

# Effect of calcium substitution on superconductivity and hole concentration in $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$

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**Abstract.** The superconducting properties of single phase  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$ ,  $0.0 \leq x \leq 0.60$  (LC) and  $0.0 \leq y \leq 0.70$  (CB), compounds with tetragonal triple-perovskite structure are studied, using X-ray diffraction for their resistivity, a.c. susceptibility, and oxygen-content.  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  (LC) samples,  $0.15 \leq x \leq 0.60$ , are superconducting with  $T_c^{R=0}$  between 40 and 74 K. With the increase in  $x$ , the oxygen content, hole concentration in the  $\text{CuO}_2$  layers as well as the  $T_c$  increase. It is interesting to find that although the hole concentration and oxygen stoichiometry of the  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  (CB) compounds increase with the increase in  $y$ , the  $T_c^{R=0}$  remains nearly constant around 74 K for  $y=0.0-0.70$ . A correlation exists between the  $T_c$  and the hole concentration for LC and CB compounds.

**Keywords.** Perovskite structure; oxygen content; hole concentration.

## 1. Introduction

The superconducting system  $\text{LaCaBaCu}_3\text{O}_z$  (abbreviated as La-1113) has been the subject of many investigations (De Leeuw *et al* 1988; Fu *et al* 1988; Engelsberg 1991; Gunasekaran *et al* 1993; Leu *et al* 1996; Yuan *et al* 1996), as it can be synthesized by following different stoichiometric compositions as the starting material. This La-1113 has a superconducting transition temperature ( $T_c$ ) of nearly 80 K, with a tetragonal triple-perovskite structure similar to tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Y-123) (Katano *et al* 1987).

Recently it has been observed (Leu *et al* 1996; Yuan *et al* 1996) that a simultaneous substitution by Ca or Sr for La as well as Ba in the  $\text{La}_{1.5-x/2}(\text{Ca/Sr})_x\text{Ba}_{1.5-x/2}\text{Cu}_3\text{O}_z$  exhibits superconductivity for  $0.15 \leq x \leq 0.8$  showing maximum  $T_c$  of 78 K for Ca and 48 K for Sr at  $x=0.45-0.75$ . To date no attempt has been made to approach La-1113 superconducting phase by replacing La by Ca in the  $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  nonsuperconductor as  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  up to  $x=0.5$  (LC), and then substituting Ca for Ba in  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  (CB).

In this paper, we report the syntheses of  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  ( $x=0.0-0.60$ ) (LC) and  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  ( $y=0.0-0.70$ ) (CB) systems. These systems are studied by X-ray diffraction for their oxygen stoichiometry, a.c. susceptibility, and resistivity. The inter-relationship between the superconductivity, dopant valency and variation in their oxygen content is dis-

cussed in relation to the hole concentration in these systems.

## 2. Experimental

A series of compounds having the compositions  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  ( $x=0.0-0.60$ ) and  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  ( $y=0.0-0.70$ ) were prepared by solid state route under identical conditions. Stoichiometric quantities of finely powdered  $\text{La}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$ , and  $\text{CaCO}_3$  (all 99.98% pure) were thoroughly mixed and heated in air at 950°C for 24 h in a platinum crucible. This reacted powder was reground and reheated in air at 950°C for further 24 h to obtain a homogeneous single phase sample. The black product obtained was pulverized and cold-pressed into pellets which were sintered at 950°C for 12 h in oxygen atmosphere, followed by slow cooling at the rate of 5°C min<sup>-1</sup> until it reached room temperature. To obtain oxygenated samples, these pellets were annealed under oxygen flow at 500°C for 24 h, followed by a slow cooling at the rate of 1°C min<sup>-1</sup> until it reached room temperature.

All samples were characterized at room temperature by X-ray diffraction using  $\text{CuK}\alpha$  radiation. The X-ray analysis revealed that all the samples were indeed single phase. The stoichiometric composition of the constituents in the samples was confirmed by EDAX analysis using JEOL scanning electron microscope. The oxygen stoichiometry of the samples was determined by iodometric titration technique. Resistivity was measured as

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a function of temperature on regularly-shaped samples, using the standard four-probe method. The a.c. susceptibility measurements were accomplished in a system with a lock-in-amplifier, and an APD cryocooler.

