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Structural and magnetic studies on $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ type superconducting oxides

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Abstract

The La-2125 type $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ ($0.1 \leq x \leq 0.5$; LDBO) compounds have been synthesized and studied as regards their structural and superconducting properties using room temperature neutron diffraction, high field dc magnetization, four-probe resistivity and iodometric double titration. The Rietveld analysis of the neutron diffraction data reveals tetragonal structure for all the samples, which crystallizes into La-123 type tetragonal structure in the $P4/mmm$ space group. Iodometric double titrations were performed to determine the oxygen content values and calculate the mobile charge carrier (hole) density. The superconducting transition temperature (T_c) increases from ~ 20 K for $x = 0.1$ to a maximum of 75 K for $x = 0.5$. The flux pinning force (F_p) and critical current density (J_c), calculated from the low temperature hysteresis loops, also increase with increasing dopant concentration. This paper presents studies on the structure and superconducting properties of all LDBO compounds in relation to the role of calcium in inducing superconductivity in the tetragonal non-superconducting oxide.

1. Introduction

Mixed oxide superconductors having structure similar to tetragonal $\text{REBa}_2\text{Cu}_3\text{O}_z$ (RE = Y or a rare earth ion) have attracted interest since several RE-123 type tetragonal structures, such as $\text{REBaCaCu}_3\text{O}_{7-\delta}$ [1], $\text{LaBa}_{1.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_\delta$ [2], $\text{La}_{2-x}\text{RE}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ [3], $(\text{Ca}_x\text{La}_{1-x})$

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($\text{Ba}_{c-x}\text{La}_{2-c+x}\text{Cu}_3\text{O}_y$ [4], $\text{La}_{3.5-x-y}\text{RE}_y\text{Ca}_{2x}\text{Ba}_{3.5-x}\text{Cu}_7\text{O}_z$ [5]), were found; these have been studied extensively in view of their structural and superconducting properties. These tetragonal superconductors are especially interesting because:

- (i) The superconducting transition temperature (T_c) depends substantially on the cationic intermixing at various atomic sites, unlike the case for the orthorhombic RE-123 superconductors where T_c depends on the optimal value of the oxygen content ($z \sim 6.9$). For the superconducting tetragonal compounds, the oxygen content value per unit cell (z) can be >7 , which is in the ‘hole overdoped’ region.
- (ii) The crystal structure of tetragonal superconductors remains tetragonal throughout the doping range, thus allowing one to circumvent the complications in interpreting experimental data arising from the ordered Cu–O chains which are observed for the orthorhombic RE-123 superconductors on structural (orthorhombic–tetragonal) transition occurring.

Some of us have studied the La-2125 ($\text{La}_2\text{Ca}_1\text{Ba}_2\text{Cu}_5\text{O}_z$) compounds in the stoichiometric form $\text{La}_{2-x}\text{RE}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ with x varying from 0 to 0.5. The La-2125 phase is obtained for $x = 0.5$, and it exhibits a maximum $T_c \sim 78(\pm 1)$ K. The $\text{La}_{2-x}\text{RE}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ type high temperature superconductors with $x = 0.1\text{--}0.5$ have been studied with different R^{3+} ions such as Nd, Gd, Pr [6–8].

The starting compound of this family, La-224 ($\text{La}_2\text{Ba}_2\text{Cu}_4\text{O}_z$; for $x = 0.0$ in $\text{La}_{2-x}\text{RE}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$), is a tetragonal triple-perovskite compound exhibiting semiconducting behaviour [6]. La-224 can be normalized to the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE-123) form, as $\text{La}_1(\text{Ba}_{1.5}\text{La}_{0.5})\text{Cu}_3\text{O}_{7-\delta}$. The structural analysis of the neutron diffraction data on La-224 shows that it is isostructural to the tetragonal RE-123 structure in the $P4/mmm$ space group [6, 7]. The bulk superconductivity in this tetragonal compound is achieved when Ca^{2+} is doped at the La^{3+} site in the nominal composition. Over the entire doping range the structure remains similar to that of tetragonal $\text{RBa}_2\text{Cu}_3\text{O}_{6+\delta}$ ($P4/mmm$) [9, 10]. T_c increases up to 75 K (± 1) for an optimum value of $x = 0.5$.

