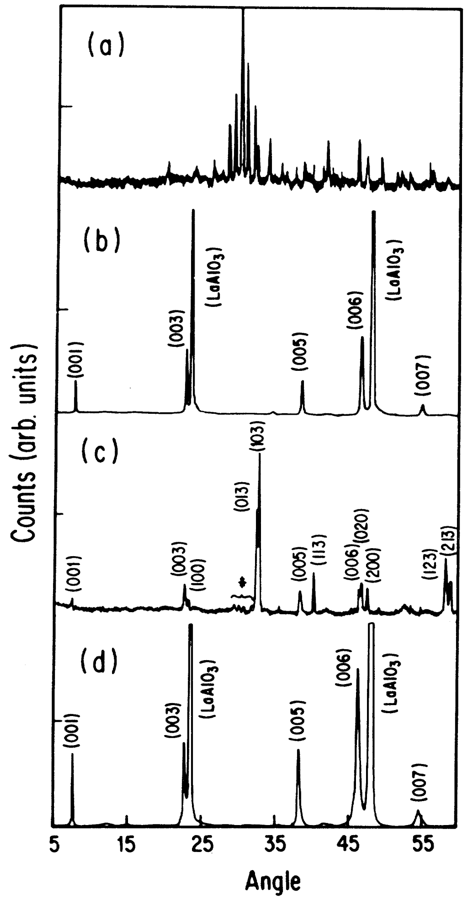

FIG. 1. X-ray-diffraction patterns of (a) the nominal composition of Lu-1:2:3, (b) $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$ (thin film), (c) $Lu_{0.8}Tb_{0.2}Ba_2Cu_3O_{7-\delta}$ bulk sample, and (d) $Lu_{0.75}Ce_{0.15}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ thin film. Patterns in (b) and (d) exhibit only (001) reflections showing the films to be highly *c*-axis oriented.

RESULTS

Thin films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ are crystalline, belong to 1-2-3 phase and are highly *c*-axis-oriented for $0 \leq x \leq 0.6$ [inferred from the fact that XRD spectra contain only (001) diffraction lines in Fig. 1(b)]. For higher values of x, multiphase films are observed. A bulk sample with $x = 0.2$ is also essentially a single-phase material as is clear from the XRD shown in Fig. 1(c). With higher concentration of Tb ($x \geq 0.3$), impurity phases ($BaTbO_3$ being the most prominent phase) start appearing in the bulk samples. Structural stability limit is much higher ($x = 0.6$) for films because in thin films, the substrate also plays a role in stabilizing the 1-2-3 phase. The films superconduct with $T_c \approx 88$ K, and $\delta T_c \approx 1$ K, typical of well-formed 1-2-3 phase. Figure 2 shows normalized resistance, $r(T) = R(T)/R(300\text{ K})$, as a function of temperature, of the bulk sample with $x = 0.2$ [Fig. 2(a)] and of films with $x = 0.1$, 0.3, 0.5 [Figs. 2(b)–(d)]. T_c is same in both film and bulk samples. The film, however, has a much better metallicity. J_c of the films was measured using patterned 10 μm wide microbridges and using 1 μV/cm criterion. J_c has been found to be greater than 10^6 A cm^{-2} at 77 K for all the films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ for x up to 0.5. The inset of Fig. 2 shows J_c as a function of temperature for a thin film of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$. J_c is found to be 3.0×10^6 A cm^{-2} at 77 K and 2.8×10^7 A cm^{-2} at 10 K.

XRD measurements showed that the bulk samples $Lu_{1-x}Pr_xBa_3Cu_3O_{7-\delta}$, with $x > 0.1$, are single-phase material. Major component of samples with $x \approx 0.1$ is the 1-2-3 phase. However, thin films of these materials, grown on ⟨100⟩MgO and ⟨100⟩$SrTiO_3$ substrates are single phase and highly *c*-axis-oriented for all concentrations x of Pr including $x = 0$. Figure 3 shows normalized resistance for films with $0 \leq x \leq 0.55$. A most notable