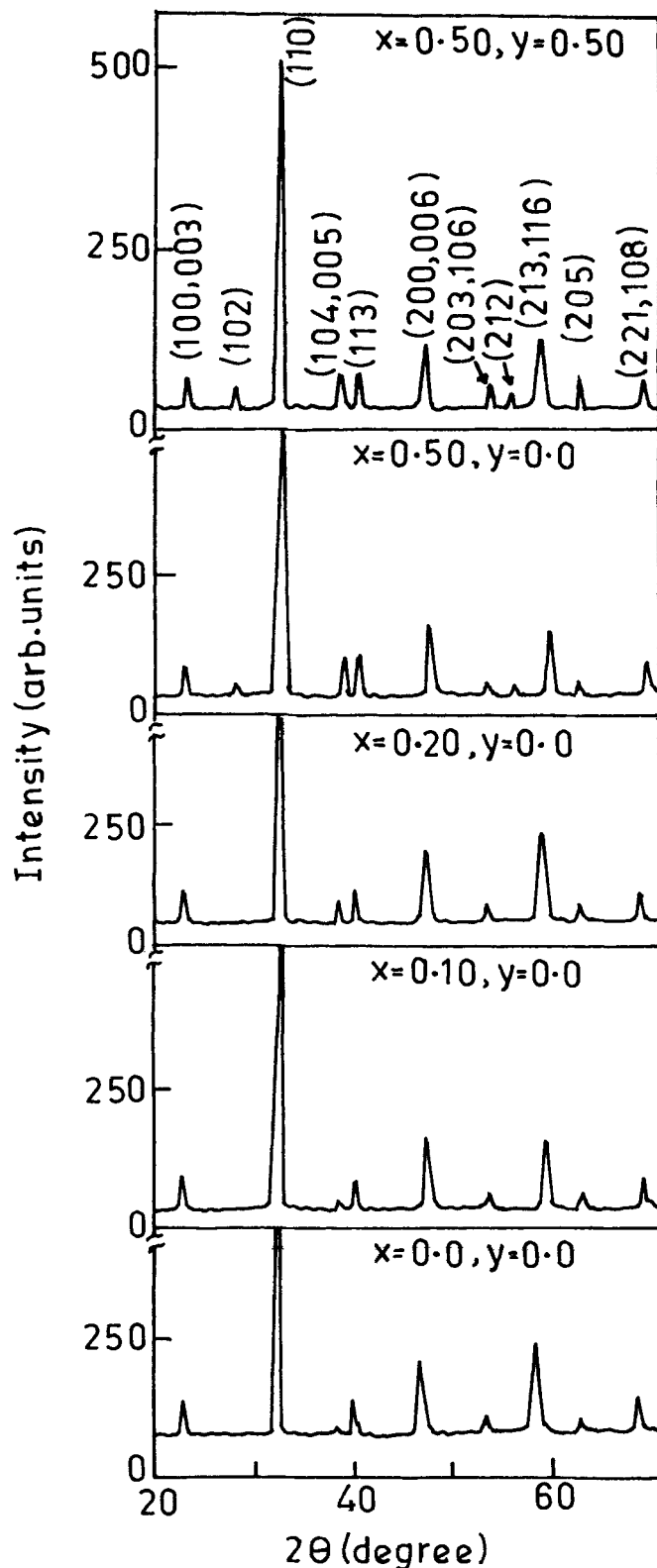
### 3. Results and discussion

Single phase materials were obtained between  $0.0 \leq x \leq 0.60$ , and  $0.0 \leq y \leq 0.70$  for LC and CB systems, respectively, as shown by the XRD patterns. Figure 1 shows the typical XRD patterns of  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  (LC) for  $x=0.0, 0.10, 0.20, 0.50$ , and  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  (CB) for  $y=0.50$ . The observed X-ray diffraction peaks modelled by modified Gaussian functions and refined unit cell parameters, and calculated using the standard least squares programme, are listed in table 1 for LC and CB samples. All the LC and CB samples maintain a tetragonal triple-perovskite structure. The  $a$  and  $c$  parameters and the unit cell volume decrease with increasing concentration,  $x$  (table 1), because  $\text{La}^{3+}$  with larger ionic radius ( $1.02 \text{ \AA}$ ) is replaced by the smaller  $\text{Ca}^{2+}$  ionic radius ( $0.99 \text{ \AA}$ ) in LC. Likewise, the  $a$  and  $c$  parameters as well as the unit cell volume of CB samples decrease with increasing Ca content,  $y$ , (table 1), as  $\text{Ba}^{2+}$  ion with larger ionic radius ( $1.34 \text{ \AA}$ ) is replaced by the smaller  $\text{Ca}^{2+}$  ion ( $0.99 \text{ \AA}$ ). Similar results have been reported for the  $\text{La}_{4-x}\text{Ca}_x\text{Ba}_3\text{Cu}_7\text{O}_z$  (Wu *et al* 1993a),  $\text{La}_3\text{Ba}_{4-x}\text{Ca}_x\text{Cu}_7\text{O}_z$  (Wu *et al* 1993b), and  $\text{La}_{3-x}\text{Ca}_x\text{Ba}_{3-x}\text{Cu}_6\text{O}_z$  (Leu *et al* 1996) series.