The structure of a typical La-2125 unit cell is shown in figure 1. This figure shows the atomic site occupancies of various cations. The La^{3+} site is occupied by La^{3+} , Ca^{2+} and substituted R^{3+} , whereas the Ba^{2+} site is occupied by La^{3+} and the remaining Ca^{2+} . This type of cationic intermixing is responsible for the superconductivity in La-2125 type compounds. We have observed that the ‘hole doping’ by Ca^{2+} at La^{3+} sites is not fully compensated by ‘hole filling’ by La^{3+} at Ba^{2+} sites; hence the increase in hole concentration, and T_c .

The mobile charge carriers (i.e., *holes*), which are responsible for superconductivity in this compound, are introduced by the substitution of Ca^{2+} for La^{3+} . These mobile p type carriers first decrease the long range magnetic ordering of Cu spins in the tetragonal non-superconductors such as La-224, and drive the system from an antiferromagnetic insulator to a metallic superconductor [11–13]. It is known that Ca^{2+} substitution creates oxygen vacancies in Cu–O₂ planes in $(\text{Y/R})_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_z$ (1–2–3 type systems) [14]. The possibility of oxygen vacancies in Cu–O₂ planes is of interest, considering that superconductivity is essentially believed to arise in Cu–O₂ planes in high T_c materials. The high temperature superconductivity in the tetragonal 1–2–3 and similar kinds of phases suggests that the Ca cations introduce holes into the bridging sites between two Cu–O₂ sheets. This alternative ‘bridging’ hole picture, as suggested by Gu *et al* [15] for $\text{LaBaCaCu}_3\text{O}_{7-\delta}$ compounds, is more general for the tetragonal high T_c cuprates than the ‘transferring’ picture associated with the orthorhombic $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phases.

We present here our studies on $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ (LDBO), among the RE-123 derived high T_c phases, including structural and superconducting property considerations. In

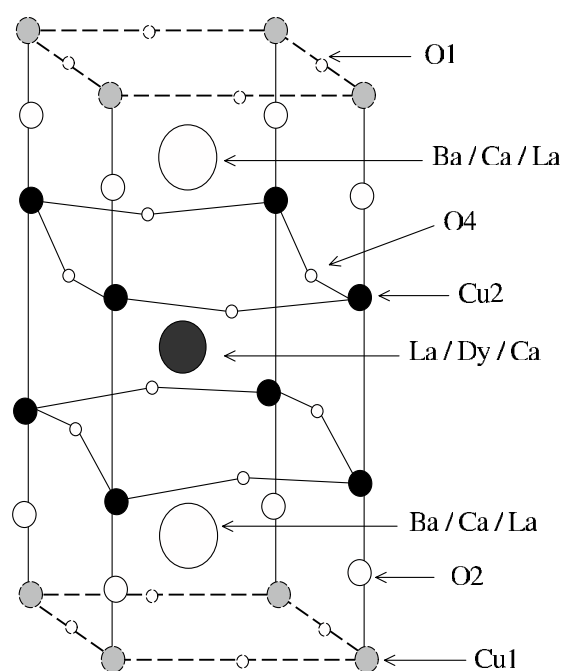


Figure 1. A typical La-2125 unit cell.

in this paper we discuss the role of calcium in introducing superconductivity in LDBO compounds by 'bridging' the CuO_2 sheets.