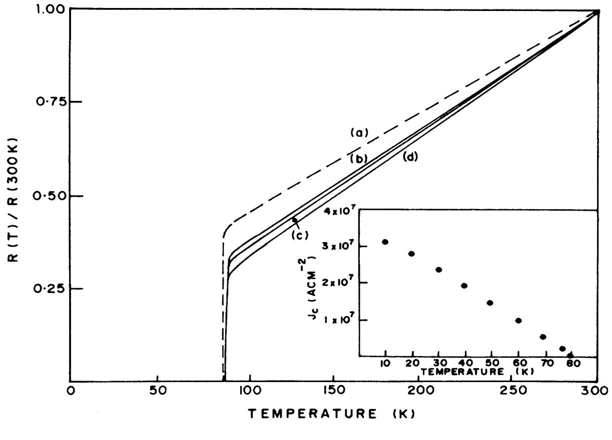

FIG. 2. (a) $r(T)$ [$=R(T)/R(300\text{ K})$] as a function of temperature of a bulk sample of $Lu_{0.8}Tb_{0.2}Ba_2Cu_3O_{7-\delta}$. (b)–(d) shows the similar plot for the thin films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ for $x = 0.1$, 0.3, 0.5. Inset shows the J_c as a function of temperature for one of the films of $Lu_{0.5}Tb_{0.5}Ba_2Cu_3O_{7-\delta}$.

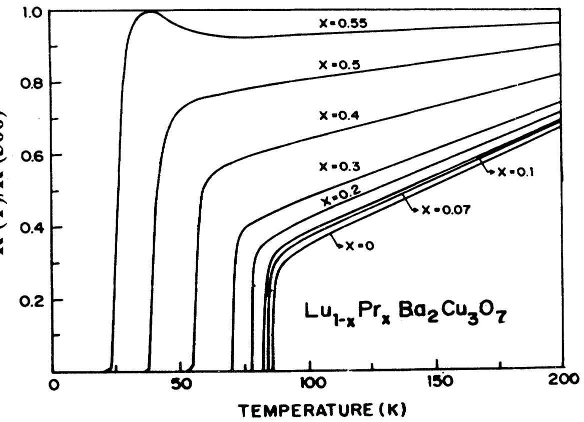

FIG. 3. $r(T)$ as a function of temperature plot of thin films of composition $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for $0.0<x<0.55$.

feature is that T_c varies rather weakly with Pr concentration in samples for $x \le 0.2$; films with large concentration of Pr ions, x as large as 0.55, are superconducting ($T_c=23$ K). Figure 4 shows normalized transition temperature $T_c(x)/T_c(x=0)$ in $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, as a function of x. This is compared with the observed behavior for the systems with $R=$Nd and Yb as reported by Xu and Guan.[8]

Superconducting properties of Ca-doped systems $Lu_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$ were studied with the idea of obtaining information about hole localization by Pr ions. We chose low concentrations of Ca ions ($y=0.1$). This is because negligible disordering of oxygen atoms takes place at such low concentrations of Ca ions, for example, as in $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$.[22]

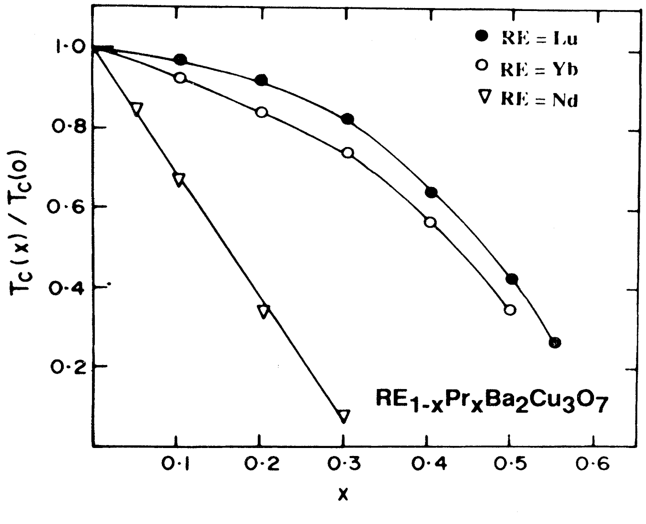

FIG. 4. Normalized superconducting transition temperature $T_c(x)/T_c(0)$ as a function of Pr concentration x, in the systems $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$: $R=$Nd [$T_c(0)=95$ K for bulk], Yb [$T_c(0)=91.5$ K for bulk], and Lu [$T_c(0)=88$ K for thin films]. Data for Nd and Yb systems are from Xu and Guan (Ref. 8). Lu-based thin films have higher T_c for $x>0.2$, e.g.. $Yb_{0.5}Pr_{0.5}$-1:2:3 sample has $T_c=33$ K, while $Lu_{0.5}Pr_{0.5}$-1:2:3 thin film has $T_c=37$ K.

