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Structure and electrical properties of lanthanum doped $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ superconductor

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Abstract

In this work we studied the effect of La-doping on phase purity, crystal structure and electrical resistivity of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ superconductor, synthesized by usual solid state reaction method. The X-ray florescence (XRF) show the stoichiometry of samples and X-ray diffraction (XRD) analysis showed the change of structure from orthorhombic to tetragonal by increasing La doping. It was found that the change of lanthanum concentrations of all our samples produce a change in the oxygen content, the ratio of lattice parameters c/a and mass density ρ_m. Electrical resistivity, using the four-probe technique, was used to find the critical temperature T_c and to put in evidence metallic and semiconducting behavior in normal state.

Key Words: Superconductors, electrical resistivity, critical temperature

1. Introduction

After the first discovery of the superconducting ceramic system La-Ba-Cu-O with critical transition temperature between (30–40) K, other families of copper-oxide based ceramics have been synthesized with higher critical temperatures ("high T_c") [1]. These oxides include the Bi-Sr-Ca-Cu-O series (T_c = 80–110 K) [2]. Bi-2223 phase is represented as an interesting phase of the Bi-Sr-Ca-Cu-O system, because it has high superconducting critical temperature and a high critical current density [3]. S As such, Bi-2223 phase is one of the most promising materials for application in high magnetic field at liquid nitrogen temperature. Generally, Bi-2223 phase has been reported for the composition $Bi_2Sr_2Ca_2Cu_3\ O_{10+\delta}$ [4]. Substitutions of Pb, Sb and Cd into Bi-sites in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ have been studied [5–7]. It has been found that small addition of Pb enhances the transition temperature from 92 to 106 K, whereas addition of (Pb + Cd) to Bi-base increase the transition temperature from 85 to 110 K. Also, some properties of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ can be improved by partial substitution of Sr^{+2} into Ba^{+2} sites and Bi by Pb and Hg. These substitutions enhance the formation of Bi-2223 and improve the superconducting properties we found that the highest transition temperatures T_c were 125 and 129 K for $Bi_{1.75}Pb_{0.25}Sr_{1.9}Ba_{0.1}Ca_2Cu_3O_{10.26}$ and $Bi_{1.75}Hg_{0.25}Sr_{1.9}Ba_{0.1}Ca_2Cu_3O_{10.271}$, respectively [8].

In the present work we have successfully prepared $Bi_2Sr_2Ca_{1-x}La_xCu_3O_{10+\delta}$ bulk polycrystalline superconductor by used solid state reaction process. We analyze the structure and study the electrical properties of La-doped $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ superconductor synthesized at optimum conditions.

2. Experimental

The synthesis of Bi-2223 samples with chemical formula $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ have been performed by solid state reaction method using appropriate stoichiometric weights of pure powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, La_2O_3 and CuO, as starting materials, according to the general chemical formulas:

$$\text{first step: } 2\ SrCO_3 + (2\text{-}x)\ CaCO_3 + 3\ CuO \rightarrow Sr_2Ca_{2-x}Cu_3O_7 + 4\ CO_2$$

$$\text{second step: } 2\ Bi_2O_3 + x\ La_2O_3 + 2\ Sr_2Ca_{2-x}Cu_3O_7 \rightarrow 2\ Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$$