2. Experimental details

All of our samples in the LDBO series were prepared by the solid-state reaction method. The high purity (99.9 + % pure) starting compounds of La_2O_3 , Dy_2O_3 , CaCO_3 , BaCO_3 and CuO were taken in stoichiometric quantities and ground thoroughly under acetone to form a homogeneous mixture. This mixture was then calcined at 900°C for 24 h in powder form. The samples were then pelletized and sintered at 940°C for 48 h with intermediate grindings. These sintered pellets were first annealed in flowing N_2 gas at 940°C for 12 h; this was followed by O_2 gas annealing for another 12 h. While cooling, the samples were first slow cooled to 500°C at 1°C min^{-1} rate, and annealed for 24 h at this temperature, and then finally slow cooled to room temperature in flowing O_2 at 1°C min^{-1} rate. The samples were characterized for phase purity and lattice constants by means of room temperature x-ray diffraction. All the samples were found to be single phase with tetragonal symmetry. A four-probe resistivity set-up was used to determine the superconducting transition temperature (T_c) using a closed cycle cryocooler. The lowest temperature which we could achieve with this system was 40 K, and hence the resistance was measured up to that temperature. A Quantum Design SQUID magnetometer was used to measure the dc susceptibility (χ) and dc magnetization values. The oxygen content was determined by an iodometric double-titration method. Powdered samples of all the compositions (~ 7 g) were used for the neutron diffraction investigation. The samples were packed in vanadium cans and exposed to a monochromatic neutron beam ($\lambda = 1.249 \text{ \AA}$). The neutron diffraction data were recorded using a 'position sensitive detector'. The analysis

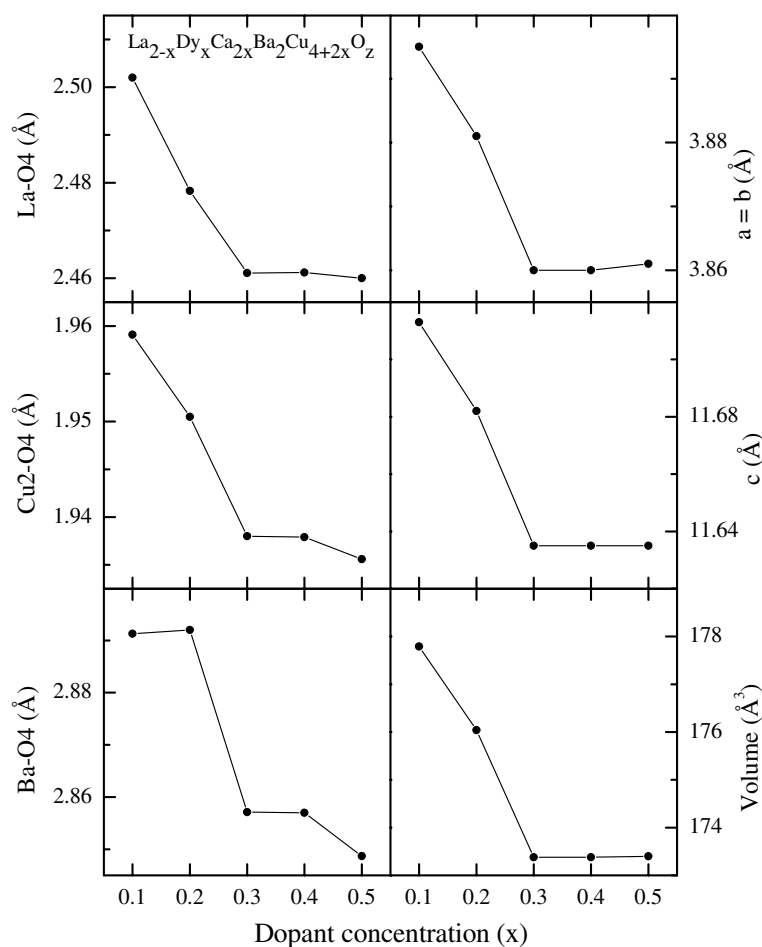


Figure 2. The variation of (selected) bond lengths and lattice parameters with increasing dopant concentration for the $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ series.

of the neutron data was done using the FULLPROF suite, employing the Rietveld refinement method [16, 17].

3. Results

3.1. Structure

The neutron diffraction experiments were performed on polycrystalline powders of LDBO compounds. The structural analysis reveals tetragonal La-123 type structure with the $P4/mmm$ space group for all samples studied in the $x = 0.1$ – 0.5 range. Detailed analysis of neutron diffraction data on $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ (with $x = 0.1$ – 0.5) by the Rietveld refinement method has been reported in [18]. A typical unit cell of the La-2125 compound is shown in figure 1.