Figure 5 shows $r(T)$ of thin films of a number of Lu-Pr-Ca combinations. All films show metallic behavior down to their respective T_c's. It is instructive to note that T_c ($=64$ K) of $Lu_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ is significantly depressed. This T_c depression, ΔT_c (≈ 22 K) is much larger than ΔT_c (≈ 10 K) observed in Y-1:2:3.[22] Thus whereas T_c is rather insensitive to chemical pressure (T_c's in Lu-1:2:3 and Y-1:2:3 are not very different), ΔT_c is a sensitive function of chemical pressure. Resistivity studies of the films of compositions $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}$ and $Lu_{0.8}Pr_{0.1}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ show that addition of Ca ions depresses T_c. This T_c depression, ΔT_c ($=5$ K), is, however, reduced with respect to the case $x=0$ (no Pr ions). For $x=0.2$, ΔT_c ($=3$ K) is further reduced. Interestingly enough, for $x=0.3$, there is an enhancement of T_c instead of depression.

Attempts to prepare single-phase thin films or bulk sample of $Lu_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$ for $x \ge 0.05$ were not successful. Not only bulk but even the films were multiphase and nonsuperconducting. However, by doping the system simultaneously with Ce and Ca ions, we obtained highly c-axis-oriented [see Fig. 1(d)] and superconducting films of $Lu_{1-x-y}Ce_xCa_yBa_2Cu_3O_{7-\delta}$. The T_c's of all the films are given in Table I. Comparison of XRD spectra of thin films of the composition $Lu_{0.75}Ce_{0.15}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$ and $Lu_{0.70}Ce_{0.15}Ca_{0.15}Ba_2Cu_3O_{7-\delta}$ showed a small increase in c-axis length indicating that at least some of the Ca ions substitute at the Lu site.

DISCUSSION

Partial substitution of Ce ions (which can exist in the trivalent or tetravalent states) resulted in multiphase materials. We would like to mention here that Th ions, which are always tetravalent, give multiphase materials.

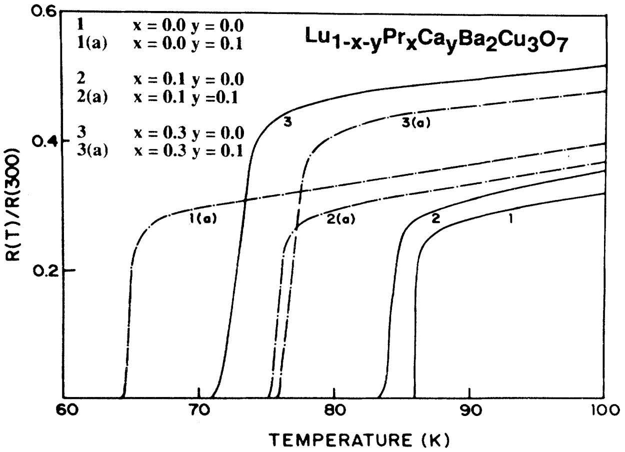

FIG. 5. Plot of $r(T)$ as a function of temperature for thin films of compositions $Lu_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$. Notice that $\Delta T_c=T_c[y=0]-T_c[y]$ is large for $x=0.0$, decreases as x increases and reverses sign for $x=0.3$.

TABLE I. Summary of data on $Lu_{1-x-y}M_xCa_yBa_2Cu_3O_{7-\delta}$ (M=Ce, Pr) and values of J_{ex} at various concentration (x) for M=Pr.

