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Crystal structure and physical properties of $R(Ba_{1-x}Sr_x)_2Cu_3O_y$ (R= Nd, Pr) prepared under reducing atmosphere

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Abstract

The effects of Sr substitution for Ba on the crystal structure, oxygen content and physical properties of polycrystalline samples of $R(Ba_{1-x}Sr_x)_2Cu_3O_y$ (R= Nd, Pr) have been investigated. The samples were prepared by sintering at a high temperature under reducing atmosphere, followed by annealing under O_2 flow. The structure parameters were refined by the Rietveld analysis of X-ray powder diffraction data. The occupation factors of each site were analyzed under the assumption that a part of Sr ions occupies the R site and pushes the same amount of R ions into the Ba site. For the R= Nd, the ratio of Sr on the Nd sites $g_{(Sr/Nd)}$ increases with x, from 0 for $x = 0$ to 0.11 for $x = 0.5$. The orthorhombicity decreases continuously with x. On the other hand, for R= Pr, the site exchange between Sr and Pr does not occur. The orthorhombicity keeps a high value until $x = 0.3$ and drastically becomes zero at $x \geq 0.3$. The electrical resistivity and the Néel temperature T_N increases with x until $x = 0.3$, and then decreases. These results show that the high decrease rate of T_c in $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ is attributed to the occupation of Ba sites by Nd and the non-superconductivity of $PrBa_2Cu_3O_y$ is not due to the occupation of Ba site by Pr. It is also suggested that the hybridization of Pr 4f and O 2p π orbitals which prevents the replacement of Pr by Sr increases with x until $x = 0.3$ and then abruptly turns to decrease.

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Keywords: $RBa_2Cu_3O_y$; Light rare earth elements; Superconducting cuprates; Sr substitution

1. Introduction

The electronic state of the CuO_2 plane of the 123 type cuprates $RBa_2Cu_3O_y$ (R: rare earth element), is influenced by many factors such as the radius, valence and distribution of R ions, the oxygen content and the corrugation of the plane itself. In the cuprates of light rare earth elements La, Pr or Nd, they have severe effects on the properties, because of large ionic radius of them. $PrBa_2Cu_3O_y$ is not superconducting but semiconducting. $LaBa_2Cu_3O_y$ and $NdBa_2Cu_3O_y$ show the superconductivity with T_c higher than 90 K only when they are prepared under an optimum condition.

So far, many investigations have been made on the Sr substituted $R(Ba_{1-x}Sr_x)_2Cu_3O_y$ [1–4]. In general, for given R, T_c and orthorhombicity decrease with increasing Sr concentration. For a given Sr concentration, both the crystal structure and T_c depend on the size of R ions. However, the values of T_c are rather scattering in the past reports for a same substance.

Previously we investigated the effect of the Sr substitution systematically on $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ prepared under various sintering conditions [5]. The optimum sintering condition to give the highest T_c was the sintering at as high temperature as possible under reducing atmosphere. The results were discussed in relation to the site distribution of Nd and Sr ions.

In this study, we picked up $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ and $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ systems to investigate the effect of the ion distribution on the electronic state of the CuO_2 plane. Here the ion distribution in the present samples prepared by sintering at a high temperature under reducing atmosphere is controlled by the substitution of Sr for Ba.

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2. Experimental

All samples of $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ and $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ were carefully prepared by the conventional solid state reaction method. For $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ the preparation condition was optimized to realize the highest T_c for each x. A mixture of the ingredients was calcined and sintered under Ar flow at 950–980 °C for $x = 0$–0.5. The final sintering and oxygenation condition were as follows; heating in a flowing $Ar:O_2 = 100:0.01$ gas at 950–980 °C for 10 h and then slowly cooled to 440 °C in this gas and kept at that temperature for 60 h under flowing O_2 and cooled to room temperature. For $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ the condition was optimized to realize the highest crystal orthorhombicity. The calcining and sintering temperature was 900–925 °C for $x = 0$–0.5.

The oxygen content determined by the thermogravimetric analysis was in the range between 6.94 and 7.01. The structure parameters were refined by the Rietveld analysis of X-ray powder diffraction data [6].

The electrical resistivity and magnetization were measured in the temperature range between 4 and 300 K.

3. Results and discussion

All the structure parameters are listed for $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ and $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ in Tables 1 and 2, respectively. In the analysis of the occupation factors, the assumption that for $x = 0$, R occupation on the Ba sites $g_{(R/Ba)}$ is 0 and for $x \neq 0$, a part of Sr ions occupies the R sites and pushes the same amount of R ions into the Ba site, $g_{(R/Ba)} = (1/2)g_{(Sr/R)}$, gives an excellent fitting. For $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$, $g_{(Sr/Nd)}$ changes with x from 0 for $x = 0$ to 0.11 for $x = 0.5$ and $g_{O(5)}$ from 0.01 for $x = 0$ to 0.48, $g_{O(4)}$ from 0.99 to 0.54, respectively (Fig. 1). On the other hand for $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$, the site exchange between Sr ions and Pr ions does not occur; $g_{(Sr/Pr)} = 0$ for $0 \leq x \leq 0.5$. The difference between $g_{O(4)}$ and $g_{O(5)}$ keeps a high value almost unity until $x = 0.3$ and drastically becomes zero at $x \geq 0.3$ (Fig. 2).