Using the BONDSTR module of the FULLPROF suite, we have calculated the bond lengths for all the compositions studied. The variation of selected bond lengths, around the conducting CuO_2 plane, is plotted as a function of dopant concentration in figure 2. The

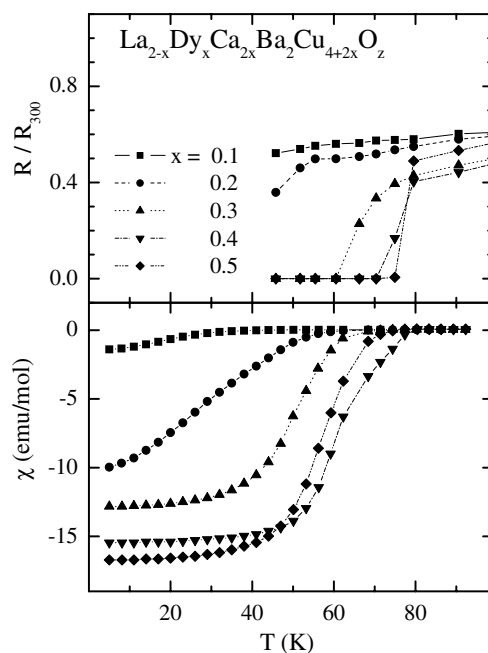


Figure 3. A combined plot of the resistance and susceptibility as a function of temperature for all samples in the $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ series.

increase in content of smaller ionic radii ions (Ca^{2+} , Dy^{3+} at the La^{3+} site and Ca^{2+} , La^{3+} at the Ba^{2+} site) results in the shrinking of these bond lengths, thus distorting the polyhedra of the perovskite block containing the superconducting CuO_2 planes. Due to the shortening of the bond lengths the unit cell parameters also decrease, in similar fashion, resulting in a reduction of the unit cell volume, resulting in turn in the bridging of the two CuO_2 planes.

3.2. Resistance and susceptibility measurements

The superconducting properties of all the LDBO samples were determined by electrical (four-probe resistance, R , measurement) and magnetic (dc susceptibility, χ) methods.

Figure 3 shows a plot of R and χ as a function of temperature for all the samples of the LDBO system in the temperature range 5–100 K. The T_c values obtained by these independent methods are in good agreement. Since the $T_c^{R=0}$ for the $x = 0.1$ and 0.2 samples were below 40 K, we determined the transition temperatures for all samples precisely, from the first derivatives of the susceptibility curves. With increasing concentration x , the superconducting transition temperature increases from ~ 20 K for $x = 0.1$ to a maximum of $T_c^{R=0} = 75$ K for the $x = 0.5$ (La-2125 phase) compound.

The values of the transition temperatures obtained from both resistivity and susceptibility measurements are given in table 1. T_c^{ON} has been plotted as a function of increasing x in figure 4.

3.3. Oxygen content determination and charge carrier density

Iodometric double titration has been performed on all the samples to calculate the oxygen content per unit formula. Using the oxygen content values obtained from iodometric titrations and Tokura's formula [19, 20], hole concentrations have been calculated. The values of the hole concentration and oxygen content per unit cell and per unit formula are tabulated in table 1.

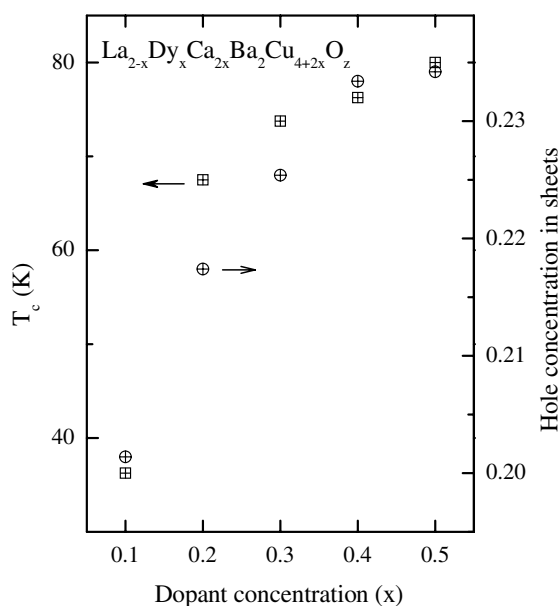


Figure 4. The increase in superconducting transition temperature (T_c^{ON}) and hole concentration (p) with increasing dopant concentration in $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$.