The values of oxygen content,  $z$ , of the LC and CB samples, as determined by an iodometric titration technique, are listed in table 2. The effective Cu valence ( $2+p$ ) or the hole concentration ( $p$ ) per  $[\text{Cu}-\text{O}]$  unit was calculated from these data and is included in table 2. It is evident from table 2 that the oxygen content ( $z$ ) as well as the hole concentration ( $p$ ) of LC and CB series increase with the increasing Ca concentration, suggesting that  $\text{Ca}^{2+}$  acts as a hole dopant. The oxygen stoichiometry of LC and CB compounds results from two counter-balanced effects: charge balance and hole doping.

Thus, increasing  $\text{Ca}^{2+}$  ( $0.99 \text{ \AA}$ ) ion substitution for  $\text{La}^{3+}$  ( $1.02 \text{ \AA}$ ) ions results in a decrease in the positive charge, which can be compensated to some extent by increasing the holes which leads to the net increase in the oxygen stoichiometry, as observed. A noteworthy fact is that while both  $p$  and  $z$  of LC and CB series increase with the increase in Ca concentration similar to  $\text{La}_3\text{Ba}_{4-x}\text{Ca}_x\text{Cu}_7\text{O}_z$  (Wu *et al* 1993b), for  $\text{La}_{1.5-x/2}\text{Ca}_x\text{Ba}_{1.5-x/2}\text{Cu}_3\text{O}_z$  (Leu *et al* 1996),  $\text{La}_{1.5-x/2}\text{Sr}_x\text{Ba}_{1.5-x/2}\text{Cu}_3\text{O}_z$  (Yuan *et al* 1996), and  $\text{La}_{4-x}\text{Ca}_x\text{Ba}_3\text{Cu}_7\text{O}_z$  (Wu *et al* 1993a) series,  $p$  increases and  $z$  decreases.

Typical resistivity results of LC and CB samples are given in figures 2 and 3, respectively. The resistive superconducting transition temperatures at zero resistance,



**Figure 1.** XRD patterns of  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  (LC) for  $x=0.0, 0.1, 0.2, 0.5$  and  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  (CB) for  $y=0.5$ .

**Table 1.** Values of unit cell parameters, unit cell volume and density of  $\text{La}_{1.5-x}\text{Ba}_{1.5-y}\text{Ca}_{x+y}\text{Cu}_3\text{O}_z$  system.

