Ceramics International 31 (2005) 533–536

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Superconducting properties of Pr-substituted $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$

W.Y. Yip, A.K. Koh, R. Abd-Shukor*

School of Applied Physics, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Received 28 November 2003; received in revised form 25 March 2004; accepted 4 May 2004

Abstract

The effect of Pr in $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ (DyPr-1113) for $x = 0.00$–0.20 cuprate superconductors prepared using the solid state reaction method are studied. The prepared samples showed a single 1113 phase. Mechanisms of partial hole transfer and pair breaking were suggested to play an important role in the suppression of the transition temperature in this system. The correlation between T_c and Pr concentration can be divided into two regions bordered near $x = 0.03$. The mechanism of hole filling causes a drastic suppression of the transition temperature for small concentration of Pr from $x = 0$ to 0.03. For $0.03 < x < 0.2$, partial hole transfer mechanism instigates any further T_c depression causing it to be almost constant.

Keywords: A. Powders; Solid state reaction; B. Porosity; C. Electrical properties; D. Oxide superconductors

1. Introduction

The discovery of superconductivity with transition temperatures (T_c) near 90 K in $YBa_2Cu_3O_{7-\delta}$ (Y-123) is still generating a great deal of interest in the material. Substitution of Y with rare-earth element R (except Ce, Pr, Pm and Tb), gives T_c similar to the $YBa_2Cu_3O_{7-\delta}$ compound. The $RSrBaCu_3O_{7-\delta}$ (R-1113) compound is isostructural with the R-123 materials where half of Ba is replaced by Sr.

The corresponding $DySrBaCu_3O_{7-\delta}$ (1113) superconducts at about 80 K in either orthorhombic or quasitetragonal structure with different thermal treatments [1]. The transition temperature of $(R_{1-x}Pr_x)Ba_{2-y}Sr_yCu_3O_{7-\delta}$ decreased with increasing Pr concentration [2]. The unique role of Pr is its superconductivity suppressing ability [3–7]. Recent works have shown that the substitution of Pr ion in the rare-earth site suppressed the superconductivity in $(Gd_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ compound [8]. For a recent review on the role of Pr in the 123 high temperature superconductors (HTSCs), see ref. [9]. Pr in the 1113 phase was suggested to be in the 3+ and 4+ state. An optimum Cu valence between 2.20+ to 2.30+ exhibits the maximum transition temperature in this phase [10].

The mechanisms that have been proposed to explain the suppression of T_c by Pr-doping include hole filling [11], pair breaking [12], hole localization [13], hole percolation [2] and hole depletion [14]. Hole filling exists when the extra electron fills the holes in the Pr-doped samples because Pr ion is substituted as a tetravalent or higher valence. The exchange interaction between the Pr magnetic moments and the spin of the mobile carriers in the CuO_2 planes causes the mechanism of pair breaking. The hole is localized due to the hybridization of the local states of the Pr ion with the conduction band states of the sandwiching CuO_2 planes. Hole depletion occurring in the CuO_2 planes is due to the charge transfer from the Cu–O pdσ band into the LM (Liechtenstein and Mazin) band.

In this paper we report the effect of Pr on the formation and superconducting properties of $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ for $x = 0$–0.2 where more insights are given in this interesting class of superconductor. The different mechanisms that suppress T_c at various Pr-doping levels are discussed.

---

* Corresponding author. Tel.: +60 3 89215904; fax: +60 3 89213777.
E-mail address: ras@pkrisc.cc.ukm.my (R. Abd-Shukor).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2004.05.029

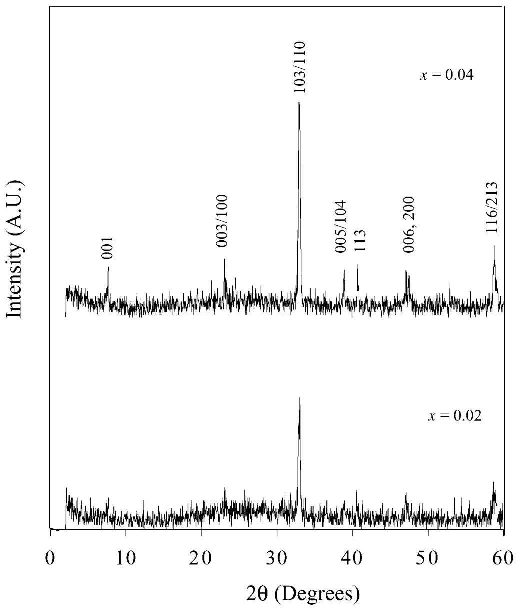

Fig. 1. X-ray powder diffraction patterns of $(Dy_{1-x}Pr_x)SrBaCu_3O_7$ with x = 0.02 and 0.04 indicating a dominant 1113 phase.