Table 1. Values of T_c obtained from resistivity and susceptibility measurements, oxygen contents from iodometric titration and the hole concentration per unit cell and in Cu-O_2 sheets.

Dopant concentration x	Transition temperature		Oxygen content (in 123 & 2125)		Hole concentration	
	$T_c^{R=0}$ (K) (± 1 K)	T_c^X (onset) (± 1 K)	per unit cell (z')	per unit formula (z)	per unit cell (p)	in CuO_2 sheets (p_{sh})
0.1	<20	38	6.90 (2)	9.66 (2)	0.266 (2)	0.200 (2)
0.2	<30	58	6.95 (2)	10.19 (2)	0.300 (2)	0.225 (2)
0.3	66	68	6.96 (2)	10.68 (2)	0.306 (2)	0.230 (2)
0.4	71	78	6.96 (2)	11.14 (2)	0.309 (2)	0.232 (2)
0.5	75	79	6.97 (2)	11.61 (2)	0.313 (2)	0.235 (2)

The increase in transition temperature with x can also be compared with the simultaneous increase of the hole concentration in sheets (p_{sh}) with x , as clearly seen in figure 4. The simultaneous increases in p_{sh} and T_c with increasing x indicate a correlation between the hole concentration and superconducting properties for these compounds.

3.4. Magnetization and determination of the critical current density

A higher critical current density in the superconductors can be achieved by blocking the movement of the flux lines. This can be achieved by means of 'defects'. The bridging of the CuO_2 sheets by Ca^{2+} is accompanied by the creation of 'flux pinning centres', as structural defects are created when a smaller ion replaces a bigger ion in the unit cell. We have therefore measured the critical current density (J_c) for all the samples at 5 K, and observed an increase in J_c with increasing dopant concentration. Figure 5 shows the moment (in emu) plotted against

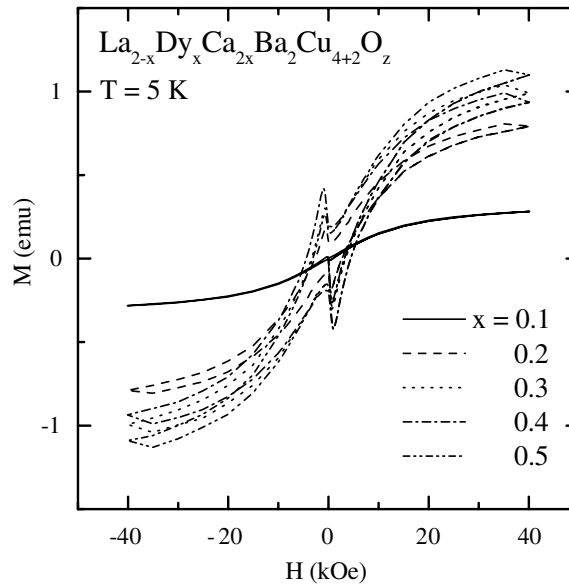


Figure 5. Hysteresis loops for $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ ($x = 0.1-0.5$) samples measured at 5 K.

the sweeping field. These $M-H$ loops were used to calculate the critical current density (J_c expressed in A cm^{-2}), given by Bean's critical state model and expressed as

$$J_c = \frac{30 [M^+ - M^-]}{D} \quad (1)$$

where M^+ and M^- are the values of the magnetization observed during the up and down cycles of the field sweeping [21, 22]. D is the average grain size calculated from the SEM micrographs and has been taken as $\sim 2 \times 10^{-4}$ cm. Figure 6 shows the variation of J_c with the applied field. With increasing x , J_c increases up to $x = 0.4$ and then decreases slightly. Thus $x = 0.4$ can be taken as the optimum doping level up to which J_c increases and enhances the flux pinning (F_p), which is the product of J_c and H at a particular temperature.