The weight of each reactant was measured by using a sensitive balance. The synthesis of the samples have been carried out by three step precursor method. In the first step, powders of $SrCO_3$, $CaCO_3$ and CuO were mixed together by using an agate mortar. A sufficient quantity of 2-propane was used to homogenize the mixture and to form slurry during the process of grinding for about 30–50 minutes. The mixture was dried in an oven at 250 $^\circ$C. The mixture was put in furnace equipped with a programmable controller, for calcinations, to remove CO_2 gas from the mixture. For this process the powder was heated to temperature of 800 $^\circ$C for three hours with a rate of 200 $^\circ$C/hr, then cooled to room temperature by the same rate of heating. In the second step, the $Sr_2Ca_{2-x}Cu_3O_7$ precursor was mixed with La_2O_3 and Bi_2O_3 to obtain the nominal compositions $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ for $x = 0.0$, 0.5, 1.0 and 1.5. The composition of prepared samples was checked by the powder XRF analysis in order to find the actual Bi/Sr/Ca/La/Cu ratio. The powder was pressed into disc-shaped pellets 1.2 cm in diameter and 0.2–0.3 cm thickness, using a hydraulic press operated to a pressure of 7 ton/cm^2. The pellets were presintered in air at 855–860 $^\circ$C for 6 hours with a circulation rate of 300 $^\circ$C /hr, then cooled to room temperature at the same rate of cooling. In the third step, the pellets were reground, repressed and resintered in oxygen (oxygen replenishment rate 0.2 L /min) at the same range of temperature for further 6 hours and then cooled to 450 $^\circ$C and annealed in oxygen for 2 hours, then cooled to room temperature by same rate of heating. The ρ-T characteristics (resistivity as a function of temperature) of these samples were measured by means of a standard d.c. four-probe technique to investigate their superconducting state. The excess of oxygen content δ as well as for measuring the critical temperatures and the mass density ρ_M have been described elsewhere [9]. The structure of the prepared samples was obtained by using X-ray diffraction meter (XRD) measurements in θ-2θ arrangement, in a range from 20 to 60 degrees. A computer program based on Cohen's least square method [10], was used to calculate the lattice parameters a and c. The volume fraction of any phase (V_{phase}) in the sample was determined by using the relation

$$V_{\text{phase}} = \frac{\sum \Gamma a}{\sum \Gamma 1 + \sum \Gamma 2 + ... + \sum \Gamma n} \times 100,$$

where Γa is the XRD peak intensity of the phase which were determined, $\Gamma 1, \Gamma 2, \ldots \Gamma n$ are the peaks intensity of all XRD.

3. Results and discussion

The composition of the $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples was determined by X-ray florescence analysis (XRF), are shown in figure 1. XRF analysis of the samples shows that the ratio of Bi:Sr:Ca(La):Cu is about 2:2:2:3.

