

## Ce and Tb Substitution for Y in $\text{YBa}_2\text{Cu}_3\text{O}_7$ Thin Films

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The kinetic differences of growth between standard solid-state synthesis and *in situ* growth by laser ablation have allowed the substitution of Ce and Tb for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  for the first time. The effects of Ce and Tb substitution on the material  $T_c$  is discussed within the framework of the existing models for the Pr system. We suggest that localization of the holes by trapping may provide a suitable mechanism to account for the observed properties of the Pr and Ce substituted compounds.

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It has been found that substitution of Y in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound by rare earths does not affect the superconducting properties nor significantly alter  $T_c \sim 92$  K [1,2]. There are three exceptions, Pr, Ce, and Tb, which also have in common the possibility of existing in a tetravalent state. It has been shown that substitution of Y by Pr does not result in superconducting material [3-14] although Pr can be easily incorporated into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  replacing Y without perturbing the orthorhombic structure. For the other two rare earths (RE), Ce and Tb, it has not been possible to obtain a single-phase compound for either partial or complete substitution under standard synthesis conditions [15].

In spite of the considerable amount of work on the characterization of material obtained by Pr substitution, the absence of superconductivity is not yet understood. Chemical substitution results and magnetic susceptibility data [16] suggest that tetravalent Pr may be responsible for the insulator and absence of superconductivity. In contrast, spectroscopic data [10-12] suggest that the Pr ion is trivalent as other RE ions when substituted into the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure. Since Ce and Tb are also readily oxidized to the tetravalent state, it is important to study the effect of their substitution for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  for comparison with Pr.

Previous attempts to synthesize material substituting Y by Ce or Tb using standard solid-state reactions resulted in mixed phases containing  $\text{REBaO}_3$  and  $\text{BaCu}_2$  reflecting the inherent instability of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [15]. Aware that Ce does not substitute for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , we noted that while typical solid-state synthesis conditions require temperatures in the range of  $950^\circ\text{C}$ , the *in situ* growth by laser ablation can take place in the range  $650$ – $750^\circ\text{C}$ . This temperature difference may lead to considerably lower diffusivities and, thus, substantially different synthesis conditions. A rough estimate, made from intermetallic oxide data [17], suggests that a  $10^2$  to  $10^3$  change in atomic diffusivity is associated with a  $200$ – $300^\circ\text{C}$  temperature difference. These thoughts suggest that at the lower deposition temperatures of the *in situ* process, the substituted phase might have sufficiently long-lived metastability to allow its synthesis.

In this paper we report methods for preparing single-phase material with partial Ce or Tb substitution and dis-

cuss their superconducting properties in light of the Pr results. We suggest hole trapping as a possible mechanism, providing one consistent explanation for the observed properties of the Pr and Ce substituted compounds.

The thin films were deposited by ablating a bulk ceramic target of the appropriate composition of  $\text{Y}_{1-x}\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  or  $\text{Y}_{1-x}\text{Tb}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  using the 248-nm line of a Lambda Physik EMG 202 operating with KrF focused onto a  $3.0 \times 1.0\text{-mm}^2$  spot. The target materials were prepared by mixing stoichiometric amounts of the oxides of Y, Ce, Tb, Cu, and  $\text{BaO}_2$  firing at  $925^\circ\text{C}$  for 12 h and repeating this process 3 times. Uniform coverage of the substrate was assured by rastering the laser beam over the target with a uniform photon fluence of approximately  $1.7 \text{ J/cm}^2$ . The films of  $5000$ – $8000\text{-\AA}$  thickness were deposited on both polished  $\text{MgO}$  and  $\text{LaAlO}_3$  single-crystal substrates at a temperature of  $730^\circ\text{C}$  in an oxygen atmosphere of 200 mT and allowed to cool to room temperature at ambient pressure of  $\text{O}_2$ .

Rutherford backscattering (RBS) measured stoichiometry of  $500\text{-\AA}$  films on Si substrates with the exception of the Ce/Ba ratio which did not yield resolvable peaks due to the small difference of atomic number. Independent confirmation of the RBS results and the Ce/Ba ratio was obtained using inductively coupled plasma spectroscopy. The structure and phase purity of the films were checked by standard x-ray diffraction. The superconducting transition was measured resistively and by ac susceptibility.