Sample (x, y)	Unit cell parameters (Å)		Volume, V (Å <sup>3</sup> )	X-ray density (g/cm <sup>3</sup> )
	a, b	c		
(0.00, 0.00)	3.926(3)	11.753(9)	181.1546(11)	6.503(3)
(0.10, 0.00)	3.908(3)	11.736(9)	179.2376(11)	6.488(3)
(0.15, 0.00)	3.899(3)	11.732(9)	178.3522(11)	6.486(3)
(0.20, 0.00)	3.891(3)	11.726(9)	177.5302(11)	6.478(3)
(0.25, 0.00)	3.888(3)	11.720(9)	177.1659(11)	6.448(3)
(0.35, 0.00)	3.885(3)	11.703(9)	176.6360(11)	6.382(3)
(0.40, 0.00)	3.884(3)	11.693(9)	176.3942(11)	6.348(3)
(0.45, 0.00)	3.881(3)	11.686(9)	176.0164(11)	6.314(3)
(0.50, 0.00)	3.878(3)	11.666(9)	175.4436(11)	6.294(3)
(0.60, 0.00)	3.899(3)	11.701(9)	177.8809(11)	6.099(3)
(0.50, 0.10)	3.874(3)	11.654(9)	174.9018(11)	6.228(3)
(0.50, 0.20)	3.867(3)	11.640(9)	174.0609(11)	6.169(3)
(0.50, 0.30)	3.863(3)	11.631(9)	173.5667(11)	6.098(3)
(0.50, 0.40)	3.858(3)	11.613(9)	172.8498(11)	6.041(3)
(0.50, 0.50)	3.850(3)	11.560(9)	171.3481(11)	5.995(3)
(0.50, 0.60)	3.824(3)	11.483(9)	167.9156(11)	5.982(3)
(0.50, 0.70)	3.803(3)	11.419(9)	165.1508(11)	5.984(3)

**Table 2.** Values for oxygen content, hole concentration and  $T_c$  of  $\text{La}_{1.5-x}\text{Ba}_{1.5-y}\text{Ca}_{x+y}\text{Cu}_3\text{O}_z$  system.

Sample (x, y)	Resistivity $T_c^{R=0}$ (K)	A.C. susceptibility $T_c^{\text{ON}} (\chi_{ac})$	Oxygen content (z)	Hole concentration (p)
(0.00, 0.00)	NS	NS	6.55(3)	0.033(3)
(0.10, 0.00)	NS	NS	6.59(3)	0.060(3)
(0.15, 0.00)	40(2)	43(2)	6.67(3)	0.113(3)
(0.20, 0.00)	45(2)	48(2)	6.72(3)	0.147(3)
(0.25, 0.00)	68(2)	70(2)	6.74(3)	0.160(3)
(0.35, 0.00)	69(2)	72(2)	6.79(3)	0.193(3)
(0.40, 0.00)	70(2)	72(2)	6.82(3)	0.213(3)
(0.45, 0.00)	71(2)	74(2)	6.81(3)	0.207(3)
(0.50, 0.00)	74(2)	76(2)	6.85(3)	0.233(3)
(0.60, 0.00)	70(2)	73(2)	6.74(3)	0.160(3)
(0.50, 0.10)	74(2)	76(2)	6.90(3)	0.267(3)
(0.50, 0.20)	73(2)	76(2)	6.92(3)	0.280(3)
(0.50, 0.30)	74(2)	75(2)	6.95(3)	0.300(3)
(0.50, 0.40)	75(2)	77(2)	7.02(3)	0.347(3)
(0.50, 0.50)	75(2)	78(2)	6.99(3)	0.327(3)
(0.50, 0.60)	71(2)	72(2)	7.05(3)	0.367(3)
(0.50, 0.70)	60(2)	66(2)	7.11(3)	0.406(3)

NS, Non superconducting

$T_c^{R=0}$ , obtained from figures 2 and 3 are listed in table 2. For  $x \leq 0.1$  LC samples, a metal to semiconducting type transition is observed. All the other LC samples ( $x = 0.15-0.60$ ) show a metallic conducting behaviour from 300 K to the superconducting transition temperature. For  $x = 0.0$  and 0.1 samples, no  $T_c$  is observed. For  $0.15 \leq x \leq 0.60$  samples,  $T_c^{R=0}$  is found between 40 K and 74 K (figure 2). In the case of CB series, all samples exhibit metallic to superconducting transitions with almost constant  $T_c^{R=0} \sim 74$  K for  $y = 0.1-0.5$ , and thereafter  $T_c^{R=0}$  decreases with increasing  $y$  for  $y = 0.5-0.7$  (table 2).

The temperature dependence of a.c. susceptibility for typical samples of both LC and CB are shown in figures 4 and 5, respectively. The onset critical temperature determined from a.c. susceptibility  $T_c^{\text{on}} (\chi_{ac})$  listed in table 2 agrees very well with the resistively found  $T_c^{R=0}$ . This shows the consistency of the measurements and the quality of samples.

