ScienceAsia 29 (2003): **31-35**

Structural Changes and Suppression of Superconductivity in Two $Re_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's (Gd, Dy) Due to Pr Doping

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Received 8 May 2002
Accepted 22 Jul 2002

ABSTRACT The structural changes and the suppression of superconductivity in the Gd- and Dy-"123" HTSC's due to the equal substitution of Pr and Ca were studied. The onset temperatures (T_c's) of the codoped $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ and $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's were measured by AC susceptibility measurements. The T_c's and rates of decrease of dT_c/dx due to Pr substitution for both series exhibited rare earth size effects. It was found that the lattice distortion defined D = (b-a)/(b+a), where a and b are the lattice parameters in the basal plane, decreases systematically as the doping is increased. A mixed (d+s)-wave symmetry model is used to explain the behaviors of both the T_c's and rates of decrease of dT_c/dx as Pr^{4+} ions are doped into the two "123" HTSC's.

KEYWORDS: RE-123 HTSC's, AC susceptibility, Pr and Ca doping, rates of suppression, rare earth size effect.

INTRODUCTION

It is now well established that the onset temperatures (T_c's) of the rare earth-"123" high temperature superconductor (the $REBa_2Cu_3O_{7-}\delta$HTSC),[1,2] exhibit a rare earth (RE) size effect. When the hole concentration (or oxygen content) is kept constant, the T_c's exhibit a dependence on the RE size, *ie*, $T_{c,larger\ ion(L)} > T_{c,smaller\ ion(S)}$. Another RE size effect has been seen in the rates of suppression of the T_c's of these HTSC's due to nonmagnetic Zn^{2+} and magnetic Ni^{2+} substitution in the Cu(2) sites in the CuO_2 layer[3-5]. Tung, *et al*.[6] have looked at the codoping of Pr and Ca into six RE based "123" HTSC's (RE = Er, Dy, Gd, Eu, Sm and Nd) and have observed a RE size effect in the rates of suppression due to the substitution, *ie*, $dT_c/dx\big|_L > dT_c/dx\big|_S$. The codoping was done in order to make the substitution an isovalent one. Changes in the hole concentrations in the HTSC's will also lead to changes in the T_c's. Andersson *et al*.[7] found that the depression of T_c due to the cosubstitution of Ca and Pr is linear with the concentration, in contrast to the accelerated decrease when only Pr is substituted.

In this paper, we wish to report on our study of the structural changes and suppression of superconductivity in the $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ and $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's due to the cosubstitution of Ca^{2+} and Pr^{4+} ions into these HTSC's. The T_c's are determined from AC susceptibility measurments. The copper valencies and lattice parameters of the HTSC's are carefully monitored. The reasons for monitoring these two properties are firstly, it is well known that the T_c's of the individual HTSC depend on the hole concentration in the 2D CuO_2 layer and secondly, the T_c's of the homologous series, $REBa_2Cu_3O_7$ and the doped "123" homologous series $RE_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$[8] vary inversely with the size of the rare earth ions, and the orthorhombic distortions in these HTSC series are affected by the size of the of the rare earth ions. Lin, *et al*[1] and Williams and Tallon[2] found that the distortion in the "RE-123" series decreased as the size of the RE ions increased. Similar decreases in the distortions were seen by Gan, Chen and Cheng,[8] in $RE_{0.9}Ca_{0.1}Ba_2Cu_3O_{7-\delta}$. Eab and Tang[9] showed that the T_c's of the $REBa_2Cu_4O_8$ HTSC's increased as the square of the orthorhombic distortion. Lin, *et al*,[1] and Gan, Chen and Cheng,[8] said that the lattice compression caused by the insertion of larger RE ions induces strains into the ceramic.