M	x	y	T_c (K)	J_{ex} (MeV)
Ce	0.05	0.05	81	
	0.1	0.1	74	
	0.15	0.05	63	
	0.15	0.10	69	
	0.15	0.15	58	
Pr	0.07		85	26
	0.05	0.05	82	
	0.1		83	38
	0.1	0.1	78	
	0.2		79	44
	0.2	0.1	76	
	0.3		70	51
	0.3	0.1	74	
	0.4		54	61
	0.4	0.1	57	
	0.5		37	65
	0.55		24	68

We also further note that $LuBa_2Cu_3O_{7-\delta}$ is stabilized in the 1:2:3 phase by any other rare earth which is in a well-defined trivalent state, such as Sm, Gd [Refs. 13 and 16]. However, when our Ce samples are simultaneously doped with Ca ions, they give single-phase materials which is a strong support to the fact that Ce ions are in tetravalent state. Addition of an equal amount of Ca ions (a divalent ion) along with Ce or Th, helps in stabilizing the phase. This clearly implies that a divalent ion is needed to counteract the excess charge due to the tetravalent Ce ions. Further, the ionic radius of Ce^{4+} (0.97 Å) is smaller than that of Lu^{3+} ions (0.98 Å). Therefore, multiphase nature of both bulk and thin films of $Lu_{1-x}Ce_xBa_2Cu_3O_{7-\delta}$, for $x \geq 0.05$, demonstrates that Ce is tetravalent in this system and that formation of thin films in the 1-2-3-phase also depends critically on the "average R radius." Addition of divalent Ca ions help stabilize the phase and restore superconductivity because (i) they are bigger and thus increase the average radius of the ions occupying the R site and (ii) they neutralize the excess positive charge of the Ce ions.

The central point of our discussion to follow is the fact that $LuBa_2Cu_3O_{7-\delta}$ is close to structural (in)stability in both bulk and thin-film forms. In one case, it is just below the stability line and in the other, just above.

As described above, superconducting properties of thin films of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ are independent of x ($0 \leq x \leq 0.6$), $T_c \approx 88$ K. $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ forms in the 1-2-3 phase in bulk as well for $0.1 \leq x < 0.3$ and exhibits high-quality superconducting behavior, see Figs. 1(c) and 2(a), with nearly same T_c as in thin films. This is rather remarkable because, $LuBa_2Cu_3O_{7-\delta}$ does not stabilize in polycrystalline form and $TbBa_2Cu_3O_{7-\delta}$ does not exist.[2,3,11–16,18] From the considerations of structural stability of $LuBa_2Cu_3O_{7-\delta}$, it is clear that Tb ions cannot be in the tetravalent state as the radius of Tb^{+4} (0.88 Å) is smaller than that of trivalent Lu ions for eightfold coordination. Thus our experiments constitute a direct experimental determination of the valence of Tb ions and rule out the possibility of Tb ions being in the tetravalent state, at least in this system. It must be emphasized that the presence of Tb ions in rather large concentration in the system $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ does not affect superconducting behavior of the films. Their superconducting properties (T_c is independent of x and J_c values are high, comparable to those reported for the best Y-1:2:3 films) bear a close similarity with those of $Lu_{1-x}R_xBa_2Cu_3O_{7-\delta}$ (R=rare-earth ion, for instance Y and Sm).[17] These results also provide a strong supporting evidence that Tb ions are trivalent in $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$. This inference is confirmed by x-ray photoemission spectroscopy measurements.[23]

The valence of Pr ions in superconducting cuprates has been a subject of great controversy. Arguments, with supporting experimental evidence, have been advanced in favor of Pr ions being trivalent, mixed valent, and tetravalent in $PrBa_2Cu_3O_{7-\delta}$ and several systems of the type $Pr_{1-x}R_xBa_2Cu_3O_{7-\delta}$. Just as in the case of Tb ions, we argue that Pr ions in $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ have to be essentially trivalent.