Figure 6a shows  $T_c$  vs oxygen stoichiometry and figure 6b shows  $T_c$  vs hole concentration of the LC and CB series, respectively. A plateau is observed for  $T_c$  around 74 K. For the sake of comparison and completeness, we

have also shown in figure 6a the variation of  $T_c$  with oxygen stoichiometry in  $\text{La}_{1.5-x/2}\text{Ca}_x\text{Ba}_{1.5-x/2}\text{Cu}_3\text{O}_z$  (LCB) (Leu *et al* 1996) and  $\text{La}_{1.5-x/2}\text{Sr}_x\text{Ba}_{1.5-x/2}\text{Cu}_3\text{O}_z$  (LSB) (Yuan *et al* 1996), and in figure 6b the variation of  $T_c$  with hole concentration in LCB and LSB. The data for both the systems was taken from Leu *et al* (1996) and Yuan *et al* (1996).

It is evident from figure 6a that there is a disagreement between the increase of  $T_c$  with oxygen stoichiometries of LC, CB, LCB (Leu *et al* 1996) and LSB (Yuan *et al* 1996), respectively. According to present work,  $T_c^{R=0}$  of LC compounds increases with increasing  $z$  from 6.55 to 6.85, and  $T_c^{R=0}$  of CB compounds remains nearly constant

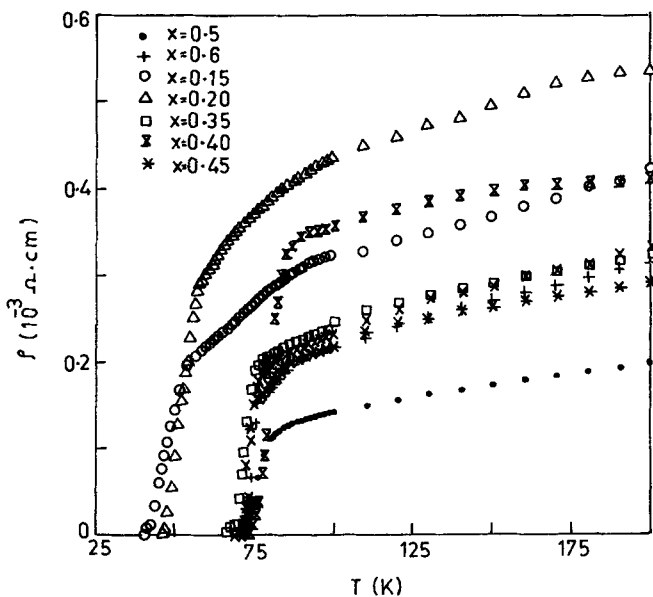


Figure 2. Resistivity vs temperature for  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$ .

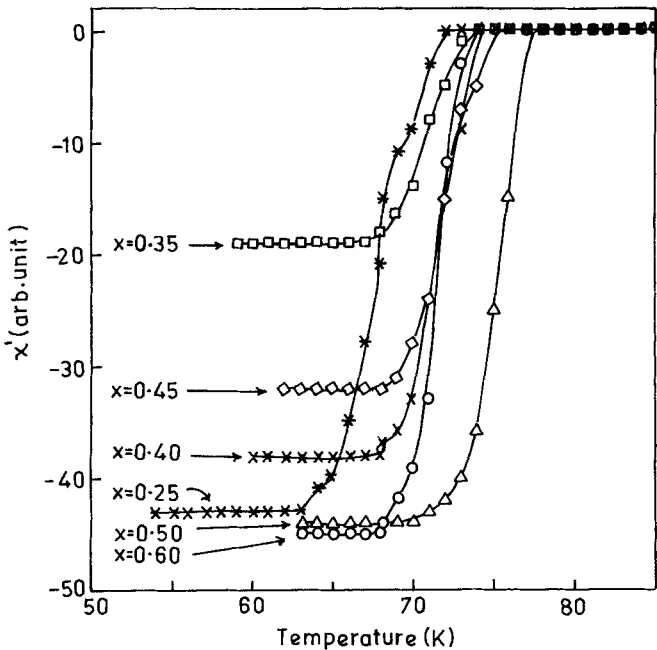


Figure 4. Temperature dependence of a.c. susceptibility for  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$ .