The first of three x-ray-diffraction spectra in Fig. 1 is the profile of a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin film while the second is a ceramic target with a small amount of Ce substitution obtained by standard methods. One can clearly see the powder lines at  $28.6^\circ$  and  $29.3^\circ$  corresponding to the  $\text{BaCeO}_3$  and  $\text{BaCuO}_2$  phases. Large changes are clearly evident in the third spectra obtained from a film deposited using the same ceramic target of Fig. 1. The impurity lines have disappeared, leaving the (001) reflections as the only prominent features excepting a small hint of the (013) reflection at  $32.3^\circ$ . The x-ray results, in conjunction with duplication of the target stoichiometry in the film, clearly demonstrate that we have been successful in synthesizing  $\text{Y}_{1-x}\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  for  $0.05 < x < 0.3$ . The *c*-axis lattice constant was found to be independent of dopant concentration with  $c = 11.69 \text{ \AA}$  for Ce and *c*

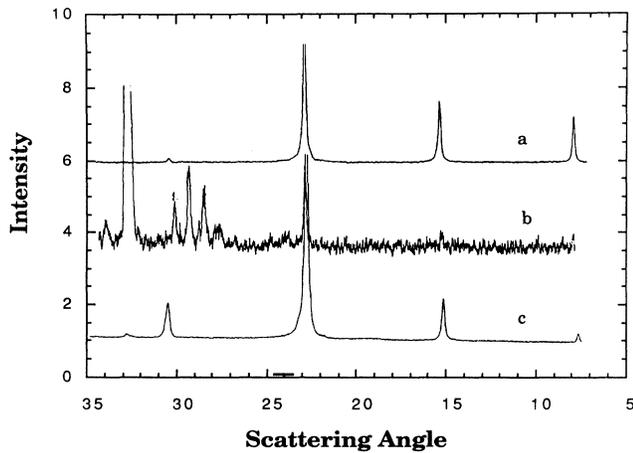


FIG. 1. X-ray profiles of, curve *a*, a thin film of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  deposited on MgO; *b*, a ceramic target of  $\text{Y}_{0.95}\text{Ce}_{0.05}\text{Ba}_2\text{Cu}_3\text{O}_7$ ; and *c*, a thin film of  $\text{Y}_{0.95}\text{Ce}_{0.05}\text{Ba}_2\text{Cu}_3\text{O}_7$  deposited on MgO.

$=11.70 \text{ \AA}$  for Tb, which compares well with  $c=11.68 \text{ \AA}$  for pure material and  $c=11.69 \text{ \AA}$  for Pr substitution. The appearance of mixed phase material onsets rather suddenly; while a relatively clean x-ray profile is observed for  $x=0.3$ , the data for  $x=0.4$  show a very strong reflection at  $28.6^\circ$  indicating the presence of a large amount of the undesired  $\text{BaCeO}_3$ .

The transport data presented in Fig. 2 show that Tb substitution has relatively little or no effect upon  $T_c$ . Although Ce substitution, as shown in Fig. 2, significantly depresses  $T_c$ , the transition widths are comparable to those measured in the Pr system [4] consistent with the absence of any substantial quantities of a second phase as also shown by x-ray data. These transport results agreed with  $T_c$  obtained by an ac inductance measurement. Films deposited from targets with  $x > 0.3$  for Ce or  $x > 0.75$  for Tb showed multiple phases by x-ray analysis with the resistive transition greatly broadened and extremely sensitive to the amount of measuring current.

The transition temperatures of films with Ce, Tb, and Pr substitution for Y are displayed in Fig. 3. The data of the Pr films are similar to previously published studies of ceramic material. While the similarity of Ce and Pr is striking, the differences with Tb substitution are obvious. Both Ce and Pr substituted films show an initially gradual decrease in  $T_c$  with increasing rare-earth concentration until about  $x=0.20$  where a more rapid falloff is observed. In sharp contrast, the Tb substitution has no appreciable effect on the transition temperature of the films. Data with Ce concentrations greater than  $x=0.3$  were not included because of their multiphase nature, apparently above the solubility limit for this experiment. It is likely that the limit can be extended by reoptimizing deposition conditions at higher Ce concentrations.

Broadly speaking, the depression of  $T_c$  with Pr doping of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has been attributed to four sources: (1)