2. Experimental details

Samples were prepared by the solid state reaction method using high purity oxide components. The $(Dy_{1-x}Pr_x))SrBaCu_3O_{7-\delta}$ samples with x = 0–0.20 were prepared by using the precursor method. Appropriate amounts of high purity (>99.99%) powders of Dy_2O_3, Pr_6O_{11}, $SrCO_3$, $BaCO_3$ and CuO were mixed completely and then ground thoroughly before the mixture were calcined at 950 °C in air for 24 h with several intermittent grindings. The resultant powders were ground thoroughly and pressed into pellets of about 13 mm diameter and 2 mm thickness. These pellets were sintered at 950 °C for 24 h followed with annealing in oxygen at the same temperature for more than 10 h. The samples were slow cooled at a rate of 60 °C/h until 500 °C and natural furnace-cooled to room temperature.

The powder X-ray diffraction (XRD) method using a Siemens D 5000 diffractometer with Cu Kα source was used to identify the resultant phases. The dc electrical resistance versus temperature measurements were carried out using the four-point probe method with silver paste contacts in conjunction with a closed cycle refrigerator from CTI Cryogenics (Model 22) and a temperature controller from Lake Shore (Model 330). A constant current source between 1 mA and 100 mA was used throughout the measurements.

Table 1
Lattice parameters, $T_{c,\ onset}$ and porosity for $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$

x	Lattice parameters			$T_{c\ onset}$ (K)	Porosity (%)
	a (Å)	b (Å)	c (Å)		
0.00	3.839(3)	3.829(10)	11.537(8)	89	13
0.01	3.843(4)	3.842(4)	11.549(6)	84	6
0.02	3.840(5)	3.840(14)	11.566(9)	82	7
0.03	3.839(8)	3.839(14)	11.546(10)	80	8
0.04	3.842(8)	3.839(14)	11.574(13)	80	15
0.06	3.832(8)	3.844(16)	11.544(10)	81	18
0.10	3.836(11)	3.835(2)	11.569(15)	81	17
0.15	3.845(3)	3.847(6)	11.550(5)	81	15
0.20	3.840(3)	3.838(9)	11.535(6)	80	14

3. Results and discussion

The powder X-ray diffraction patterns of all $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ samples showed mainly a single 1113 phase. Fig. 1 shows the pattern for x = 0, 0.02 and 0.04 which indicates that Dy-1113 phase (space group, *P4/mmm*) is dominant (Fig. 1). No systematic change in the lattice parameters is observed with various Pr contents (Table 1). Scanning electron micrographs of the x = 0 and 0.06 samples are shown in Fig. 2a and b. In general the $x \geq 0.06$ samples showed grainy feature with less than 5 μm in size.

The electrical resistance versus temperature curves are shown in Figs. 3 and 4. All the samples show a metal-like