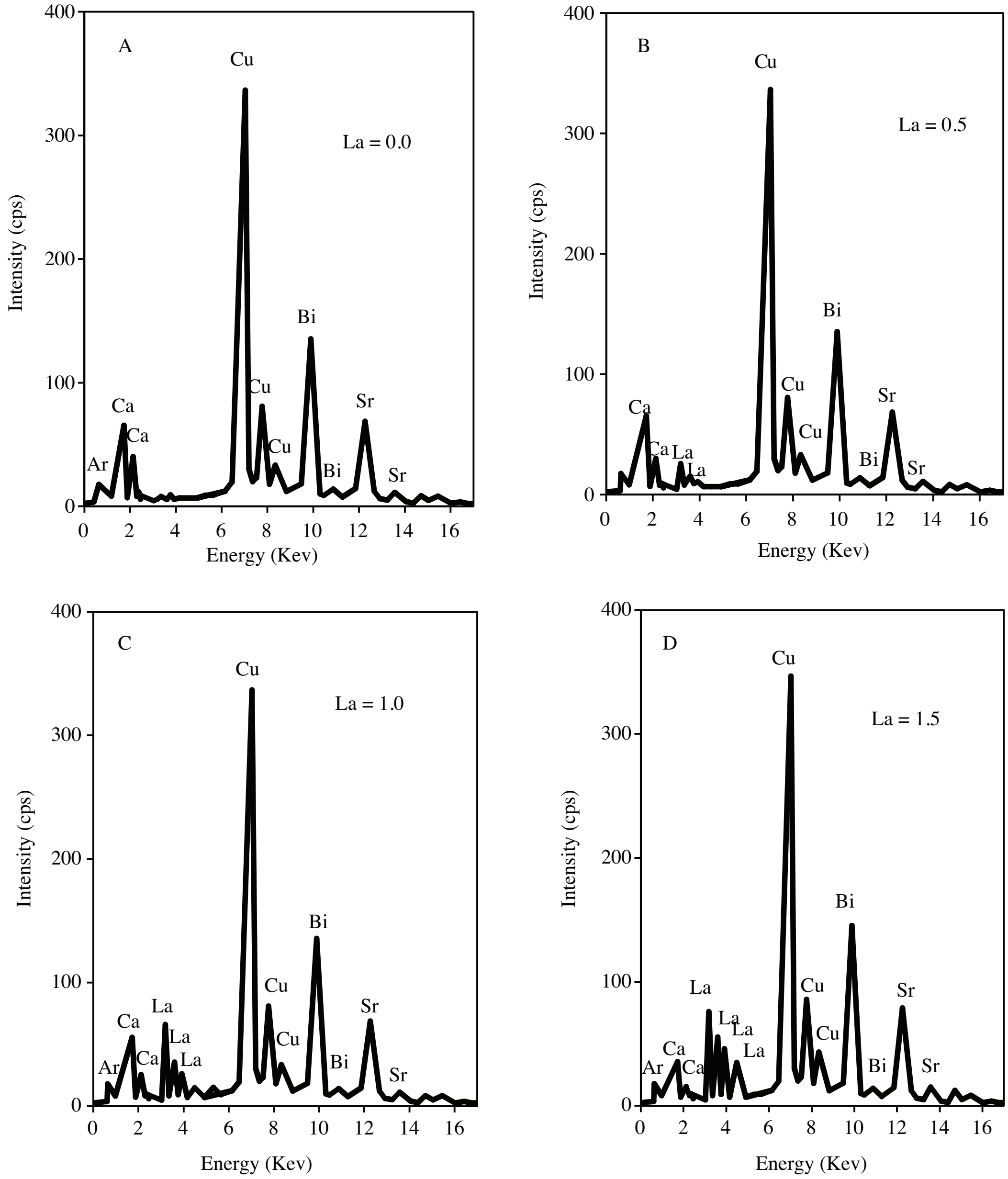

Figure 1. XRF patterns of the $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples (with x = 0.0, 0.5, 1.0 and 1.5 or samples A, B, C and D).

X-ray diffraction (XRD) patterns of the La-doped Bi-based superconductors are shown in Figure 2. The positions and intensities of the diffraction peaks reveals that our samples mainly consists of the a major

2223 phase (high T_c phase/H phase), minority 2212 phase (low T_c phase/L phase) and a small amount of a unidentified minor species. The comparison between the relative intensities of XRD patterns of the La doped samples with the relative intensities of the same reflections of the sample with $x = 0.0$ La shows a decrease of H-phase and increase of L-phase with increasing La doping. The lattice parameters of Bi-2223 phase were calculated by using the d-values and (hkl) reflections of the observed x-ray diffraction pattern through the software program based on Cohen's least square method. The obtained parameters a, b, c and the ratio c/a presented in the table shows orthorhombic structure for samples A, B and tetragonal structure for samples C and D, respectively. The c-axis lattice constant and c/a ratio increases with increasing lanthanum as compared with this has no lanthanum content,. This result may be explained by the larger ionic radius of La^{+3} (2.74 °) than that of Ca^{+2} (2.23 °).

Table. Values of critical transition temperature, lattice parameters (a, b, c, c/a), excess oxygen δ and mass density ρ_M for the $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples.

Samples	$T_{(off)}$ (K)	$T_{(on)}$ (K)	δ	a (Å)	b (Å)	c (Å)	c/a	ρ_M (g/cm^3)
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$	89	101	0.23	5.431	5.427	37.18	6.846	1.59
$Bi_2Sr_2Ca_{1.5}La_{0.5}Cu_3O_{10+\delta}$	109	117	0.18	5.411	5.412	37.29	6.891	1.56
$Bi_2Sr_2Ca_{1.0}La_{1.0}Cu_3O_{10+\delta}$	—	—	0.14	5.405	5.405	37.33	6.906	1.52
$Bi_2Sr_2Ca_{0.5}La_{1,5}Cu_3O_{10+\delta}$	—	—	0.07	5.401	5.401	37.35	6.915	1.51