Lin, *et al*, hypothesized that the strain induces a charge redistribution between the charge reservoir layer and the CuO_2 layer. The strain (which could also arise from the orthorhombic distortion) can induce a

modification of the pairing interaction responsible for the Copper pairing in the HTSC's. Evidence for this is seen in the shape of the order parameter, which is that of a four leaf clover with one pair of leaves larger than the pair perpendicular to them.[10] The modification would lead to the (**s**+**d**)-model of super-conductivity proposed by Beal-Monod and Maki.[11] In this paper, we will attempt to explain our observed dependence of the T_c's and of the rates of decrease, dT_c/dx, due to Pr substitution into the two HTSC's in terms of a (**s**+**d**)-wave theory of superconductivity developed by one of the present authors (IMT).[12] In two recent papers, Tang and coworkers[13, 14] have shown that the RE size effects in the rates of depression due to substitutions of magnetic Ni^{2+} ions and of non magnetic Zn^{2+} ions into the "RE-123" HTSC's could be explained within the framework of this theory.

Materials and Methods

The HTSC's were prepared by the standard ceramic method. Stoichiometric amounts of Dy_2O_3, Gd_2O_3, Pr_6O_{11}, $CaCO_3$, $BaCO_3$ and CuO were carefully weighed and mixed to obtain the compounds, $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ and $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ (with x = 0.0, 0.025, 0.05, 0.075 and 0.1). The mixed powders were calcinate at 930°C for 24 hrs to achieve the solid state reaction. The calcinated lumps were reground and pressed into pellets of about 9 mm in diameter under an uniaxial pressure of 2000 psi. The pellets were then sintered for another 24 hours at 940°C in a crucible furnace. Shortly before the end of sintering step, flowing oxygen gas was introduced in the chamber. The pellets were cooled to room temperature at a cooling rate of 1° per minute in a flowing O_2 atmosphere. The pellets were subjected to a second sintering under the same conditions.

The XRD patterns of the specimens of both series were obtained. In Fig 1 and 2, we show the XRD patterns of the $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ and $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ ceramics for x up to 0.30. Blow ups of the patterns for x = 0.10, 0.20 and 0.30 of both series show the formation of an impurity phase (as evident by additional peaks at $2\theta \approx 28°$) and so we have not carried out further measurements on these specimens. In Table I, we list the values of the lattice parameters determined from the XRD patterns. As can be seen, the **c**-axes of both ceramics increased in a monotonic fashion as Ca^{2+} and Pr^{4+} ions were substituted for Dy. More importantly, we found that the lattice distortion D (=(**b**-**a**)/(**b**+**a**)) decreased monotonically as the impurity ions were substituted. The lattice distortions is larger in the "Dy-123" series than they are in the "Gd-123" series. The reason for the lattice distortion being smaller in the ceramics having the larger rare earth ion is that larger

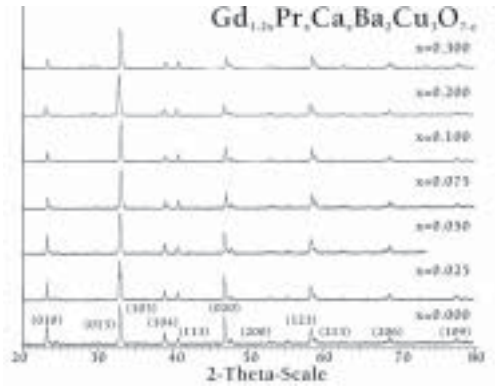

Fig 1. XRD Patterns For the $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_7$d HTSC's (x = 0.0 - 0.3). Blowups of the patterns for x = 0.1, 0.2 and 0.3 show impurity peaks around 2q = 28°.

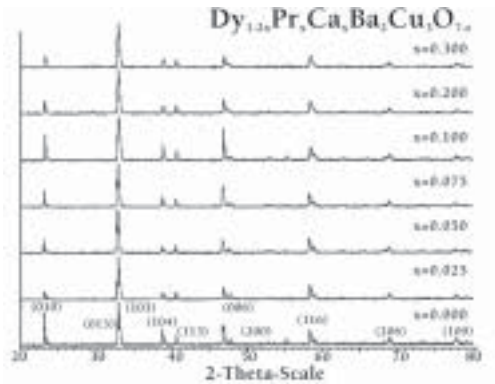

Fig 2. XRD Patterns For the $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's (x = 0.0 - 0.3). As with Fig 1, blowups of the patterns for x = 0.1, 0.2 and 0.3 show impurity peaks around 2θ = 28°.