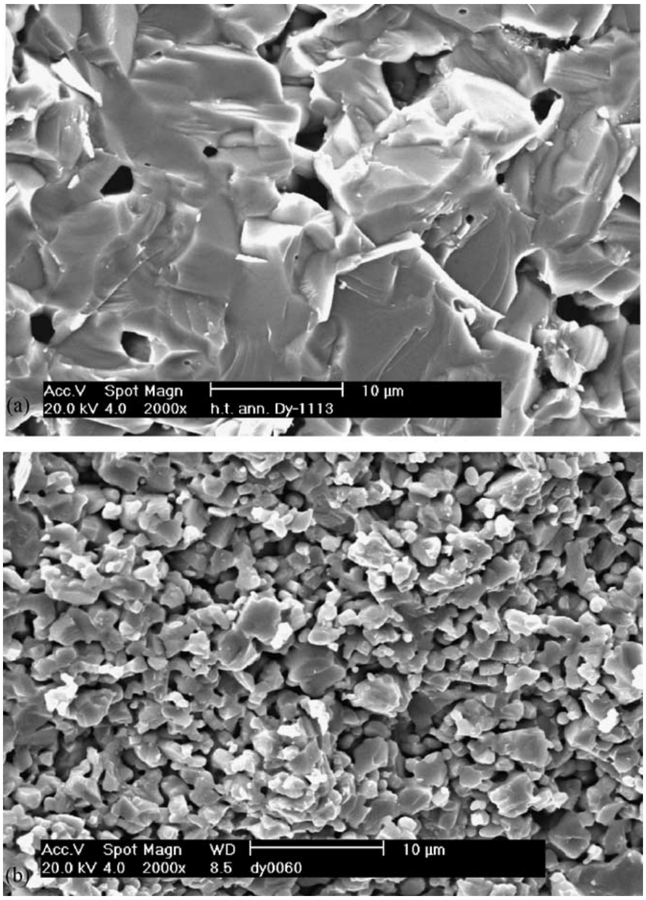

Fig. 2. Scanning electron micrographs of (a) $DySrBaCu_3O_{7-\delta}$ and (b) $Dy_{0.94}Pr_{0.06}SrBaCu_3O_{7-\delta}$.

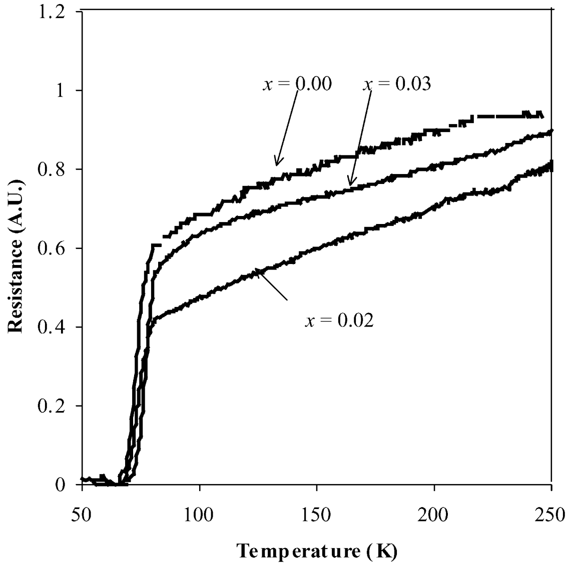

Fig. 3. Electrical resistance vs. temperature curves of $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ for $x = 0.00$, 0.02 and 0.03.

normal state behaviour with the resistance changes linearly with temperature. The undoped sample shows the highest $T_{c,\ onset}$ of 90 K. The doped samples show $T_{c,\ onset}$ from 80 K to 85 K (Table 1). Substitution of Pr suppresses the superconductivity of the samples. $T_{c,\ onset}$ drops dramatically until $x = 0.03$. $T_{c,\ onset}$ becomes almost constant from $x = 0.03$ to 0.20 (Fig. 5). Mechanism of partial hole transfer and pair breaking may play an important role in the suppression of the transition temperature. Mechanism of hole filling causes the drastic depression of $T_{c,\ onset}$ for the small $x = 0$–0.03. Later, partial hole transfer instigate the T_c depression and causes the $T_{c,\ onset}$ to be almost constant for $x = 0.03$–0.2. For higher x, mechanism of pair breaking plays a significant role resulting in the drastic drop of $T_{c,\ onset}$ [15].

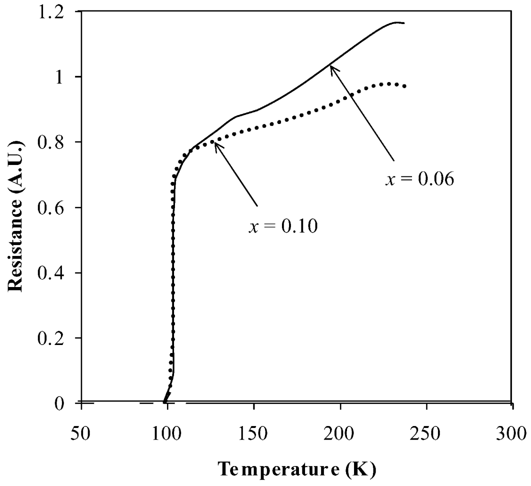

Fig. 4. Electrical resistance vs. temperature curves of $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ for $x = 0.06$ and 0.10.

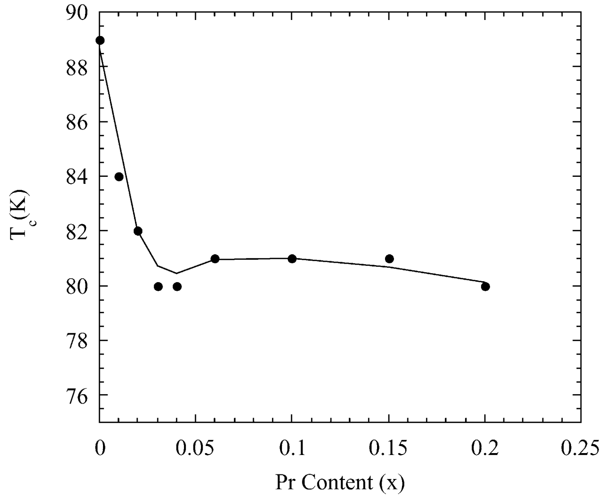

Fig. 5. T_c vs. Pr content (x) of $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ (the solid line is to guide the eye).

