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Investigation of structure and transport properties of $\text{Gd}_{1-x-z}\text{Pr}_x\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system†

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Abstract

The granular $\text{Gd}_{1-x-z}\text{Pr}_x\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (GdPrCa-123) high-temperature cuprate superconductor samples were prepared and characterized. The electrical resistivity of Pr-free samples show a reduction in T_c with increasing Ca content. For these samples, the $T_c(z)$ curve is nonlinear and a plateau appears at $z \approx 0.05$ – 0.15 . With increasing Ca concentration, the lattice parameter a increases. Moreover, it is observed that the in-plane Cu(2)–O(2) bond distance increases with increasing Ca content. On the other hand, the Cu(2)–O(2)–Cu(2) angle increases and the CuO_2 plane becomes flatter with successive Ca doping, which causes the suppression of superconductivity. The same bond distances in Pr–Ca substituted samples decrease slowly with increasing Ca doping, but increase with increasing Ca concentration after an optimum value. In addition, the electrical resistivity of Pr–Ca-doped samples shows an increase of T_c with Ca doping up to an optimum value, whereafter it begins to decrease. We suggest that the competition of two effects, the number of holes and the flattening of CuO_2 planes by Ca doping, results in a nonlinear decrement in the $T_c(z)$ curve.

1. Introduction

Most of the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R-123) materials are found to be superconducting with a T_c in the 90 K range. R is Y or rare earth ions except Tb, Ce, Pm and Pr. Pr is the only element that can form the 123 phase, but the Pr-123 compound is a semiconductor. Destructive effects of Pr substitution in high-temperature cuprate superconductors have not been well understood. For example, the substitution of Pr for Gd in $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (GdPr-123) shows a lower T_c . This T_c reduction with increasing x does not agree with Abrikosov–Gor'kov (AG) pair breaking theory [1]. In order to further investigate the effects of the Pr ion for these compounds, Ca^{2+} was chosen as the second dopant in GdPr-123.

The substitution of Ca^{2+} for R or other elements in superconductor compounds has provided many interesting results. The superconducting 123-phase has been achieved by substituting Ca for Pr in $\text{Pr}_{0.5}\text{Ca}_{0.5}$ -123 compound, without the presence of Y or any other rare earth element [2]. The increase

of T_c with Ca doping was first shown in $\text{Y}_{1-x-y}\text{Pr}_x\text{Ca}_y$ -123 [3]. In compounds with oxygen deficiency, the substitution of Ca for R increases T_c [4–6], but in samples which are annealed in oxygen it decreases T_c [7–13]. In the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_6$ system partial Ca doping for Y causes the system to become a superconductor [6]. In $\text{Pr}_{0.5}\text{Ca}_{0.5}$ -123 [2], $\text{Y}_{1-x-y}\text{Pr}_x\text{Ca}_y$ -123 [3, 14] and $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$ ($\delta \approx 0$) [15], the reason for the increasing T_c is the creation of mobile holes in CuO_2 planes due to Ca doping in the system. In $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ca}_x\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ [16], the reason for the recovery of superconductivity is the ion-size effect at the Ba site: some Ca ions locate on the Y site due to their similar ionic radii, and some of the Pr ions then begin to move toward the Ba site. The Pr ion at the Ba site would have much less effect on T_c , because at the Ba site the Pr–O bond length is greater than that at the Y site. Therefore, the interaction between the Pr and the O 2p magnetic moments decreases, resulting in the increase in T_c [16]. On the other hand, for the cases of $\text{Er}_{1-y}\text{Ca}_y$ -123 [7], $\text{Y}_{1-y}\text{Ca}_y$ -123 [14], $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ca}_x\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ [16] and, fully oxygenated, $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{0.8}, \text{Sr}_{0.2})_2\text{Cu}_3\text{O}_z$ systems [10, 12], the substitution of Ca decreases T_c . These observations have

† Part of this paper was presented at the MSM-99 conference [25].

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been explained on the basis of effects such as over-doping, the dilution of the magnetic interaction, the pair breaking effect by Ca doping and the excess Ca acting as impurity phase. Ca doping has been the basis of more studies which reveal many interesting results [17–23].

It is observed that, besides hole doping, Ca substitution results in interesting structural changes in superconducting systems [6, 9, 16], such as: (i) flattening of the CuO_2 planes, (ii) a contraction of the in-plane Cu–O bond distance and (iii) a decrease in the Cu–Cu bond distance between planes.