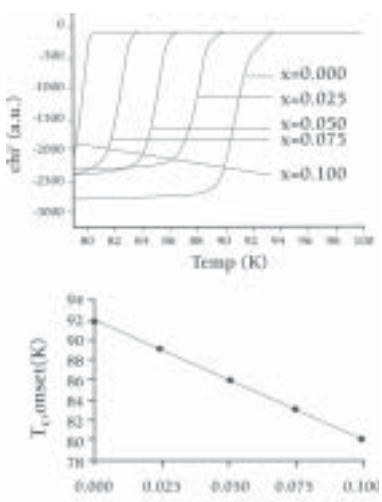

Fig 3. Real Part of the AC susceptibility (c') of $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's (x = 0.0, 0.025, 0.05, 0.075 and 0.1) and the dependence of T_c on concentration of Pr (and Ca). The transition temperature, T_c, is defined as temperature at which diamagnetism sets in.

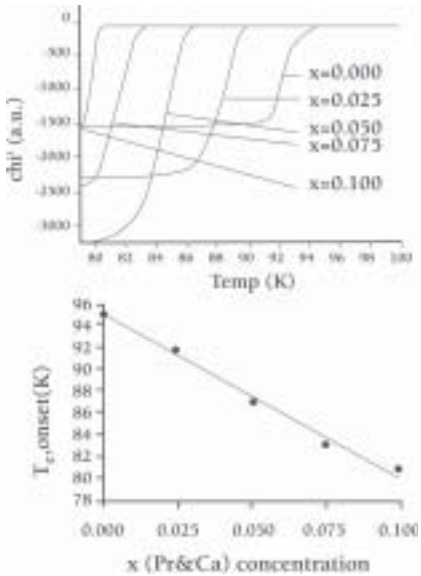

Fig 4. Real Part of the AC susceptibility (c') of $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's (x = 0.0, 0.025, 0.05, 0.075 and 0.1) and the dependence of T_c on concentration of Pr (and Ca).As with Fig 3, the transition temperature T_c is defined as temperature at which diamagnetism sets in.

Table 1. Properties of $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ and $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ Lattice parameters, Orthorhombicity, Copper valency and Transition temperature.

$Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$						
X	a(Å)	b(Å)	c(Å)	D=(b-a)/(b+a)	Copper valency	T_c (K)
0.000	3.8144	3.8819	11.5708	0.0087	2.25	91.9
0.025	3.8150	3.8807	11.5711	0.0085	2.23	89.3
0.050	3.8163	3.8795	11.5724	0.0082	2.25	85.9
0.075	3.8172	3.8788	11.5729	0.0080	2.25	83.2
0.100	3.8179	3.8780	11.5738	0.0078	2.23	80.2
0.200	3.8187	3.8763	11.5742	0.0074	2.22	*
0.300	3.8201	3.8749	11.5753	0.0071	2.25	*

$Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$						
X	a(Å)	b(Å)	c(Å)	D=(b-a)/(b+a)	Copper valency	T_c (K)
0.000	3.8307	3.8830	11.6613	0.0068	2.23	94.7
0.025	3.8319	3.8825	11.6626	0.0065	2.25	91.4
0.050	3.8327	3.8820	11.6637	0.0064	2.23	86.5
0.075	3.8333	3.8812	11.6651	0.0062	2.22	82.3
0.100	3.8345	3.8807	11.6659	0.0060	2.24	80.1
0.200	3.8357	3.8798	11.6668	0.0057	2.25	*
0.300	3.8361	3.8784	11.6681	0.0055	2.23	*

RE ions retard the collapse of one dimensional CuO chains toward each other as the oxygen ions are removed from the O^{2-} along the **a** axis in the single CuO plane lying between the BaO plane in the pervoskite structure. This also explains why the distortion decreases as Pr^{4+} and Ca^{2+} ions are incorporated. Replacement of some of the smaller Gd^{3+} or Dy^{3+} ions by larger Pr^{2+} ions would further hinder the collapse of the CuO chains toward each other.