The electrical resistivity at room temperature for the $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ samples with $x = 0.01$–0.2 are shown in Fig. 6. The resistivity increases with Pr content. A steep increase in resistivity is observed near $x = 0.15$. This behaviour is not related to the porosity or the microstructure because a change in microstructure is observed at $x \geq 0.06$.

In conclusion, samples with nominal starting compositions $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ have been prepared and studied by electrical resistance, X-ray powder diffraction, scanning electron microscopy, and electrical resistivity at room temperature. The manner in which superconductivity was suppressed in this system has been uncovered. T_c depression in the Pr-substituted material can be divided into two regions bordered near $x = 0.03$ with different mechanisms of suppression. Mechanism of partial hole

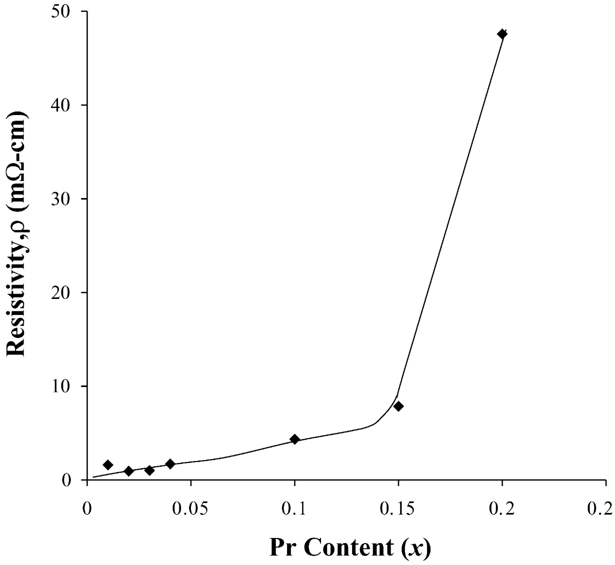

Fig. 6. Normal state electrical resistivity at 300 K of $(Dy_{1-x}Pr_x)SrBaCu_3O_{7-\delta}$ (the solid line is to guide the eye).

transfer causes the drastic suppression of T_c in the low Pr content region while pair breaking was suggested to play an important role in the $x = 0.03–0.2$.

Acknowledgements

This research has been supported by Ministry of Science, Technology and the Environment of Malaysia (IRPA 09-02-02-0072 EA199). W.Y. Yip would like to thank UKM for the travel grant.

References

[1] X.Z. Wang, P.L. Steger, Physica C 196 (1992) 247–251.
[2] M. Muroi, R. Street, Physica C 253 (1995) 205–216.
[3] Z. Tomkowicz, Physica C 320 (1999) 173.
[4] H.B. Radousky, J. Mater. Res. 7 (1992) 1917.
[5] S.R. Ghorbani, P. Lundquist, M. Anderson, M. Valldor, Ö. Rapp, Physica C 353 (2001) 77.
[6] J. Ye, Z. Zou, A. Matsushita, K. Oka, Y. Nishihara, Physica C 341–348 (2000) 525.
[7] M. Muroi, R. Street, Physica C 314 (1999) 172.
[8] M.R. Mohammadizadeh, H. Khosroabadi, M. Akhavan, Physica B 321 (2002) 301.
[9] M. Akhavan, Physica B 921 (2002) 265.
[10] S. Nakajima, M. Kikuchi, Y. Syono, N. Kobayashi, Y. Muto, Physica C 167 (1990) 57.
[11] J.J. Neumeier, T. Bjornholm, M.B. Maple, J.K. Schuller, Phys. Rev. Lett. 63 (1989) 2516.
[12] Y. Xu, W. Guan, Phys. Rev. B 45 (1992) 3176.
[13] J.C. Chen, Y. Xu, M.K. Wu, W. Guan, Phys. Rev. B 53 (1996) 5839.
[14] A.I. Liechtenstein, I.I. Mazin, Phys. Rev. Lett. 74 (1995) 1000.
[15] X. Sun, X. Zhao, W. Wu, X. Fan, X.G. Guang Li, H.C. Ku, Physica C 309 (1998) 63–67.