

Effect of substitution of Ce on superconducting properties of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ system

R R KOTHAWALE^{1,*}, B N DOLE² and S S SHAH³

¹Department of Physics, Shri Shivaji College, Barshi, Solapur 413 411, India

²Department of Physics, P.E.S. College of Engineering, Aurangabad 431 002, India

³Department of Physics, Dr. B.A. Marathwada University, Aurangabad 431 004, India

*Email: rk19395@yahoo.com

Abstract. We have investigated the superconducting properties of the $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ system with $x = 0.00, 0.02, 0.04, 0.08$ and 0.1 by X-ray diffraction and magnetic susceptibility. The substitution of Ce for Ca has been found to drastically change the superconducting properties of the system. X-ray diffraction studies on these compounds indicate decrease in the c -parameter with increased substitution of Ce at Ca site and volume fraction of high T_c ($2 : 2 : 2 : 3$) phase decreases and low T_c phase increases. The magnetic susceptibility of this compound shows that the diamagnetic onset superconducting transition temperature (onset) varies from 109 K to 51 K for $x = 0.00, 0.02, 0.04, 0.08$ and 0.1 . These results suggest the possible existence of Ce in a tetravalent state rather than a trivalent state in this system; that is, $\text{Ca}^{2+} \rightarrow \text{Ce}^{4+}$ replacement changes the hole carrier concentration. Hole filling is the cause of lowering T_c of the system.

Keywords. Superconductivity; $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$; Ce substitution.

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1. Introduction

In the Bi-based system, three phases are observed with the general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ where $n = 1$ (2201), $n = 2$ (2212) and $n = 3$ (2223), with corresponding superconducting temperatures of 10 K, 85 K and 110 K respectively. These phases were isolated by Chu *et al* in 1988 [1], but $n = 3$ phase is very difficult to prepare in pure form as it undergoes a change to the 2212 (85 K) phase. Partial substitution of Pb for Bi has been found to help the growth of the 2223 phase [2–4]. In many high T_c superconducting families of compounds, the rare-earth plays an important role in establishing the proper structure. The substitution of Ca^{2+} (divalent) by trivalent rare-earth elements in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{4+\delta}$ (2212) causes a drastic change in the carrier concentration and results in transition from superconductor to an insulator [5–10]. Many reasons have been suggested for the decrease in the carrier concentration such as structural modulations or change in oxygen stoichiometry or change in the Cu valency or both [11]. The magnetic interaction of the rare-earth ions with electrons/holes responsible for superconductivity is generally found to be very weak in this oxide system so that superconductivity is not

affected by the presence of magnetic rare-earth ions which otherwise act as pair breakers in many systems [12].

The transition temperature of the system decreases with Eu, Gd, Ce substitution, when the percentage of the dopant is increased. Experimental interpretation has been given but not satisfactorily explained yet. Some have suggested reasons such as change in copper valency or anisotropy of the *c*-axis. Substitution of yttrium in 2223 system gives very interesting results, such as increase in transition temperature with low concentration related to a change of the average oxidation state of copper [13]. We have substituted Ce^{3+} with very small concentration (0.00 to 0.1) in the lead-doped 2223 system. The X-ray diffraction and ac susceptibility studies have been done as a function of Ce substitution and discussed here.

2. Experimental details

The samples of the system $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Ce_xCu_3O_{10+\delta}$ with concentration $x = 0.00, 0.02, 0.04, 0.08, 0.1$ were prepared by conventional solid-state reaction route. The stoichiometric proportions of the starting materials, $Bi_2O_3, PbO, SrCO_3, CaCO_3, Ce_2O_3$ and CuO , were taken. Then the powders were mixed and ground for 3 h in agate and mortar pestle and precalcined at $800^\circ C$ for 240 h. The calcined powders were ground and re-

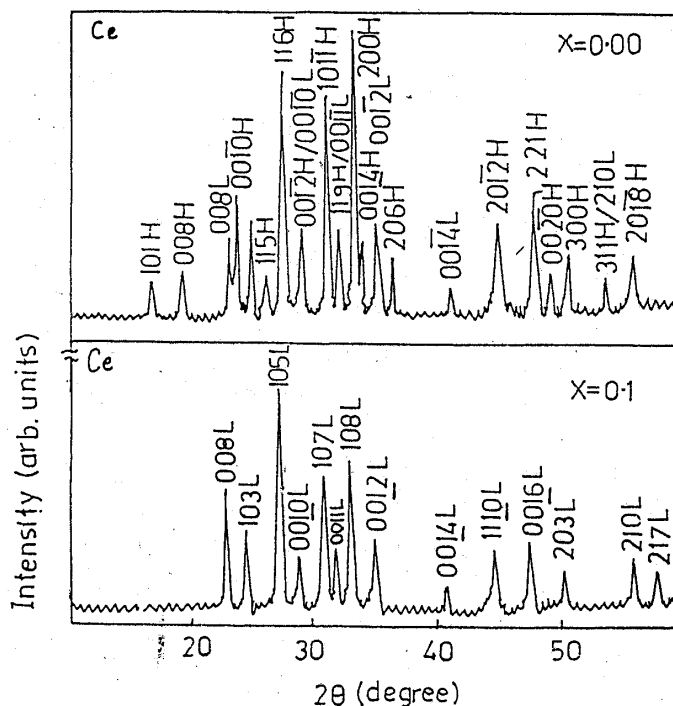


Figure 1. X-ray diffraction pattern of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Ce_xCu_3O_{10+\delta}$ system.