The standard iodometric method was used to determine the copper valencies. The hole concentration in the HTSC's must be carefully monitored since the T_c's of the HTSC's depend on this parameter. Zhang and Sato[15] reported that the transition temperatures depend in a parabolic manner on the hole concentration in the CuO_2 layers present in the HTSC's. The values of the hole concentration in the different specimens are listed in Table I. In this study, the T_c's of the HTSC's are defined as the temperature at which diamagnetism first appears in the specimens. This is done by looking for the onset temperature in the real part of the AC susceptibility. The AC susceptibility measurements were done using an AC field of 20 Oe at 1500 Hz. and in zero DC field. In Fig 3, we show the real part of the ac susceptibilities of the $Dy_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-}\delta$ HTSC's (x = 0.0, 0.025, 0.050, 0.75 and 0.1). Also in Fig 3, the dependence of the onset temperatures on the concentrations of Pr and Ca is shown. The same information for the $Gd_{1-2x}Pr_xCa_xBa_2Cu_3O_{7-\delta}$ HTSC's is shown on Fig 4. The values of the transition temperature are listed in Table 1.

Discussion

We first note that the T_c of the undoped host "Gd-123" HTSC (94.7 K) is higher than that of the undoped "Dy-123" HTSC (91.9 K). These results are in keeping with those of Lin, et al.[1] and Williams and Tallon.[2] In a study based on a phenomenological Ginzburg Landau approach, Tang, et al.[16] established that the correlation between the T_c and the size of the rare earth was a correlation between the T_c and the square of the orthorhombic distortion D. The rare earth ion size effect arises because the distortion is correlated to the size of the rare earth ion. The observed T_c's (onset temperatures) of the host "Gd-123" (94.6 K) and "Dy-123" (92 K) HTSC's are consistent with "rare earth ion size effect" as are the rates of suppression of superconductivity, -1.53 K/atm.% for the Gd HTSC and -1.18 K/atm. % for the Dy HTSC.

To understand how the rare earth ion size affects the rate of suppression of supercon-ductivity in the "RE-123" HTSC, we must first point out that the suppression of the T_c could be due to three mechanisms, hole depletion, electron localization arising from increased dis-ordering resulting from the substitution,

and pair breaking by the Pr magnetic moment. The co-substitution of Pr and Ca should eliminate the hole depletion resulting from the replacement of trivalent rare earth ions by Pr^{4+} ions. Looking at the Cu valencies of the two "RE-123" series, we see that the valencies for the doped "Gd-123" HTSC's are in the range 2.23-2.25 and those for the doped "Dy-123" are in the range 2.22-2.25. The near constant valencies of the two HTSC series would be a good reason to eliminate the hole depletion as a possible cause for the systemmatic decreases in the T_c's of the two "RE-123" HTSC's. The systematic changes in **c**-axis length and in the orthorhombic distortion as the substitution levels increase dose not point to an increased (random) disordering of the crystal structure. This leaves us with pair breaking as the most likely mechanism for the suppression of superconductivity when equal amounts of Pr^{4+} and Ca^{2+} ions replace the trivalent rare earth ions in the "RE-123" HTSC's.

The mixed (***d*** + ***s***)-wave symmetry model was introduced to explain the presence of a ***s***-wave component in the order parameter of a "Y-123" HTSC. Kouznetsov, *et al*,[10] obtained evidence that the shape of the order parameter is that of a four leaf clover with one pair of leaves larger than the pair perpendicular to them. In a pure ***d***-wave HTSC, the four leaves are of the same size. Since this new feature has only been seen in orthorhombic distorted HTSC's, it was conjectured that the ***s***-wave component is in some way connected to the distortion. Tang and coworkers[12-14] and others[17] have assumed that the orthorhombic distortion induces a modification of the pairing interaction, so that the new interaction would be invariant under the new set of operations for which the orthorhombic distorted crystal remains invariant. Such an interaction could be

$$V_{pairing}(\mathbf{k},\mathbf{k'}) = \eta(\phi)V_d\eta(\phi') + \beta(D)\{ V_{ani} (\eta(\phi) + \eta(\phi')) + V_{iso} \} - \mu \qquad (1)$$

where V_d is the strength of the interaction for the ***d***-wave pairing; V_{ani} and V_{iso}, the strengths of the induced non separable anisotropic interaction and isotropic interaction; $\beta(D)$, a parameter which depends on the orthorhombicity and which becomes zero in the absence of the distortion; $\eta(\phi)$, a basis function for a representation of the crystal symmetry group and μ is the Coulomb repulsion term.