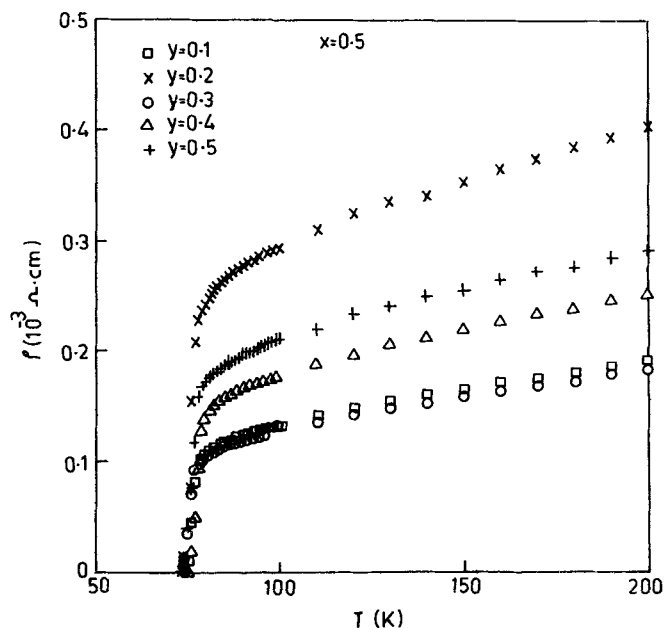


Figure 3. Resistivity vs temperature for  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$ .

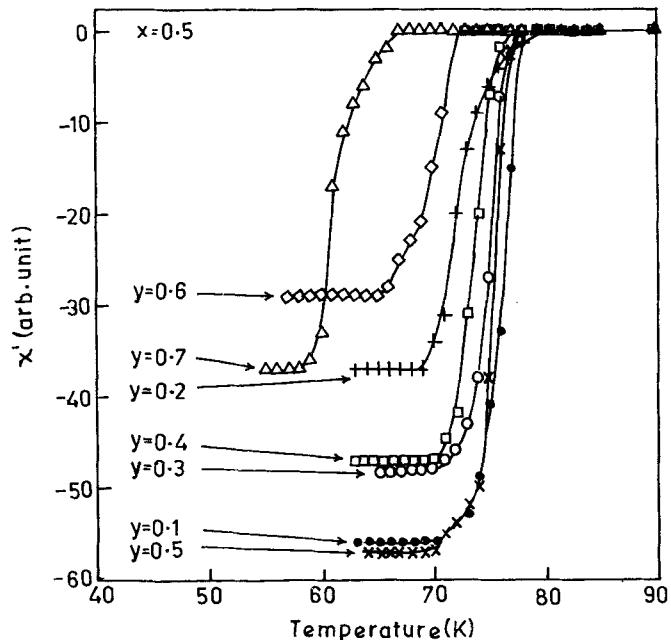


Figure 5. Temperature dependence of a.c. susceptibility for  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$ .