As described above, Pr ions stabilize the system $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ in 1-2-3 phase, even if they are present in rather small concentration (x as small as 0.1), both in bulk as well as in thin-film form. This situation is similar to that encountered in the case of $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ system, and unlike that for Ce substitution. As the radius of Pr ions in the tetravalent state (0.96 Å) is smaller, like Ce ions, than that of Lu ions, the lattice cannot be stabilized in the 1:2:3 phase if Pr ions are tetravalent. Further, as the redox potential of Tb ($Tb^{4+}+e^- \rightarrow Tb^{3+}$: $E^0=3.1$ V) is close to that of Pr ($Pr^{4+}+e^- \rightarrow Pr^{3+}$: $E^0=3.2$ V),[24] we suggest that just as terbium, Pr also would be in a trivalent state as both terbium and praseodymium occupy the same lattice site with a similar environment. Although it has been suggested that part of the Pr ions occupy the Ba site in the 1:2:3 structure, a recent report on observation of superconductivity in La-1:2:3 with T_c of 88 K again implies that the valence state of Pr seems to play a crucial role in depressing superconductivity.[25] In this context, our results establish that Pr ions are essentially in trivalent state in $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and the mechanism by which it depresses T_c must be of trivalent origin. At the same time, it has been suggested that some of the substituted Pr ions might enter the Ba site. However, from the neutron-diffraction studies on $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, several authors have shown that nearly all Pr occupies the rare-earth sites. A complete review on this aspect is given by Radousky.[7] We believe a similar behavior of Pr is expected in this system also. The primary mechanism of depression of superconductivity in our material is due to its occupation of the rare-earth site. Moreover the possibility of Pr occupying the Ba site is again challenged by the observation of superconductivity with a T_c of 88 K in $LaBa_2Cu_3O_{7-\delta}$ (Ref. 25) (where La^{3+} is larger than Pr^{3+}), which again implies that such disordering may not be the primary effect in depressing superconductivity for Pr.

Unlike in the $Lu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ system, T_c of the bulk as well as thin-film samples of $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ does vary with x. As shown in Fig. 4, however, T_c does not vary substantially in the films containing low concentration of Pr ions ($x \leq 0.2$). This Pr dependence of T_c is very similar to that observed in $Yb_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ wherein, it should be pointed out, the size of Yb ions is close to that of Lu ions. It must be contrasted with that of the systems $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (R=Nd, Sm, Eu, and Gd) wherein Pr ions depress T_c rather strongly. In Fig. 4, we compare the normalized superconducting transition temperature $T_c(x)/T_c(0)$ of $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (this work) with that of $Yb_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Nd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[8] From these considerations, it follows that the Pr ions suppress T_c via two physically different, but connected, mechanisms in the host lattices having R ions with a large radius (such as Nd^{3+} ions) and the R ions with a relatively smaller radius (such as Yb^{+3} and Lu^{+3} ions). Besides the mechanisms connected with the valence state of Pr ions and their large $4f$ conduction-electron wave-function overlap, some authors have also considered Abrikosov-Gorkov (AG) pair breaking due to the Pr moments as a possible mechanism of T_c suppression. The AG equation is given by[26,27]

$$\ln[T_{c(0)}(x=0)/T_{c(0)}(x)] = \psi[1/2+1/\{2\pi\tau_s T_{c(0)}(x)\}]-\psi(1/2) , \quad (1)$$

where

$$\tau_s^{-1}=(2\pi/K_\beta)n_i N(E_f)J_{\rm ex}^2(g-1)^2 j(j+1) . \quad (2)$$

ψ is the digamma function, $J_{\rm ex}$ is interaction parameter, n_i is the concentration of Pr ions, g and j are, respectively, the Lande g factor and total angular momentum of the Hunds rules ground state of Pr^{+3}. $N(E_f)$ is the density of states at the Fermi level which we take to be $=0.44$ states/eV atom spin following Neumeier *et al.*[28]

Table I gives the values of $J_{\rm ex}$ for various concentrations of Pr. It is clear that the interaction parameter increases as the concentration of Pr increases suggesting that a more complex mechanism is operating.

Soderholm[29] has suggested that for Pr ions to influence superconducting properties of the systems $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, it is essential that their ground state be magnetic and also that there should be significant $4f$ conduction-electron hybridization. Following this line of approach, we propose a simple model to account for the observed behavior of Pr ions in the superconducting cuprate systems:

Pr ions are in a trivalent state, with a significant hybridization of their $4f^2$ electrons with conduction electrons. Whether their crystal-field ground state is magnetic (J=4, M_J=+/−4) or nonmagnetic (J=4, M_J=0) depends upon the unit-cell volume V of the crystal structure of the host matrix. We postulate that in the 1-2-3 lattice, there is a critical cell volume $V_{\rm cr}$ such that the ground state of Pr ions is magnetic for $V > V_{\rm cr}$ and nonmagnetic for $V < V_{\rm cr}$. In $PrBa_2Cu_3O_{7-\delta}$ and also in the host lattices with R=Nd (for example), Pr ions are magnetic as in these cases, $V > V_{\rm cr}$ and, therefore, superconductivity is largely suppressed due to magnetic interaction. On the other hand, $V < V_{\rm cr}$ in the host lattices with R=Yb or Lu. This is the reason why the trend of variation of T_c with the concentration of Pr ions is different in $Lu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ or $Yb_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Nd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as described above.

It is conceivable that the host lattices, which have $V < V_{\rm cr}$ for low concentration x of Pr ions, expand sufficiently and the cell volume V increases with x, so that $V \rightarrow V_{\rm cr}$ and the nature of the ground state of Pr ions changes (nonmagnetic→magnetic) for certain values of x. When this happens, Pr ions suppress T_c more effectively via magnetic interaction. This is what happens in Lu- and Yb-based host lattices for large values of x.

Since Pr ions are trivalent, they cannot annihilate holes; they can only localize holes through the $4f$ conduction-electron hybridization. Introducing divalent Ca ions in place of trivalent Lu ions in $LuBa_2Cu_3O_{7-\delta}$ leads to a significant reduction of T_c due to the generation of extra holes (overdoping) in the matrix. When Ca and Pr ions are introduced simultaneously, two competing processes, namely, generation of extra holes due to the introduction of Ca ions and localization of holes by the Pr ions take place. For low Pr concentration (x=0.1 and 0.2) hole localization is marginal, we observe a decrease in T_c due to overdoping. For higher Pr concentration ($x > 0.2$), where there is considerable hole localization, introduction of Ca ions restores the hole density towards the optimum and there is an increase in T_c. The observations of Neumeier *et al.*[28] can also be explained as above. In samples of $Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$, T_c decreases for x=0.1 and y=0.05 and 0.1. It increases for x=0.15 and low values of y (<0.1) but decreases for y=0.1. For x=0.2 it increases for y=0.1. These observations fit into the overall pattern suggested by our mechanism, since one would expect that Pr would be in magnetic ground state for values of x in the Y-Pr-Ca 1:2:3 system lower than those in the Lu-Pr-Ca system.

There are other high-T_c materials such as $Pb_2Sr_2Ca_{0.5}Pr_{0.5}Cu_3O_{7-\delta}$ ($T_c \approx 60$ K) and $TlSr_2Ca_{0.4}Pr_{0.6}Cu_2O_{7-\delta}$ ($T_c \approx 70$ K) containing Pr ions in fairly high concentration. Their T_c, however, is close to that of their Gd analogs.[30,31] According to our model, Pr ions are trivalent in these materials also, having nonmagnetic crystal-field ground states.

To conclude, our work constitutes a direct experimental determination of valence of Pr and Tb ions in the $Lu_{1-x}M_xBa_2Cu_3O_{7-\delta}$ system and shows that they are trivalent. The main thrust of our argument is based on the sensitivity of the stability of the structure of the parent system $LuBa_2Cu_3O_{7-\delta}$ to the average ionic radius at the Lu site in bulk ceramic samples. Our data on thin films of $Lu_{1-x}Ce_xBe_2Cu_3O_{7-\delta}$ demonstrate that formation of thin films in the 1:2:3 phase also depends critically on the average R radius. As Tb ions are trivalent, their effect on superconductivity is no different from that of other trivalent R ions. Because trivalent Pr ions have somewhat extended $4f$ wave function, they have stronger overlap with conduction electrons. Our results on Ca-doped and Ca-free films of Lu-Pr systems bring out very clearly the effect of releasing additional holes by Ca ions and the localization of holes due to Pr ions. Pr ions depress T_c more effectively if their crystal-field-split ground state is magnetic. Whether the ground state of Pr ions is magnetic or nonmagnetic is related to a critical size of the unit-cell volume of the 1-2-3 structure. If the ground state is nonmagnetic, Pr ions suppress T_c only due to the hole localization. We suggest that similar considerations apply to other high-T_c superconductors containing Pr ions.

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