Following the steps of *refs*. 12-14, we arrive at the following set of coupled equations for the two components of the order parameter at $T = T_c$;

$$\{1-\beta(D)\lambda'_{iso}\, 2\pi T_c \sum \tfrac{1}{\omega_n+x\alpha_s}\}\, \Delta_s - \beta(D)\lambda'_{ani}\, 2\pi T_c \sum \tfrac{1}{\omega_n+x\alpha_d}\Delta_d = 0 \qquad (2a)$$

and

$$-\beta(D)\,\lambda'_{ani}\, 2\pi T_c \sum \tfrac{1}{\omega_n+x\alpha_s}\Delta_s + \{1 - \lambda'_d\, 2\pi T_c \sum \tfrac{1}{\omega_n+x\alpha_d}\}\, \Delta_d = 0 \qquad (2b)$$

where ω_n is the Matsubara frequency and is equal to $\pi T_c(2n + 1)$; $\lambda_i = N(0)V_i/(1 + \beta(D)V_{iso})$ with i = d, iso or ani; x, the mole fraction of the Pr ions; $\alpha_s = 1/\tau_S$ with τ_S being the life time due to the spin flip scattering by the Pr ion; and $\alpha_d = 1/\tau_N + 1/\tau_S$ with τ_N being the life time of the carriers due to normal scattering by the Pr ions. For spin flip scattering by rare earth ions,

$$1/\tau_S = (\pi^2/4)N(0)\Im^2(g-1)^2J(J+1) \qquad (3)$$

where $\Im$ is the exchange interaction; g, the Lande g factor for the Pr ion and J is the total angular momentum.

T_c is the temperature at which non zero values of the two component first become possible. Differentiating the resulting expression with respect to x and then setting x equal to zero, we obtain the following expression for the rate of suppression

$$\frac{dT_c}{dx} = \frac{\pi}{4} C \{ \lambda_d \alpha_d - \beta(D)B \} \qquad (4)$$

where

$$B = \{(\lambda_{iso}\lambda_d - \beta(D)\lambda_{ani}^2)X_{co}(\alpha_s + \alpha_d) - \lambda_{iso} \alpha_s \} \qquad (5a)$$

and

$$C^{-1} = \{ \lambda_d + \beta(D)[\lambda_{iso} - 2(\lambda_{iso}\lambda_d - \beta(D) \lambda_{ani}^2)X_{co}] \} \qquad (5b)$$

with

$$X_{co} = 2\pi T_{co} \sum \frac{1}{|\omega n|} \cdot \qquad (5c)$$

For the RE size effect to hold, *ie*, $dT_c/dx\,|_L > dT_c/dx\,|_S$, we need

$$\frac{1 - \beta(D_L)B^*}{1 +\beta(D_L)C^*} > \frac{1 - \beta(D_S)B^*}{1 + \beta(D_S)C^*} \cdot \qquad (6)$$

if we assume that the only difference between two "RE-123" HTSC's is their orthorhombicity. In the above, $B^* = B/\lambda_d\alpha_d$ and C^* are the terms of C^{-1} which are proportional to $\beta(D)$ divided by λ_d. The inequality is satisfied if $\beta(D_S) > \beta(D_L)$. Looking at the values of the orthorhombicities of the two host superconductors, we find the values of the orthorhombicities for the "RE-123" having the larger ion size has the smaller value of the orthorhombicity, 0.0074 for the "Gd-123" and 0.0151 for the "Dy-123" (noting again that Gd^{3+} radii > Dy^{3+} radii). Summarizing, we find the responses of the "RE-123" HTSC's to different levels of doping all exhibit a RE size effect, $dT_c/dx\,|_L > dT_c/dx\,|_S$, and that the RE size effect is accounted for by a mixed (***d*** + ***s***)-wave symmetry model.

ACKNOWLEDGEMENTS

Two of the authors (NC&PW) would like to thank the Thailand Research Fund for granting them the Royal Golden Jubilee PhD Fellowship and the Postgraduate Education Research Program in Chemistry for partial financial support to make this research possible.

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