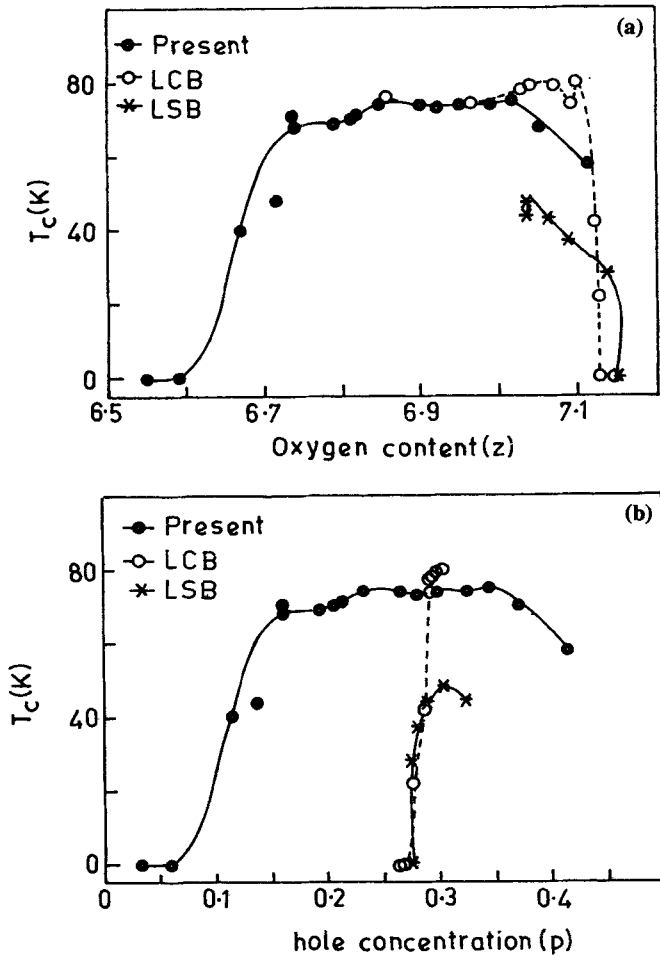
despite increase in  $z$  from 6.85 to 7.02, and thereafter it decreases. In contrast, the  $T_c^{R=0}$  of LCB (Leu *et al* 1996) and LSB (Yuan *et al* 1996) compounds increases with decreasing  $z$  from 7.15 to 7.04 (figure 6a). There is a similarity in the increase of  $T_c$  with hole concentration among LC, CB, LCB (Leu *et al* 1996) and LSB (Yuan *et al* 1996) series though the actual variation in  $p$  is different for all the compounds.

The lanthanum stoichiometry of LC series is reduced from 1.50 to 0.90 as  $x$  increases from 0.0 to 0.60. Since the lanthanum stoichiometry is greater than one and there is only one  $\text{Y}^{3+}$  site in a  $\text{YBa}_2\text{Cu}_3\text{O}_z$  triple-perovskite unit cell, some of the  $\text{La}^{3+}$  ions must occupy the  $\text{Ba}^{2+}$  site for all the LC compounds. As shown in table 2, the hole concentration increases with decreasing lanthanum stoichiometry up to  $x=0.50$  and thereafter it decreases for  $x=0.60$ , being off stoichiometry in the LC series.

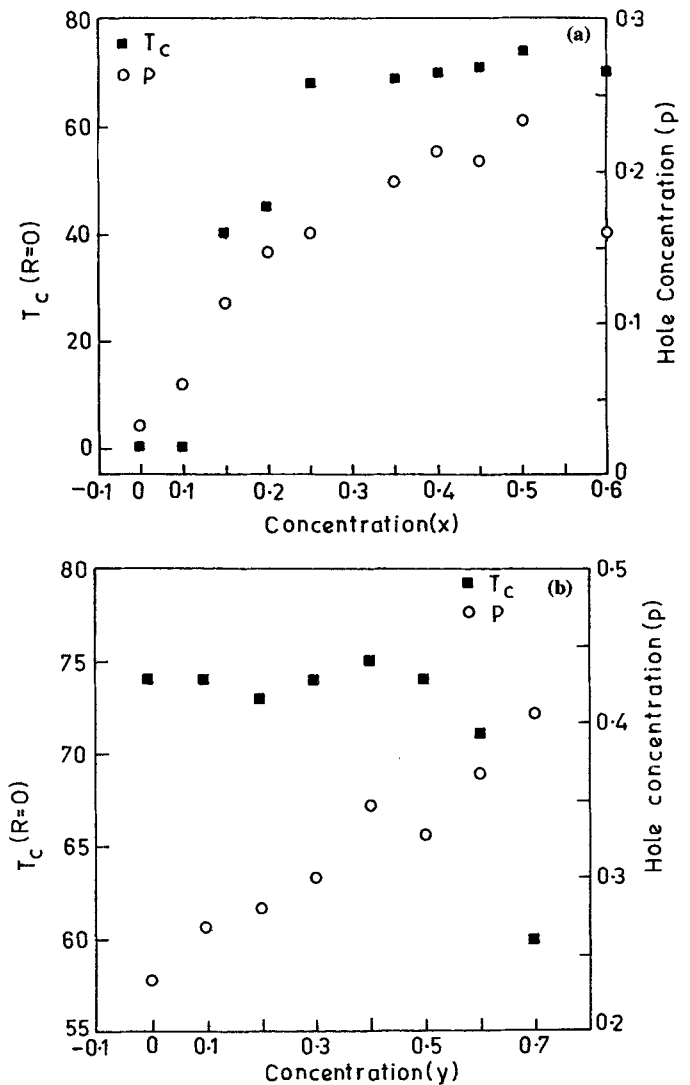
Similar trend is observed for  $T_c^{R=0}$  vs lanthanum stoichiometry (table 2). The  $T_c^{R=0}$  of  $x=0.6$  samples decreases from 74 K to 70 K due to decrease in  $p$  and