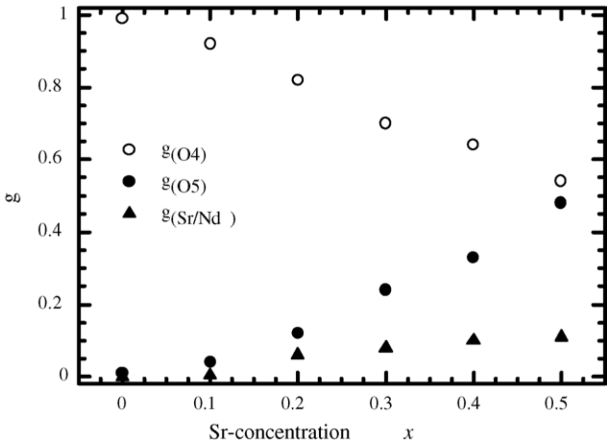

Fig. 1. The x dependence of occupation factors for $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$.

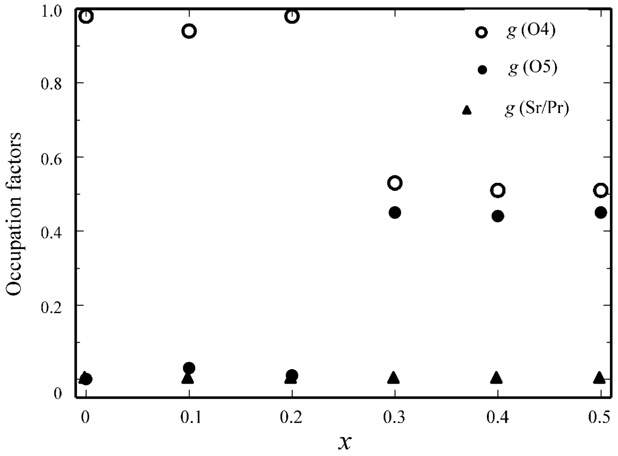

Fig. 2. The x dependence of occupation factors for $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$.

The superconducting transition temperature T_c and the orthorhombicity of $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ are

Table 1
Structure parameters for $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ obtained by Rietveld analysis of the X-ray powder diffraction data

	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
a (nm)	0.38649(2)	0.38646(7)	0.38656(4)	0.38702(9)	0.38690(9)	0.38667(1)
b (nm)	0.39163(2)	0.39043(9)	0.38954(5)	0.38856(0)	0.38757(7)	0.38691(0)
c (nm)	1.176(7)	1.174(1)	1.171(9)	1.169(9)	1.167(3)	1.163(7)
y	7.00	6.96	6.94	6.94	6.97	7.02
$z_{(Ba,Sr)}$	0.1810(8)	0.1816(1)	0.1817(4)	0.1821(3)	0.1824(4)	0.1824(5)
$z_{Cu(2)}$	0.3503(6)	0.3499(6)	0.3507(9)	0.3507(4)	0.3515(5)	0.3494(3)
$z_{O(1)}$	0.1593(1)	0.1622(3)	0.1648(6)	0.1627(9)	0.1653(1)	0.1654(8)
$z_{O(2)}$	0.3667(1)	0.3719(1)	0.3700(0)	0.3687(7)	0.3633(2)	0.3573(5)
$z_{O(3)}$	0.3772(3)	0.3702(7)	0.3770(6)	0.3782(5)	0.3812(5)	0.3809(7)
$g_{Sr/Nd}$	0.0	0.004	0.06	0.08	0.10	0.11
$g_{O(4)}$	0.99	0.92	0.82	0.70	0.64	0.54
$g_{O(5)}$	0.01	0.04	0.12	0.24	0.33	0.48
R_{WP} (%)	9.53	8.92	8.46	7.81	8.12	7.10
S	1.80	1.85	1.70	1.51	1.66	1.51

Table 2
Structure parameters for $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ obtained by Rietveld analysis of the X-ray powder diffraction data

	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
a (nm)	0.38565(3)	0.38542(9)	0.38560(3)	0.38720(5)	0.38644(5)	0.38638(2)
b (nm)	0.39238(7)	0.39197(5)	0.39069(4)	0.38727(7)	0.38698(5)	0.38690(8)
c (nm)	1.1699(1)	1.1688(1)	1.1663(8)	1.1656(5)	1.1625(6)	1.1628(4)
y	6.98	6.97	6.99	6.98	6.95	6.96
$z_{(Ba,Sr)}$	0.1787(0)	0.1797(2)	0.1787(0)	0.1778(7)	0.1781(5)	0.1780(3)
$z_{Cu(2)}$	0.3543(3)	0.3510(7)	0.3524(5)	0.3526(9)	0.3468(1)	0.3512(7)
$z_{O(1)}$	0.1651(3)	0.1678(0)	0.1660(7)	0.1570(6)	0.1563(4)	0.1616(9)
$z_{O(2)}$	0.3785(7)	0.3789(8)	0.3696(6)	0.3825(4)	0.3867(8)	0.3873(2)
$z_{O(3)}$	0.3777(2)	0.3767(7)	0.3712(4)	0.3694(1)	0.3728(6)	0.3529(0)
$g_{Sr/Pr}$	0.0	0.0	0.0	0.0	0.0	0.0
$g_{O(4)}$	0.98	0.94	0.98	0.53	0.51	0.51
$g_{O(5)}$	0.0	0.03	0.01	0.45	0.44	0.45
R_{WP} (%)	9.23	10.27	9.87	8.78	8.66	8.68
S	1.65	1.89	1.86	1.71	1.68	1.64