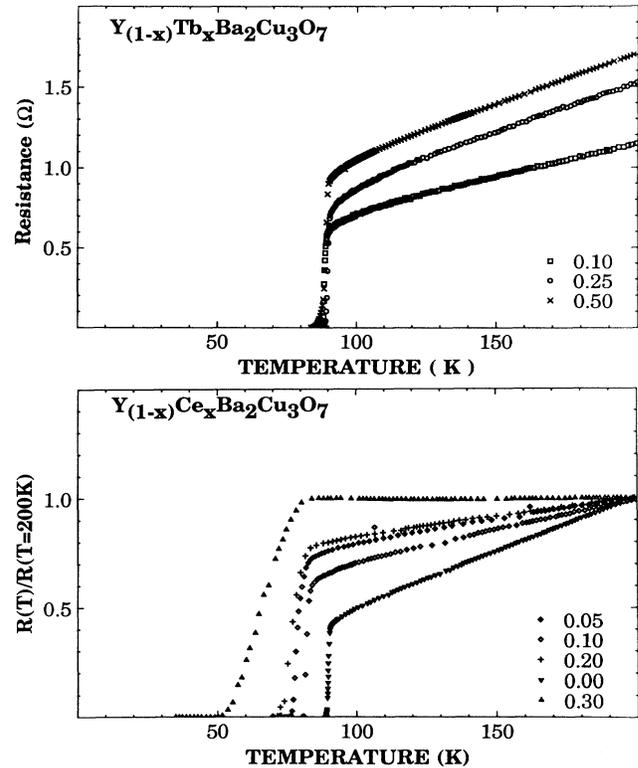


FIG. 2. Resistive data from films with Tb or Ce substituted for Y.

The magnetic Pr ion acts as a pair breaker; (2) a +4 ion rather than a +3 rare-earth ion leads to hole filling in the conduction band; (3) the extended  $f$  shell of Pr hybridizes strongly with the O  $2p$  level in the  $\text{CuO}_2$  plane; and finally (4) the Pr ion acts in some fashion to localize the formerly mobile holes. None of these proposed explana-

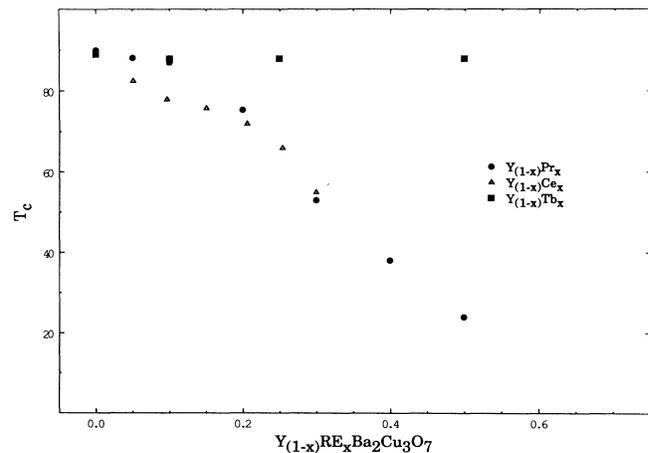


FIG. 3. Plot of the transition temperature determined by  $R=0$  vs the amount of substitution of Y by Ce, Pr, and Tb.

tions have been totally without objections.

It is well known that  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is highly sensitive to the density of holes in the  $\text{CuO}_2$  planes with hole density a function of the oxygen stoichiometry [18]. Therefore, if one assumes that the Pr ion substitutes as a +4 ion rather than +3, as the majority of the lanthanide series, the extra electron donated to the conduction band might backfill a hole state generated by the oxygen thereby depressing  $T_c$ . The most convincing evidence for this line of reasoning comes from the experiments of Neumeier *et al.* [6]. Their data show that although the effect of Pr is to depress  $T_c$ , further replacement of Y by Ca partially restores  $T_c$ . The increase of  $T_c$  with the Ca substitution is then taken as indicative of compensation of the +4 ion by the +2 ion [5]. The experimental data for  $T_c$ , including the recent work on Y-free films [15], are well described by a simple equation with Pr and Ca concentrations as the independent variables:

$$T_c(x,y) = T_{c0} - A(\alpha - \beta x + y)^2 - Bx, \quad (1)$$

where  $x$  and  $y$  represent the Pr and Ca concentrations, respectively. The linear term in the Pr concentration with the coefficient  $B$  was rationalized as due to the pair-breaking depression of  $T_c$  as well as accounting for the incomplete restoration of  $T_c$  with Ca compensation. Indeed, this picture has intuitive appeal as a conceptually simple way of explaining the dependence of  $T_c$  on Pr and Ca concentration as well as the magnetic data suggestive of a Pr moment of  $2.5\mu_B$ , close to the  $2.4\mu_B$  of the +4 ion [6]. However, the presence of tetravalent Pr is inconsistent with available spectroscopic data. Since neither x-ray-absorption near-edge structure (XANES) [10] nor x-ray photoemission spectroscopy (XPS) [11,12] measurements have been able to detect the presence of the +4 Pr ion, it was concluded for spectroscopic experiments that Pr is in a +3 state instead.

The data presented in Fig. 3 show that the change in  $T_c$  with increasing Ce concentration is nearly identical to the data for Pr. This result may at first appear to confirm the argument of hole backfilling by a +4 ion. In fact, the close similarity would require nearly identical values of the parameters used in the phenomenological model for an accurate representation of the data. However, in the case of Ce, the +4 ion is a closed shell precluding the possibility of any pair-breaking interaction due to coupling to dopant spins. This then implies that a more likely explanation of the linear term in the phenomenological model of Neumeier *et al.* [6] for Pr is of nonmagnetic origin as well.