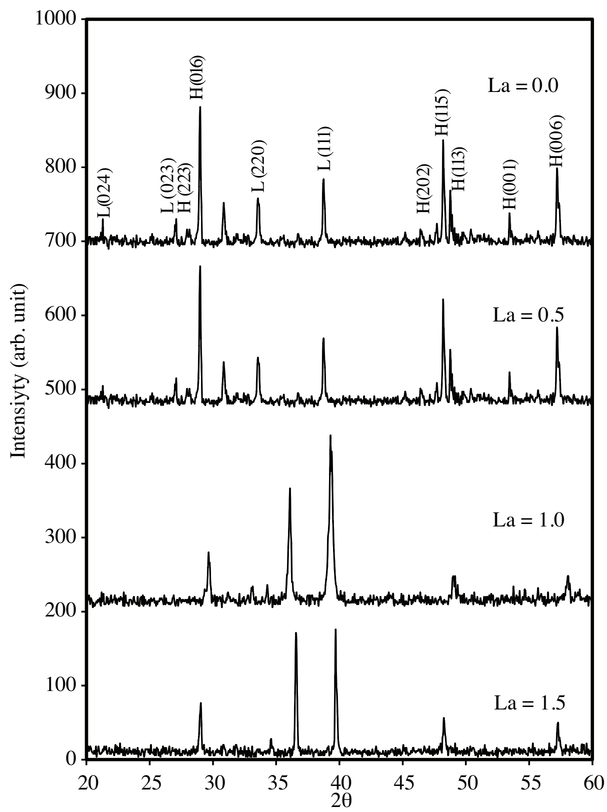

Figure 2. XRD patterns of $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples ($x = 0.0$, 0.5, 1.0 and 1.5).

Figure 3 and figure 4 shows the decreases of mass density ρ_M and excess oxygen (δ) with increasing La content, that will be decreasing the critical transition temperature $T_{c(on)}$ and $T_{c(off)}$. Because increasing of La content causes a decrease in the percentage of oxygen, which makes them less than an optimum value, which in turn gives the greatest value for the critical temperature, this may lead to the transfer of superconducting material to semiconducting.

The ratio of lattice parameter c/a increases with increasing La concentration (Figure 5). The deformation in the c-axis adjusts the amount of change Ca by La.

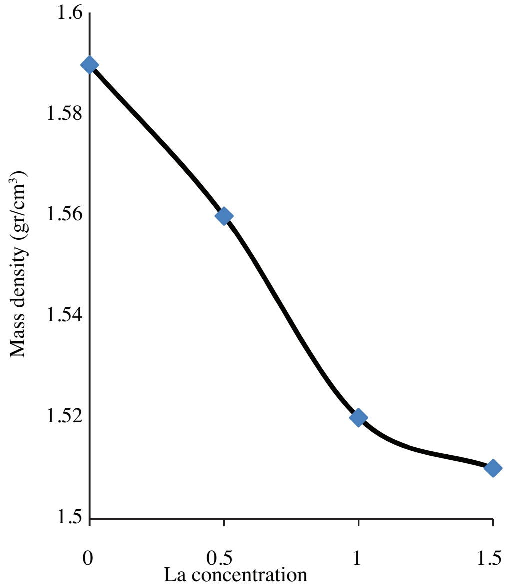

Figure 3. Mass density as function of La concentration for $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples.

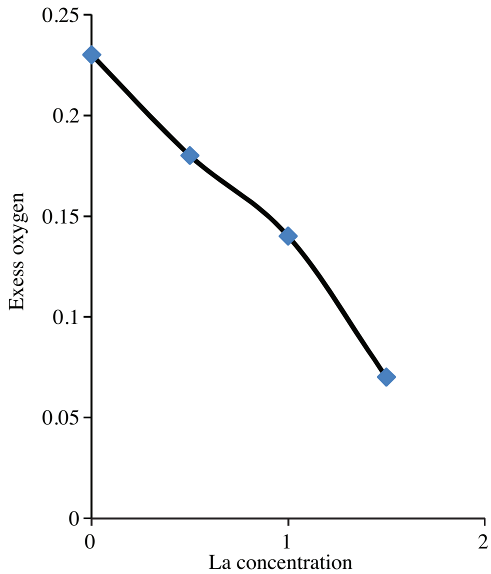

Figure 4. Excess oxygen as function of La concentration for $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples.

The temperature dependence of resistivity function of temperature for $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples (x = 0.0, 0.5, 1.0 and 1.5) is presented in Figure 6. By increasing La content, the normal state resistivity change from metal to semiconductor behavior.

Figure 6 show that at high temperature, samples $x = 0.0$ (sample A- $Bi_2Sr_2Ca_2Cu_3O_{10.23}$) and $x = 0.5$ (sample B-$Bi_2Sr_2Ca_{1.5}La_{0.5}Cu_3O_{10.18}$) presented in normal state metallic behavior, with critical transition temperature at zero resistance$T_{c(off)}$ = 109 and 89 K, and the transition temperature $T_{c(on)}$ = 101 and 117 K respectively. For the sample with x= 1.0 (sample C-$Bi_2Sr_2Ca_{1.0}La_{1.0}Cu_3O_{10.14}$) the superconducting transition is absent; but in the high temperature region electrical resistivity exhibits a metal behavior. Sample with x = 1.5 La (sample D- $Bi_2Sr_2Ca_{0.5}La_{1.5}Cu_3O_{10.07}$) exhibits a semiconductor behavior.