In this paper we will report our experimental observations on the structural and electrical properties for the case of Ca doping in GdPr-123 compounds.

2. Experiment

$\text{Gd}_{1-x-z}\text{Pr}_x\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples with $0.0 \leq x \leq 0.3$ and $0.0 \leq z \leq 0.35$ were prepared by a conventional solid-state reaction technique. Stoichiometric amounts of 99.9% purity compounds, Gd_2O_3 , Pr_6O_{11} , CaCO_3 , BaCO_3 and CuO , were thoroughly mixed, ground and calcined in air at 850°C for 24 h in an alumina crucible. Calcination was repeated twice with intermediate grinding. The black product was then pressed into pellets. To obtain fully oxygenated samples the samples were annealed in an oxygen flow for 24 h at a temperature of 930°C , followed by slow cooling for 10 h to room temperature.

The crystal structures of the samples were characterized by powder x-ray diffraction using $\text{Cu K}\alpha_1$ radiation, and a Geol Model GDX-8030 diffractometer. The diffraction patterns were analysed using the Rietveld method.

The resistivity measurements were carried out using a four-probe technique. The applied ac current was 9.3 mA with a frequency of 70 Hz in the temperature range 10–300 K. The sizes of the samples were about $10 \times 3 \times 1.5 \text{ mm}^3$. The electrical leads were attached to the samples by silver paste. The electrical resistivity of the samples at room temperature were about 0.1Ω . Temperature stabilization was achieved to $\pm 10 \text{ mK}$ using a Lake Shore-330 temperature controller with a Pt resistor and a GaAs diode.

3. Results and discussion

The x-ray diffraction pattern analysis revealed that all the samples were predominantly single phase, having an orthorhombic structure with $Pmmm$ symmetry. Moreover, the diffraction patterns of some samples were taken before and after a sintering process. It is seen that the main peaks of the PrBaO_3 , BaCuO_2 and CaCu_2O_3 impurity phases at $2\theta = 28.9^\circ$, $2\theta = 29.3^\circ$ and $2\theta = 33.94^\circ$, respectively, dramatically decrease in intensity after the sintering process. The CaCu_2O_3 and BaCuO_2 impurity phases are less than about 1% in the samples having high levels of Pr and Ca concentrations; and no other impurity phases are detected. In figure 1, it is seen that by doping high concentrations of Pr and Ca into Gd-123, BaCuO_2 and CaCu_2O_3 impurity phases appear in the system. The presence of these phases shows that excess Ca doping acts as an impurity in the system.

We analysed the x-ray patterns using the Rietveld method. The lattice parameters of the samples are obtained, and presented in table 1. It is observed that the orthorhombic

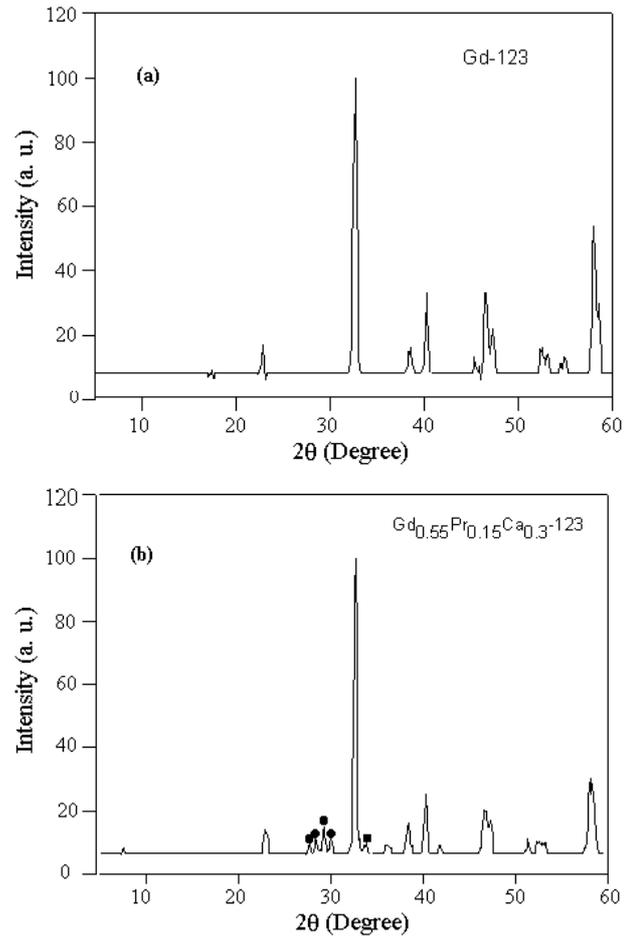


Figure 1. X-ray diffraction patterns of GdPrCa-123 samples: (a) $x, z = 0.0$, (b) $x = 0.15, z = 0.3$. ● indicates BaCuO_2 and ■ indicates CaCu_2O_3 impurity phases.

distortion of samples, $((b - a)/(b + a)) \times 100$, decreases with the increase of the Pr and Ca concentrations, in agreement with ErPrCa-123 [7].