The Dy^{3+} moment at low temperature has no influence on the superconducting properties. This is obvious because in the La-2125 unit cell La site is far removed from the Cu-O plane and therefore the magnetic moment has no influence.

4. Discussion

Superconductivity in the orthorhombic RE-123 oxides is manifested by the 'transfer of holes' from the *charge reservoir* Cu-O chain to the conductive Cu-O₂ sheets, but the conduction of charge carriers between two conducting CuO₂ layers in tetragonal Ca doped RE-123 phases should be different since there are no chains in the tetragonal 1-2-3 phase. The Ca cations at the RE site in RE-123 systems introduce the necessary holes between the two CuO₂ sheets which couple the conductive sheets in the tetragonal 1-2-3 phases; this is called 'bridging' of the CuO₂ sheets.

The substitution of Ca^{2+} at La^{3+} sites leads to the creation of holes at La^{3+} sites, which bridges the two CuO₂ sheets resulting in the 'turning on' of the superconductivity in the LDBO (La-2125 type) system studied here. The results of Rietveld analysis show an increase in Ca^{2+}

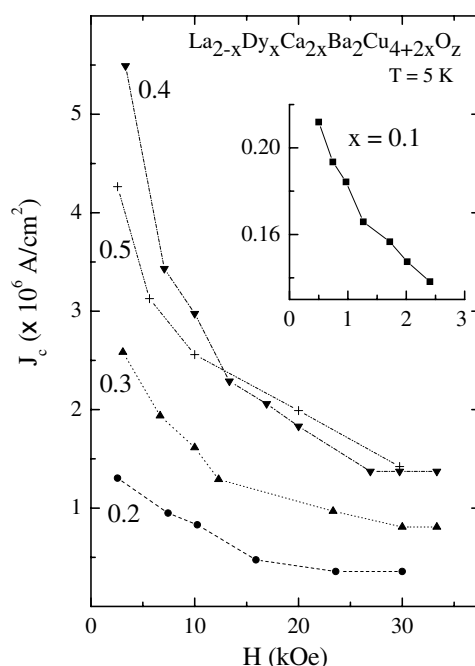


Figure 6. Critical current density (J_c) as a function of varying field for $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ ($x = 0.1-0.5$) compounds calculated at 5 K. The inset shows J_c versus H for the $x = 0.1$ sample.

content at the La^{3+} site, which is reflected in an increase in the hole concentration. This, in the LDBO system, is supported by the iodometric titration results also (figure 4). Thus, we can confidently attribute the increase in superconducting transition temperature to the increase in the concentration of Ca^{2+} at La^{3+} sites, which helps in increasing the mobile charge carrier concentration.

The local charge environment in the CuO-LaO-CuO layer (the perovskite block) is affected by Ca doping. The bridging of the CuO_2 planes by Ca^{2+} substitution leads to the shortening of the bond lengths in the perovskite block, as a result of which the unit cell volume also decreases. Defects introduced in the Cu-O_2 planes due to substitution of Ca^{2+} for La^{3+} (i.e., an extra hole) result in the conduction of charge carriers through this bridged path. The bridging of two Cu-O layers causes buckling of the conducting plane and results in the creation of centres for flux trapping, which can be attributed to the simultaneous increase in T_c , J_c and F_p with increasing dopant concentration.

5. Conclusion

Superconductivity is induced in a non-superconducting $\text{La}_2\text{Ba}_2\text{Cu}_4\text{O}_z$ phase by simultaneous addition of CaO and CuO along with Dy^{3+} substitution. Dy^{3+} has been found to stabilize the crystal structure, and have no pronounced effect on the superconducting transition temperature. Ca^{2+} substitution helps in inducing superconductivity by creating holes at La^{3+} sites, resulting in the bridging of the two conductive CuO_2 sheets. The maximum T_c which has been achieved for the LDBO system is 75 K, and this can be correlated with the optimum hole concentration value. We observe here that Ca^{2+} plays a significant role in introducing superconductivity in

the $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ system and creating 'pinning centres' by the addition of extra holes, which results in increases of the critical current density and flux pinning but without inducing any structural transition.

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