The hybridization of the Pr 4*f* shell with the O 2*p* has also been proposed as responsible for the loss of superconductivity and the metal-insulator transition. The band hybridization effects are supported by several spectroscopy experiments as well as by high-pressure transport data [6,11,13]. That is, for the early rare earths (Ce and Pr) the overlap is sufficient to significantly perturb the band

structure of the  $\text{CuO}_2$  plane, quenching superconductivity and metallic conduction. In contrast, hybridization becomes negligible for the higher- $Z$  rare earths due to the lanthanide contraction. However, as before, there are issues which leave some question as to the internal consistency of this argument. If this were the explanation then the data of Neumeier *et al.* [6] would be difficult to explain. It is surprising that the band structure may be perturbed in a fashion such that Ca accidentally compensates the perturbation with the Ca/Pr ratio very nearly equal to 1 for all Pr concentrations. Our data are also difficult to rationalize within this picture. Why should Nd not show any hint of the effect as a neighbor to Pr and yet Ce behaves identically to Pr? Unfortunately, it appears that the body of experimental data existing for Pr cannot be explained within a single model.

An alternative may be a model in which the Pr provides a channel for effectively localizing the carriers. Localizing carriers in this low-mobility, narrow-band system might be exceptionally easy in light of the very strong electron-phonon coupling which is near the limit for self-trapping [18]. As shown by Emin and Holstein [19] in such a system the barrier for self-trapping is lowered or vanishes in the presence of very small perturbations. Since Ce and Pr are relatively stable as a +4 ion, evidenced by their common occurrence in mixed valence solids, when substituted as +3 ions in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure the hole state associated with the +4 valence is likely to be positioned near the Fermi level within the range of the conduction band. In addition, while the spatial extent of  $f$  electrons in  $\text{REBa}_2\text{Cu}_3\text{O}_7$  is relatively small, the lighter rare earths, such as Ce and Pr, will have a larger radial extent increasing hybridization with the conduction band in the  $\text{CuO}_2$  plane. Thus, substitution of Pr or Ce may strongly influence the nature of the carriers in the  $\text{CuO}_2$  plane, perhaps resulting in small polaron formation. This polaron in the  $\text{CuO}_2$  plane, pinned in the vicinity of the perturbation that led to its formation (i.e., the Ce or Pr ion), effectively removes a hole from participation in the conduction band lowering  $T_c$ .

The overall effect of a hole trapped in the vicinity of the rare-earth ion may result in behaviors that can be associated with a tetravalent ion in some cases and trivalent in others depending upon the experimental technique. For instance, the measured magnetic moment of the ion, which indicates tetravalent behavior, reflects that the spin of the hole must be opposed to the spin of the rare-earth's  $f$  shell in order to hybridize, thereby reducing the effective moment of the ion. In contrast, if the hole is trapped or localized in the plane rather than on the ion, high-energy spectroscopies such as XANES and XPS will reflect those features associated with a +3 ion as observed. The chemical substitution data [15] can also be understood within the hole localization model since Ca provides additional holes compensating for those trapped in the neighborhood of the Pr or Ce atom. One would

then expect that Ca compensates the perturbation with a Ca/Pr ratio nearly equal to 1. Similarly, the spin trapped in the plane would also provide a magnetic pair breaker in strong contact with the superfluid both for Pr as well as for nonmagnetic Ce. Consequently, the phenomenological equation used by Neumeier *et al.* [6] to describe Pr substitution should also provide a suitable description of Ce substitution in agreement with the data of Fig. 3.

This type of trapping as a mechanism to quench superconductivity could be plausible in materials such as Pr, Ce, and Tb, commonly found in a tetravalent state. Then, the attractive potential felt by the hole depends critically on the proximity in energy of the +4 ion state. The +4 state then furnishes a nearby virtual state that can be used to locally lower the energy of the hole. In the case of Tb, the lanthanide contraction is sufficient to reduce the overlap such that the perturbation is too weak to localize a hole. The bound-hole picture then provides an explanation which brings all the experimental data into one consistent picture.

We have shown that *in situ* laser deposition can be used as a synthesis tool to grow single-phase materials not possible with standard methods. This offers unique possibilities in terms of exploring structure-property relationships in these complicated systems. Here we have shown that substitution of Ce for Y in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is analogous to the well studied Pr substitution. The new example of an insulating rather than superconducting lanthanide substitution led us to propose a model in which the charge-carrying holes are trapped in the vicinity of the rare-earth ion. The attractive potential may be a result

of the small energy difference between the trivalent and tetravalent states.

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