Moreover, by assigning appropriate scattering factors to each ion, the positions of the O(2), O(3), O(4) and Cu(2) ions and the values of occupation (in per cent) of atomic sites of Gd, O(1), O(2), O(3) and O(5) are determined as variables. We also define the relative Gd, Pr and Ca ion contents. It is then observed that the oxygen content in the CuO_2 planes (O(2), O(3)) is constant, and that it is more mobile at Cu–O chain (O(1), O(5)) layers. The variation of above-mentioned parameters is then followed, depending on the doping concentrations of Pr and Ca ions (table 2).

In table 2, the site occupations of Gd, Pr and Ca and the atomic positions of Cu(2), O(2), O(3) and O(4) in the lattice are given for GdPrCa-123 samples with various Pr and Ca ion concentrations.

For $\text{Gd}_{1-z}\text{Ca}_z$ -123 samples, it is seen that both the lattice parameter a (in agreement with the ErCa-123 [7], YCa-123 [9] and $\text{Y}_{0.4}\text{Pr}_{0.6}\text{Ca}_x\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ [16] systems) and the in-plane Cu(2)–O(2) bond length (in agreement with [9]) increase with increasing z . The Cu(2)–O(2)–Cu(2) angle in CuO_2 planes also increases with increasing z . On the other hand, CuO_2 planes become flatter with increasing Ca ion concentration, in agreement with [9]. The flattening of the

Table 1. Lattice parameters, unit cell volume and orthorhombicity for granular GdPrCa-123 samples.

Sample (x, z)	Lattice parameter (\AA)			v (\AA^3)	$\frac{b-a}{b+a} \times 100$
	a	b	c		
(0.00, 0.00)	3.8445	3.9094	11.680	175.551	0.837
(0.00, 0.05)	3.8545	3.9079	11.698	176.221	0.688
(0.00, 0.15)	3.8547	3.9139	11.676	176.164	0.762
(0.10, 0.05)	3.8571	3.9114	11.764	177.493	0.699
(0.10, 0.10)	3.8481	3.8824	11.684	174.560	0.444
(0.10, 0.15)	3.8579	3.8887	11.742	176.152	0.398
(0.10, 0.20)	3.8507	3.8846	11.724	175.373	0.438
(0.15, 0.10)	3.8386	3.8877	11.640	173.710	0.635
(0.15, 0.15)	3.8362	3.8757	11.668	173.487	0.512
(0.15, 0.20)	3.8439	3.8896	11.698	174.898	0.591
(0.15, 0.30)	3.8504	3.8902	11.729	175.697	0.514
(0.20, 0.20)	3.8480	3.8996	11.664	175.026	0.666
(0.25, 0.00)	3.8557	3.9114	11.692	176.331	0.717
(0.30, 0.00)	3.8524	3.9044	11.669	175.538	0.670
(0.30, 0.15)	3.8499	3.9048	11.697	175.853	0.708
(0.30, 0.20)	3.8725	3.8942	11.739	177.040	0.283

Table 2. Per cent occupation of atomic sites N_{Gd} , N_{Pr} and N_{Ca} of Gd, Pr and Ca ion positions and $Z_{Cu(2)}$, $Z_{O(2)}$, $Z_{O(3)}$ and $Z_{O(4)}$ of Cu(2), O(2), O(3) and O(4), respectively, for granular GdPrCa-123.