Table 1. X-ray diffraction results of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ compounds.

High T_c phase				
Ce con. x	Volume fraction of (2223) phase	a -Parameter of high T_c phase (Å)	c -Parameter of high T_c phase (Å)	Cell volume (Å ³)
0.00	65	5.40	37.010	1079.212
0.02	48	5.40	36.983	1078.424
0.04	36	5.398	36.942	1076.431
0.08	17	5.397	36.918	1075.333
0.1	00	5.395	36.894	1073.837
Low T_c phase				
Ce con. x	Volume fraction of (2212) phase	a -Parameter of low T_c phase (Å)	c -Parameter of low T_c phase (Å)	Cell volume (Å ³)
0.00	35	3.818	30.848	449.675
0.02	52	3.812	30.752	446.868
0.04	66	3.810	30.715	445.862
0.08	83	3.806	30.682	444.446
0.1	100	3.801	30.627	442.487

calcined again at 810°C for 32 h. The mixture was ground again and pressed into pellets. The samples were sintered at 850°C for 24 h and annealed by furnace cooling to room temperature. The samples were examined by X-ray diffraction at room temperature using JEOL X-ray diffractometer to determine their phase purity and lattice parameters. Ac susceptibility measurement of the samples were performed using lock-in amplifier in the temperature range 4.2–300 K to obtain the nature of Ce ions.

3. Results and discussion

The powder X-ray diffraction studies on the Ce-substituted (at Ca site) Bi-2223 samples suggest that these are in mixed phase. The observed peaks can be indexed on the basis of tetragonal structure which are shown in figure 1. The lattice parameters obtained from a least square fit of the observed d values are calculated. The c -lattice parameter and cell volume of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ system decrease with increasing Ce substitution at Ca site. The volume fraction of high T_c (2223) phase decreases with increase in low T_c (2212) phase. The decrease in c -parameter, cell volume and volume fraction of high T_c (2223) and low T_c (2212) phases with Ce concentration is shown in table 1. These results suggest the possible existence of Ce in a tetravalent state rather than trivalent state in this system where trivalent Ce ion is replacing the Ca^{2+} ion since the size of Ce^{3+} is comparable to that of Ca^{2+} , while Ce^{4+} is smaller.

Figure 2 shows the ac susceptibility measurement as a function of temperature for all samples from room temperature to liquid helium temperature. It is noted that $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ is superconducting with diamagnetic superconducting T_c onset of

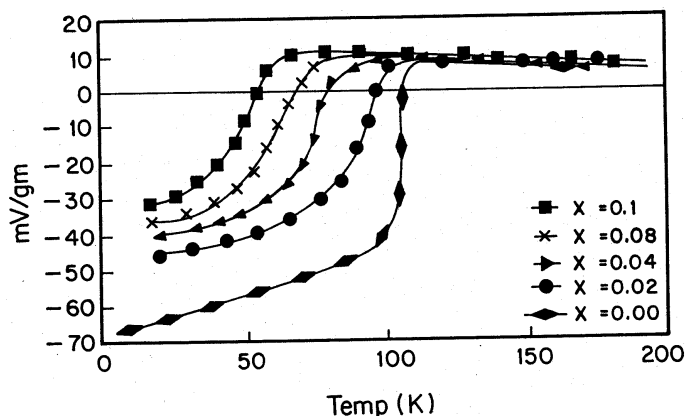


Figure 2. Ac susceptibility for $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ compounds.

Table 2. Ac susceptibility results of $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2-x}\text{Ce}_x\text{Cu}_3\text{O}_{10+\delta}$ compounds.

Ce con. x	$T_c(0)$ (K)	T_c (onset) (K)	$\Delta T_c = T_c(\text{onset}) - T_c(0)$ (K)
0.00	109	115	6
0.02	88	99	11
0.04	75	90	15
0.08	65	81	16
0.1	51	68	17

115 K which decreases drastically even for very small Ce concentration. The superconducting onset temperature for $x = 0.02$ is 99 K and transition temperature is 88 K. The superconducting onset temperature of sample $x = 0.1$ is 68 K and transition temperature is 51 K with transition width $\Delta T_c(0) = 17$ K. ΔT_c is calculated using the formula $\Delta T_c(0) = T_c(\text{onset}) - T_c(0)$ of all the samples and given in table 2. The decrease in T_c may possibly be due to hole filling as Ce^{4+} replaces Ca^{2+} . It may be mentioned here that Ce can exist in 3+ or in 4+ or in an intermediate valence state, the trivalent state being the most commonly observed. The ionic size of Ce^{3+} is comparable to that of Ca^{2+} while the ionic size of Ce^{4+} is smaller than that of Ca^{2+} .

4. Conclusion

A systematic study of Ce substitution at Ca site in the nominal composition of Bi 2 : 2 : 2 : 3 is reported here. Results of X-ray diffraction, decrease in c -parameter and cell volume of high T_c phase for small Ce concentrations and ac susceptibility measurements show that Ce substitution at Ca site drastically decreases the onset T_c and transition temperature thereby indicating that Ce exist in the nearly 4+ state in Bi-2223 system. Hence, Ce substitution provides comparatively more hole filling than the other rare-earths.

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