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Structural studies and T_c dependence in $La_{2-x}Dy_xCa_yBa_2Cu_{4+y}O_z$ type mixed oxide superconductors

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Abstract. A new series of mixed oxide superconductors with the stoichiometric composition $La_{2-x}Dy_xCa_yBa_2Cu_{4+y}O_z$ ($x = 0.0 - 0.5$, $y = 2x$) has been studied for structural and superconductiong properties. Our earlier studies on $La_{2-x}(Y/Er)_xCa_yBa_2Cu_{4+y}O_z$ series, show a strong dependence of T_c on hole concentration (p_{sh}). In the present work, the results of the analysis of the neutron diffraction measurements at room tempreature on $x = 0.3$ and 0.5 samples are reported. It is interesting to know that Ca substitutes for both La and Ba site with concomitant displacement of La onto Ba site. Superconductivity studies show that maximum T_c is obtained for $x = 0.5$, $y = 1.0$ sample ($T_c \sim 75$ K), for $La_{1.5}Dy_{0.5}Ca_1Ba_2Cu_5O_z$ (La-2125).

Keywords. Oxide superconductors; $La_{2-x}Dy_xCa_yBa_2Cu_{4+y}O_z$; structural studies; T_c dependence; neutron diffraction.

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1. Introduction

It is a well-established fact that the non-superconducting $La_3Ba_3Cu_6O_z$ (La-336), $LaBaCu_2Oz$ (La-112) and $La_2Ba_2Cu_4O_z$ (La-224) systems, all having La : Ba : Cu ratio of 1 : 1 : 2, can be made superconducting by the simultaneous addition of CaO and CuO along with rare-earth doping at La site [1,2]. Our earlier studies on $CaCuO_2$ layer addition in La-224 system yielded a stoichiometric composition of $La_{2-x}(Y/Er)_xCa_yBa_2Cu_{4+y}O_z$ where $y = 2x$. The structural and superconducting property studies showed that, superconductivity improves from non-superconductor to maximum $T_c \sim 78$ K, with increasing Ca content up to $x = 0.5$, thus giving a superconducting $La_{1.5}(Y/Er)_{0.5}Ca_1Ba_2Cu_5O_z$ (La-2125) phase [3]. In the present work an attempt is made to see the effect of substituting rare-earth ion, Dy^{3+} (ionic radius 0.910 Å) having large intrinsic magnetic moment, for La^{3+} (ionic radius 1.02 Å). The substitution of Dy at La site provides stability to the structure.

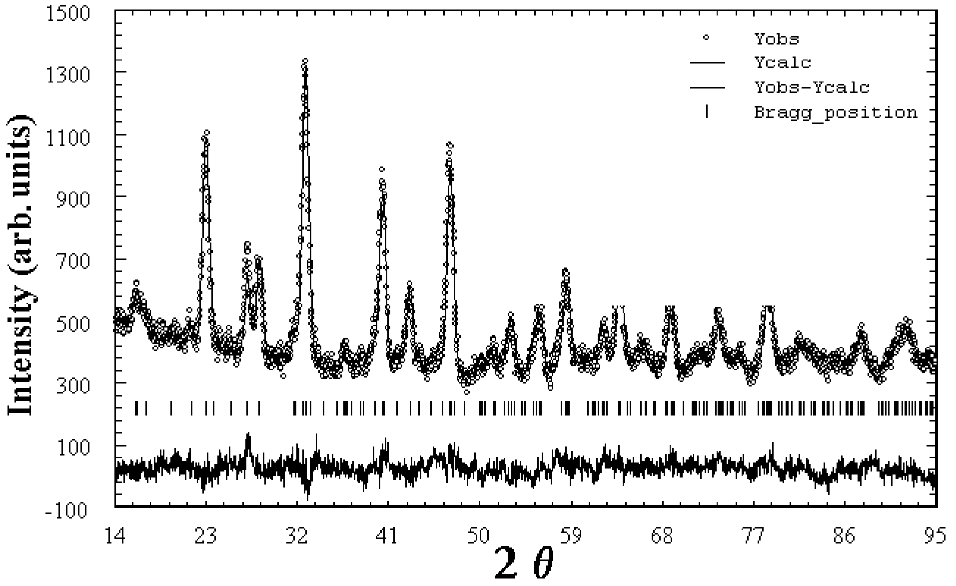

Figure 1. Rietveld fitted neutron diffraction plot for $La_{1.5}Dy_{0.5}Ca_1Ba_2Cu_5O_z$ sample.

2. Experimental

Samples with the stoichiometric composition $(La_{2-x}Dy_x)Ca_yBa_2Cu_{4+y}O_z$ $(y=2x)$, $0.1 < x < 0.5$ were synthesized using solid-state reaction method. The details of synthesis steps are the same as those reported in ref. [3]. The X-ray diffraction (XRD) patterns were fitted with least square method and they clearly indicate the single phase and tetragonal structure. Neutron diffraction studies were carried out on the two samples on 'powder diffractometer' at Dhruva Reactor (BARC) using neutrons of wavelength 1.094 Å. Figure 1 shows the Rietveld fitted pattern for $La_{1.5}Dy_{0.5}Ca_1Ba_2Cu_5O_z$ (La-2125) sample. The diffraction patterns were refined using Reitveld profile refinement program, FULLPROF. The results of Reitveld refinement are listed in table 1.

