Effect of calcium substitution on superconductivity and hole concentration in La$_{1.5}$Ba$_{1.5}$Cu$_3$O$_7$

NIKESH A SHAH, D G KUBERKAR, B T SAVALIA, M R GONAL$^1$, RAM PRASAD$^1$ and R G KULKARNI$^*$

Department of Physics, Saurashtra University, Rajkot 360005, India

$^1$Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract. The superconducting properties of single phase La$_{1.5-x}$Ca$_{x+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ $(0 \leq x \leq 0.60)$ (LC) and $0 \leq y \leq 0.70$ (CB), compounds with tetragonal triple-perovskite structure are studied, using X-ray diffraction for their resistivity, a.c. susceptibility, and oxygen-content. La$_{1.5-x}$Ca$_{x+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ (LC) samples, $0.15 \leq x \leq 0.60$, are superconducting with $T_c = 0$ between 40 and 74 K. With the increase in $x$, the oxygen content, hole concentration in the 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 LaCa$_{0.5+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ (CB) compounds increase with the increase in $y$, the $T_c$ 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 LaCaBaCu$_3$O$_7$ (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 YBa$_2$Cu$_3$O$_7.6$ $(Y=123)$ (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 La$_{1.5-x}$Ca$_x$Sr$_x$Ba$_{1.5-x}$Cu$_3$O$_7$ 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 La$_{1.5}$Ba$_{1.5}$Cu$_3$O$_7$ nonsuperconductor as La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_7$ up to $x = 0.5$ (LC), and then substituting Ca for Ba in LaCa$_{0.5+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ (CB).

In this paper, we report the syntheses of La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_7$ $(x = 0.0-0.60)$ (LC) and LaCa$_{0.5+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ $(y = 0.0-0.70)$ (CB) systems. These systems are studied by X-ray diffraction for their oxygen stoichiometry, a.c. susceptibility, and resistivity. The interrelationship between the superconductivity, dopant valency and variation in their oxygen content is discussed in relation to the hole concentration in these systems.

2. Experimental

A series of compounds having the compositions La$_{1.5-x}$Ca$_x$Ba$_{1.5}$Cu$_3$O$_7$ $(x = 0.0-0.60)$ and LaCa$_{0.5+y}$Ba$_{1.5-y}$Cu$_3$O$_7$ $(y = 0.0-0.70)$ were prepared by solid state route under identical conditions. Stoichiometric quantities of finely powdered La$_2$O$_3$, BaCO$_3$, CuO, and 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 powders 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$^{-1}$ 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$^{-1}$ until it reached room temperature.

All samples were characterized at room temperature by X-ray diffraction using 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...
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 \(\text{La}_{0.5-x}\text{Ca}_x\text{Ba}_3\text{Cu}_3\text{O}_7\) (LC) for \(x=0.0, 0.10, 0.20, 0.50\), and \(\text{LaCa}_{0.65}\text{Ba}_{0.35-y}\text{Cu}_3\text{O}_7\) (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 Å) is replaced by the smaller \(\text{Ca}^{2+}\) ionic radius (0.99 Å) in LC. Likewise, the \(a\) and \(c\) parameters as well as the unit cell volume of CB samples decrease with increasing \(\text{Ca}\) content, \(y\), (table 1), as \(\text{Ba}^{2+}\) ion with larger ionic radius (1.34 Å) is replaced by the smaller \(\text{Ca}^{2+}\) ion (0.99 Å). Similar results have been reported for the \(\text{La}_{0.5-x}\text{Ca}_x\text{Ba}_3\text{Cu}_3\text{O}_7\) (Wu et al 1993a), \(\text{LaCa}_{0.65}\text{Ba}_{0.35-y}\text{Cu}_3\text{O}_7\) (Wu et al 1993b), and \(\text{La}_{0.5-x}\text{Ca}_x\text{Ba}_3\text{Cu}_3\text{O}_7\) (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 \([\text{Cu-O}]\) 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 \(\text{Ca}\) 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 Å) ion substitution for \(\text{La}^{3+}\) (1.02 Å) 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 \(\text{Ca}\) concentration similar to \(\text{LaCa}_{0.65}\text{Ba}_{0.35}\text{Cu}_3\text{O}_7\) (Wu et al 1993b), for \(\text{La}_{0.5-x}\text{Sr}^{2+}\text{Ba}_{0.5-x}\text{Cu}_3\text{O}_7\) (Leu et al 1996), \(\text{La}_{0.5-x}\text{Sr}^{2+}\text{Ba}_{0.5-x}\text{Cu}_3\text{O}_7\) (Yuan et al 1996), and \(\text{La}_{0.5-x}\text{CaCa}_x\text{Cu}_3\text{O}_7\) (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 \(\text{La}_{0.5-x}\text{Ca}_x\text{Ba}_3\text{Cu}_3\text{O}_7\) (LC) for \(x=0.0, 0.1, 0.2, 0.5\) and \(\text{LaCa}_{0.65}\text{Ba}_{0.35-y}\text{Cu}_3\text{O}_7\) (CB) for \(y=0.5\).](image-url)