The critical temperatures at various lanthanum are summarized in the table. As shown in this table, the increase of lanthanum from x = 0.0 to 1.5 leads to decrease in critical temperatures.

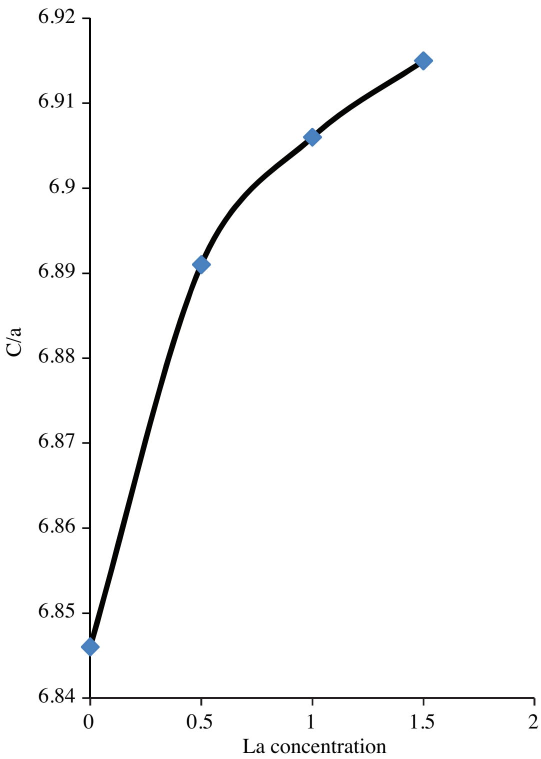

Figure 5. The ratio of lattice parameters c/a as function of La concentration for $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples.

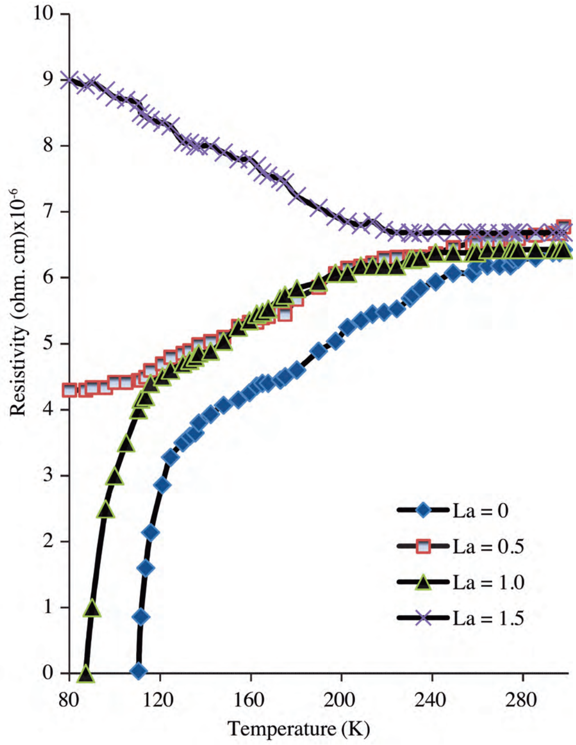

Figure 6. The resistivity as function temperature for $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ samples (x = 0.0, 0.5, 1.0, and 1.5).

4. Conclusions

Four Bi-based polycrystalline samples $Bi_2Sr_2Ca_{2-x}La_xCu_3O_{10+\delta}$ (x = 0.0, 0.5, 1.0 and 1.5) were synthesized by solid state reaction method. By increasing La concentration, the content of Bi-2223 phase (H -phase) decrease and the content of Bi-2212 phase (L-phase) increase. XRD analysis show orthorhombic structure for samples with x= 0.0 and x= 0.5 La and tetragonal structure for samples with x = 1.0 and x = 1.5 La, respectively. The increase of La concentration is the increase of the c-axis lattice constant. The mass density ρ_M and oxygen content δ decreases by increasing La content, and the ratio of lattice parameters c /a increases with increasing La concentration. The partial substitution of Ca with La lead to the decrease of critical transition temperature and the change from superconductor to insulating behavior of electrical resistivity functions of temperature.

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