3. Results and discussion

Figure 2 shows the resistive behavior of all the samples in the series. The normalized resistance vs. temperature measurements were taken using standard four-probe method. Iodometric double titration method was employed to determine the oxygen content of the sample. The normalized resistance vs. temperature plots of these sample shows an improvement in transition temperature (for zero resistance), T_c with increasing Ca concentration. As Ca increases, T_c increases and the maximum $T_c \sim 75$ K for $x = 0.5$ is achieved.

The analysis of XRD data shows that the unit cell volume decreases with increasing Ca, due to the substitution of La^{3+} (1.22 Å) by smaller ions like Ca^{2+}(1.06 Å) and Dy^{3+} (0.91 Å). The Rietveld analysis of neutron diffraction data gives the exact site

Table 1. Parameters obtained from neutron diffraction analysis for $La_{2-x}Dy_x Ca_yBa_2Cu_{4+y}O_z$ for $x = 0.3$ and 0.5 ($y = a$) samples.

Parameters	x, y	
	(0.3, 0.6)	(0.5, 1.0)
Space group	P4/mmm	p/4mmm
$a = b$ (Å)	3.8770 (2)	3.8670 (2)
c (Å)	11.6878 (8)	11.6766 (8)
Lattice parameters ($a = b$, c) Å	3.8710 (2)	3.8640 (2)
(from XRD)	11.5871 (8)	11.6675 (8)
La/Dy/Ca (1/2, 1/2, 1/2)		
N_{La}	0.500	0.300
N_{Dy}	0.180	0.300
N_{Ca}	0.280	0.400
Ba (1/2, 1/2, z)		
Z	0.183	0.186
N	1.200	1.200
La @ Ba (1/2, 1/2, z)		
Z	0.183	0.186
N	0.520	0.600
Ca @ Ba (1/2, 1/2, z)		
Z	0.183	0.186
N	0.080	0.200
Cu (1) (0, 0, 0)		
N	0.760	0.930
Cu (2) (0, 0, z)		
Z	0.352	0.352
N	2.000	2.047
O (1) (0, 1/2, 0)		
N	0.915	0.985
O (2) (1/2, 0, z)		
Z	0.164	0.165
N	1.981	1.988
O (4) (0, 0, z)		
Z	0.370	0.370
N	4.004	4.031
Oxygen content (z', z)	6.90 (2), 11.50 (2)	7.00 (2), 11.67 (2)
Oxygen content from iodometric titration (z', z)	6.867 (2), 11.445 (2)	6.98 (2), 11.64 (2)
T_c (K)	~ 66	~ 75
R-Factor	6.22	5.82
χ^2	1.527	1.489

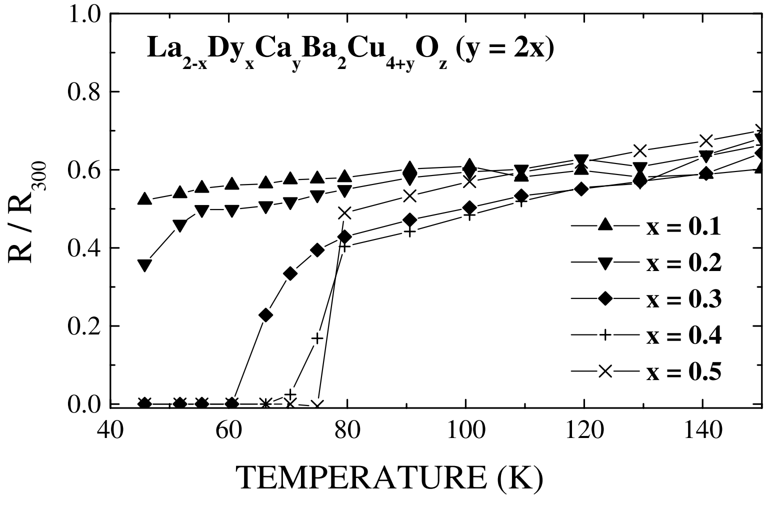

Figure 2. Normalized resistance vs. temperature plot for $(La_{2-x}Dy_x)Ca_yBa_2Cu_{4+y}O_z$; $0.1 < x < 0.5$; $y = 2x$ system.

occupancies, atomic positions and oxygen content. It can be seen from the Rietveld analysis on $La_{2-x}Dy_xCa_yBa_2Cu_{4+y}O_z$, $y = 2x$, series of samples that Ca^{2+} goes to La^{3+} and Ba^{2+} sites. With the increase in Ca concentration, the displacement of Ca onto La site increases which contributes to the improvement in superconductivity, due to the hole doping. There is concomitant displacement of La onto Ba site also. The non-superconducting $La_2Ba_2Cu_4O_z$ (La-224) becomes superconducting by the addition of $CaCuO_2$ with maximum $T_c \sim 75$ K for $La_{1.5}Dy_{0.5}Ca_1Ba_2Cu_5O_z$ (La-2125) resulting due to the Ca-occupying La-site which is hole doping.

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