$z$ . In other words, the hole concentration increases as the amount of  $\text{La}^{3+}$  ions in the  $\text{Ba}^{2+}$  site decreases up to  $x=0.5$ .

In order to demonstrate the effect of Ca substitution in  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  on the correlation between superconductivity and hole concentration ( $p$ ), we have shown in figure 7,  $T_c$  and  $p$  vs Ca concentration ( $x$  or  $y$ ). It is evident from figure 7a that both  $T_c$  and  $p$  for LC series increase with increasing  $x$  up to  $x=0.5$  showing a correlation between  $T_c$  and  $p$ . For the CB series,  $p$  increases with increasing  $y$  up to 0.70 (figure 7b), while  $T_c$  remains nearly constant up to  $y=0.50$  and thereafter it decreases for  $y>0.5$  due to excess hole doping beyond an optimum value of 0.333 (table 2). This clearly shows that Ca acts, in both LC and CB series, as hole dopant.



**Figure 6.** a.  $T_c$  vs oxygen stoichiometry ( $z$ ) for LC, CB, LCB<sup>5</sup> and LSB<sup>6</sup> series and b.  $T_c$  vs hole concentration ( $p$ ) for LC, CB, LCB<sup>5</sup> and LSB<sup>6</sup> series.



**Figure 7.** a.  $T_c$  and hole concentration ( $p$ ) vs  $x$  for  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  and b.  $T_c$  and hole concentration ( $p$ ) vs  $y$  for  $\text{LaCa}_{0.5+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$ .

The observed increase in  $T_c^{R=0}$  by Ca substitution in  $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  is explained on the basis of the oxygen effect, assuming it is real. The oxygen content,  $z$ , of a superconductor is directly related to the hole concentration  $p$ , which controls the superconductivity. The concentration of holes can be varied by varying the Ca doping concentration. It is evident from figure 6a that  $T_c^{R=0}$  increases from 0 to 75 K as  $z$  increases from 6.55 to 7.02 with corresponding increase of  $x$  and  $y$  from 0.0 to 0.50 (table 2). The trend is clear: both oxygen content as well as hole concentration increase as the samples are doped with higher concentrations of  $\text{Ca}^{2+}$  for  $\text{La}^{3+}$ , and  $\text{Ba}^{2+}$ . The  $T_c^{R=0}$  of LC and CB series increases with increasing  $x$  and  $y$ , as  $p$  increases up to the optimum value of 0.340 at  $x+y=0.50+0.40=0.90$ . Our results of LC series agree with the  $T_c$  oxygen content behaviour observed in orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , in which  $T_c$  increases with increasing oxygen content from 6.50 to 6.85 (Mckinnon *et al* 1988).

#### 4. Conclusions

Reducing the lanthanum stoichiometry in the  $\text{La}_{1.5-x}\text{Ca}_x\text{Ba}_{1.5}\text{Cu}_3\text{O}_z$  compounds, the amount of  $\text{La}^{3+}$  ions in the  $\text{Ba}^{2+}$  site is reduced, resulting in an increase in oxygen stoichiometry and hole concentration of the superconducting  $\text{CuO}_2$  layers. As a result, only one superconducting single phase, with tetragonal triple-perovskite structure, is observed for  $0.0 \leq x \leq 0.60$  which shows an increase in  $T_c^{R=0}$  from 0 to 74 K as  $x$  increases from 0.0 to 0.50. The superconductivity of the  $\text{La}_{1.5-x}\text{Ca}_{x+y}\text{Ba}_{1.5-y}\text{Cu}_3\text{O}_z$  compounds is found to correlate with the hole concentration for  $0.0 \leq x \leq 0.60$  and  $0.0 \leq y \leq 0.70$ .

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