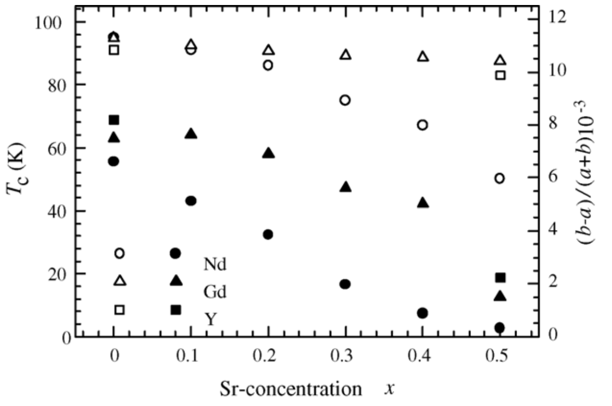

Fig. 3. The x dependences of T_c and the orthorhombicity for $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$, $Y(Ba_{1-x}Sr_x)_2Cu_3O_y$ and $Gd(Ba_{1-x}Sr_x)_2Cu_3O_y$; open symbols for T_c and solid symbols for orthorhombicity.

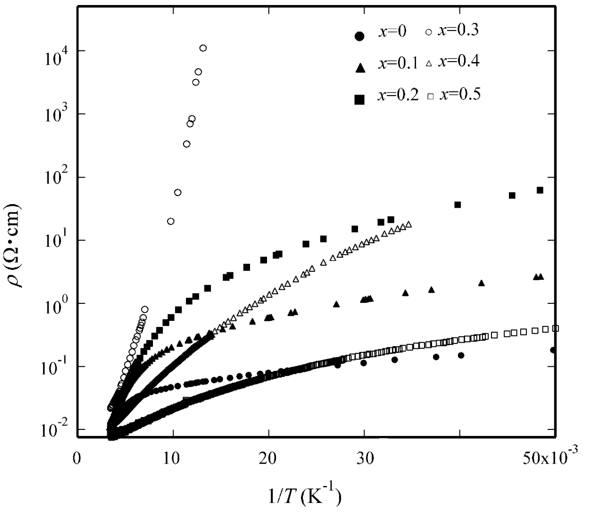

Fig. 4. The temperature dependence of the logarithmic electrical resistivity for $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$.

plotted against x with those of $Y(Ba_{1-x}Sr_x)_2Cu_3O_y$ and $Gd(Ba_{1-x}Sr_x)_2Cu_3O_y$ for the comparison (Fig. 3) [1,7]. Ions with small ionic radius like Y and Gd are considered not to occupy the Ba site.

All the compounds $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$ are semiconducting. The magnitude of electrical resistivity increases with x until $x = 0.3$ then decreases. The temperature dependence changes also at $x = 0.3$ (Fig. 4). Various magnetic parameters are listed in Table 3. The values of the effective magnetic moment are near to that of Pr^{3+}. The Néel temperature T_N increases with x, from 16.8 K for $x = 0$ to 20.6 K for $x = 0.3$ and then decreases. These tendencies of T_N and the electrical resistivity indicate that the hybridization of Pr 4f and O 2p π orbitals increases with x until $x = 0.3$.

Table 3
Various parameters appearing in the modified Curie Weiss law for $Pr(Ba_{1-x}Sr_x)_2Cu_3O_y$

x	T_N (K)	χ_0 (emu/mol)	θ_p (K)	C (emu K/mol)	μ_{eff} (μ_B)
0	16.8	0.8×10^{-3}	−5.20	0.89	2.67
0.1	18.8	1.5×10^{-3}	−7.45	0.82	2.56
0.2	19.8	2.3×10^{-3}	−10.25	0.69	2.35
0.3	20.6	0.7×10^{-3}	−13.58	0.92	2.72
0.4	18.8	0.6×10^{-3}	−13.07	0.87	2.64
0.5	16.2	0.7×10^{-3}	−17.32	1.07	2.93

4. Conclusion

It is shown that the high decrease rate of T_c in $Nd(Ba_{1-x}Sr_x)_2Cu_3O_y$ is attributed to the occupation of Ba sites by Nd and the non-superconductivity of $PrBa_2Cu_3O_y$ is not due to the occupation of Ba site by Pr. The strong hybridization of Pr 4f and O 2p π orbitals which prevents the replacement of Pr by Sr increases with x until $x = 0.3$ and then turns to decrease. The orthorhombicity keeps a high value under the existence of Pr 4f and O 2p π hybridization.

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