x, z	N_{Gd}	N_{Pr}	N_{Ca}	$Z_{Cu(2)}$	$Z_{O(4)}$	$Z_{O(3)}$	$Z_{O(2)}$
0.00, 0.00	1.000	0.000	0.000	0.3381	0.1374	0.3586	0.3596
0.00, 0.05	0.940	0.000	0.040	0.3469	0.1462	0.3674	0.3684
0.00, 0.15	0.848	0.000	0.148	0.3346	0.1339	0.3550	0.3560
0.00, 0.25	0.756	0.000	0.257	0.3412	0.1406	0.3617	0.3627
0.10, 0.05	0.831	0.081	0.031	0.3376	0.1369	0.3580	0.3590
0.10, 0.10	0.794	0.094	0.094	0.3383	0.1376	0.3587	0.3597
0.10, 0.15	0.736	0.086	0.136	0.3423	0.1416	0.3627	0.3637
0.10, 0.20	0.689	0.089	0.189	0.3456	0.1450	0.3661	0.3671
0.15, 0.10	0.731	0.131	0.081	0.3377	0.1370	0.3581	0.3591
0.15, 0.15	0.681	0.131	0.131	0.3374	0.1368	0.3579	0.3586
0.15, 0.20	0.654	0.154	0.204	0.3419	0.1413	0.3624	0.3634
0.15, 0.30	0.546	0.146	0.296	0.3526	0.1520	0.3731	0.3741
0.30, 0.15	0.548	0.298	0.148	0.3313	0.1307	0.3518	0.3528
0.30, 0.20	0.499	0.298	0.198	0.3427	0.1420	0.3631	0.3641

CuO_2 planes decreases the internal crystallographic pressure of the system, which may also be responsible for the decrease of the superconducting transition temperature [24]. In samples with constant content of the Pr ion (for example 10%), but with various Ca ion contents, it is seen that the lattice parameter a decreases with the increase of Ca until an optimum value of Ca doping, and after that, with a further increase of Ca, it increases. The same tendency is observed for the samples with 15% of the Pr ion (table 1). The decrease in the lattice parameter a may be attributed to the fact that the holes introduced go into the anti-bonding orbital of Cu $3d_{x^2-y^2}-O 2p_x$ or $-O 2p_y$, and hence the in-plane Cu(2)-O(2) bond length and the lattice parameter a decrease. We have also seen that the angle of Cu-O-Cu bonds (buckling angle) decreases with increasing Ca concentration in these samples to some value of Ca doping, after which it increases.

The oxygen contents of the samples, $(7 - \delta)$, are obtained by the Rietveld method. Table 3 shows the oxygen content of some GdPrCa-123 samples. It is shown that the oxygen content of Pr-Ca-doped samples is effectively constant (within 0.6%) with respect to the increase of Pr and Ca concentrations. The average oxygen content of the samples was found to be about 6.87 ± 0.02 .

Table 3. Oxygen contents of GdPrCa-123 samples.

Sample x, z	Oxygen content ($7 - \delta$)
0.00, 0.00	6.874
0.00, 0.05	6.880
0.00, 0.15	6.856
0.10, 0.05	6.862
0.10, 0.10	6.863
0.10, 0.15	6.870
0.10, 0.20	6.878
0.15, 0.10	6.862
0.15, 0.15	6.861
0.15, 0.20	6.870
0.15, 0.30	6.892
0.20, 0.20	6.865
0.30, 0.15	6.849
0.30, 0.20	6.872

Figure 2 shows the changes of the transition temperature against the Ca content for two concentrations of Pr (i.e. 10 and 15%). The electrical measurements of these samples show that T_c increases with increasing Ca, and, after an optimum value of doping, T_c decreases. The increase of T_c and the decrease of the

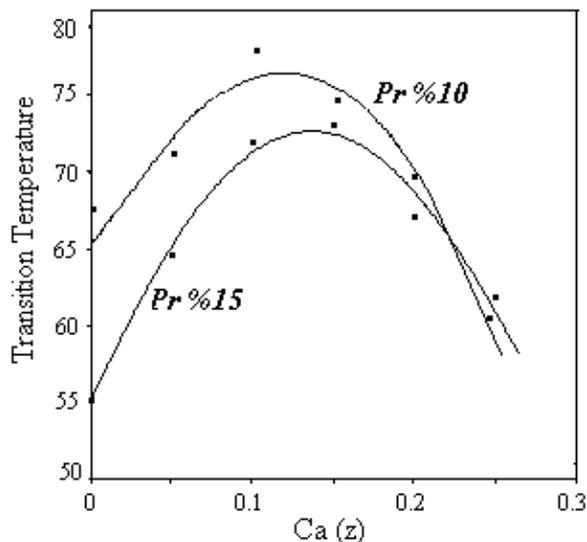


Figure 2. Transition temperature against Ca concentration for GdPrCa-123 samples, having 10 and 15% Pr ion concentrations. The full curves are guides to the eye.

lattice parameter a (the left-hand part of figure 2) correspond to hole doping by Ca. The decrease of T_c and the increase of the lattice parameter a after the optimum value of Ca doping (the right-hand part of figure 2), correspond to the presence of the over-doping effect of Ca.

Moreover, in figure 2, we observe that in comparison with 10% Pr, the 15% Pr curve is shifted both vertically and horizontally. With the increase of the Pr concentration, T_c decreases (vertical shift) and Ca content at maximum increases (horizontal shift), in agreement with [3, 14, 23]. The Ca content at the maximum of the curve for the compound with 10% Pr is about 10%, and for the compound with 15% Pr the Ca content is about 15%. The corresponding Ca concentrations determined by Tung *et al* [23] are less than 5% with 10% Pr, 10% with 15% Pr and 15% with 20% Pr. The decrease of T_c due to the increase in the Pr concentration could be affected by pair breaking by magnetic moments of the Pr ion, hole filling by excess electrons of Pr (due to the Pr excess valance of +3.86 instead of +3 [1]) and mobile hole localization. These factors cause a vertical shift in the curve. The horizontal shift is because of the presence of more electrons in the system due to the increase in the Pr concentration. To counteract the effect of these electrons, more Ca ions are required.

Figure 3 shows the transition temperature against Ca concentration for GdCa-123 samples. The electrical measurements of the $Gd_{1-z}Ca_z$ -123 samples show that the transition temperature decreases with increasing z , and this reduction is nonlinear. In this curve, a plateau in the range $z \cong 0.05$ – 0.15 is observed. The $T_c(z)$ relationship does not agree with the result for the YCa-123 compound by Neumeier *et al* [3]. If the $T_c(z)$ relationship in [14] (related to a YCa-123 compound) is investigated more carefully, it can be seen that the data of [14] also do not follow the proposed procedure in [3], and a nonlinear curve is more suitable.

Based on the above observations, we suggest that the decrease of T_c with increasing Ca content can be attributed to over-doping and the flattening of CuO_2 planes. The presence of these two intergrain disorders, and their competition in

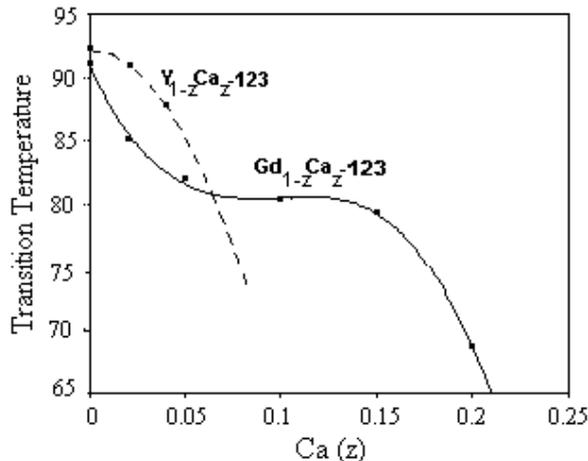


Figure 3. Transition temperature against Ca concentration for granular $Gd_{1-z}Ca_z$ -123 compounds. The broken curve is a fit to the data taken from [3].

different regions of the $T_c(z)$ curve (figure 3) has caused a nonlinear curve. The observed increase of T_c up to an optimum value of Ca doping in Pr–Ca-doped samples, suggests that each superconductor compound accepts an optimal hole concentration according to its inherent properties, and excess hole doping no longer increases T_c .

4. Conclusions

For $Gd_{1-z}Ca_z$ -123 compounds, T_c decreases nonlinearly with an increase of the Ca content and, in association, the lattice parameter a increases and CuO_2 planes become flatter. For Pr–Ca-doped samples ($Gd_{1-x-z}Pr_xCa_z$ -123) with a constant concentration of Pr, T_c increases with increasing Ca, and the lattice parameter a and the $Cu(2)$ – $O(2)$ – $Cu(2)$ angle decrease; i.e. the buckling is more intense in CuO_2 planes for this particular region of Ca concentration. After an optimum concentration of Ca doping, T_c decreases, and the lattice parameter a and the angle of the CuO_2 planes increase with increasing Ca. Based on these observations we suggest that besides the hole doping effect, Ca ion doping gives rise to interesting structural changes, for example the flattening of the CuO_2 planes. The competition of the two effects, overdoping of holes and flattening of the CuO_2 planes, seems to give rise to a nonlinear $T_c(z)$ curve for GdCa-123 samples. We also suggest that each superconductor compound, according to its inherent properties, accepts an optimum hole concentration.

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