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Charge carrier localization and metal to insulator transition in cerium substituted (Bi,Pb)-2212 superconductor

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ABSTRACT

We report on the details of carrier localization and metal to insulator transition in (Bi,Pb)-2212 by substituting Ce at its Sr site ($0.2 \leq x \leq 1.0$). Structural and compositional analysis confirm good homogeneity of Ce distribution in the (Bi,Pb)-2212 matrix. The resistivity measurements show that $x = 0.2$ sample is a superconductor while those with $x > 0.2$ are insulators. Resistivity in the insulating regime ($0.4 \leq x \leq 1.0$) is analyzed using a generalized hopping approach. The increase in normal state resistivity and disorder of the samples leads to a metal to insulator transition at $0.2 < x \leq 0.4$ and the insulating phases exhibit Mott's variable range hopping phenomenon. Around the transition, a dimensional change over from two to three dimensions is observed in the variable range hopping regime. Results show that substitution reduces the carrier concentration of (Bi,Pb)-2212, leads to suppression of superconductivity and metal to insulator transition in the system by localizing the electronic states at the Fermi level.

1. Introduction

The interplay of localization and superconductivity is of fundamental interest in the physics of electrons in strongly correlated and disordered systems such as the high temperature superconductors (HTSCs). Disorder in a metallic system can cause localization of the electronic states in the vicinity of the Fermi level and therefore lead to a metal to insulator transition (MIT), known as the Anderson's MIT [1]. Several authors have theoretically shown that the Anderson localization and superconductivity are not mutually exclusive and that the Anderson's theorem is still valid in a narrow region, around the mobility edge [2–4]. Although the electronic density of states at the Fermi level remains finite, the ground state of a disordered system is an insulator due to the spatial localization of the electronic wave functions. On the other hand, a metallic system can become superconducting if there exists a finite attractive interaction among the electrons.

In the original BCS theory, the itinerant electrons form a macroscopic wave function, $\psi = (n_c)^{1/2}e^{i\varphi}$, where n_c is the Cooper pair density and φ is the macroscopic phase. This superconducting ground state can be changed to an insulating ground state either through the disorder induced localization which causes a decrease of carrier density or by the spatial inhomogeneity which causes a loss of macroscopic phase. It has been reported that intra-grain disorder induced by doping or by elements deficiency [5,6] reduces the effective coupling strength of cuprate superconductors and results in smaller carrier density whereas inter-grain disorder arising from grain boundary defects, reduces the coupling between grains and thus destroys the phase φ. As a consequence, the electrical properties of cuprates change from insulating ($d\rho/dT < 0$) to metallic ($d\rho/dT > 0$) due to the fact that all high-T_C cuprates lie close to a metal–insulator transition [7,8]. A coexistence of superconductivity and localization has previously been observed for the latter case in granular superconductors in which small, metallic clusters become superconducting and are coupled through Josephson junctions [9]. The former case occurs in homogeneous systems by a decrease of critical temperature, T_C with increase of disorder. HTSCs are examples of homogeneous systems and in recent years the rare-earth (RE) substitution studies in HTSCs have attracted considerable attention. It has been reported that different aliovalent substitutions or changes in the oxygen stoichiometry can effectively alter the concentration of carriers in the HTSC systems, resulting in a MIT [8,10–12]. MIT can also be caused by photo-induced laser treatment in which the photo-induced

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electron–phonon anharmonicity plays a crucial role in the transition [13].

The interplay near the MIT between randomness, Coulomb repulsion and the pairing mechanism that creates superconductivity is a topic of intense debate. In two dimensions, this interplay becomes particularly interesting, since the lower critical dimension for both the localization and superconductivity is two. A number of previous studies of ultra thin film superconductors have established that increasing the disorder by increasing the sheet resistance results in the suppression of superconductivity in two dimensions [14].

$Bi_2Sr_2CaCu_2O_8$ [Bi-2212] is a HTSC and the presence of Cu–O planes in this system, strongly suggests the presence of two dimensional (2D), physical and electronic properties which makes it suitable for the above investigations. So, in the present work, we report the effect of disorder and localization on the MIT and superconducting properties of $Bi_{1.7}Pb_{0.4}Sr_2Ca_{1.1}Cu_{2.1}O_{8+\delta}$ [(Bi,Pb)-2212] system which is a HTSC, through the substitution of a rare-earth, cerium (Ce) at its Sr site. Ce is substituted in this material over a wide range ($0.2 \le x \le 1$), to explore both the superconducting and insulating regions in the temperature doping phase diagram of (Bi,Pb)-2212 system. Here Pb is also substituted in the Bi-2212 system due to the established beneficial effects of Pb, like its role in the homogenization and stabilization of the Bi-2212 phase and also in increasing its T_C, and therefore makes the system more useful for the above investigations [15,16]. Detailed evaluation of the structural and resistivity parameters of the insulating phases in $Bi_{1.7}Pb_{0.4}Sr_{2-x}Ce_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ system is also explored which provide an excellent insight and understanding about the electronic conduction and the variable range hopping (VRH) mechanism in this material.

2. Materials and methods

$Bi_{1.7}Pb_{0.4}Sr_{2-x}Ce_xCa_{1.1}Cu_{2.1}O_{8+\delta}$ ($0.2 \le x \le 1$) samples were prepared by solid state synthesis route, using high purity chemicals of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and CeO_2 (Aldrich >99.9%). Stoichiometric amounts of the ingredients were accurately weighed using an electronic balance (*Mettler AE 240*), thoroughly mixed and ground using an agate mortar and pestle, and then subjected to a three stage calcination process in air at temperatures, 800 °C/15 h, 820 °C/30 h, and 840 °C/60 h with a heating rate of 3 °C/min. Intermediate wet grinding was done between each stages of calcination. After calcination, the samples were pelletized using a cylindrical die of 12 mm diameter, under a force of 80 kN. The pellets were then heat treated at 885 °C for 120 h (60 + 60) in two stages, with one intermediate re-pressing under the same stress.

Phase analysis of the samples was done using X-ray diffraction (XRD) (*Philips X'pert Pro*) employing an X'celerator and monochromator at the diffracted beam side. Phase identification was performed using *X'Pert High score software*, in support with *ICDD-PDF 2* database. Microstructural examinations of the samples were done using scanning electron microscopy (JEOL JSM 5600 LV). Elemental analyses of the samples were done using energy dispersive X-ray analysis attached to the SEM. The electrical transport properties of the samples from 64 K to 300 K were measured using the four probe method. A Lakeshore temperature controller (*Model: 340*) was used to accurately monitor the temperature.

3. Results and discussion

The samples are labelled as Ce2, Ce4, Ce6, Ce8 and Ce10, initially with respect to the nominal x values (0.2, 0.4, 0.6, 0.8 and 1.0, respectively) and later on with respect to the actual Ce concentrations (0.19, 0.38, 0.56, 0.72 and 0.85, respectively), obtained from the EDAX analysis. The normalized XRD patterns of the samples after sintering at 855 °C/120 h are shown in Fig. 1. In all samples, the major phase detected is (Bi,Pb)-2212. But from $x = 0.6$ onwards, some additional peaks are also observed along with the (Bi,Pb)-2212. By analyzing the patterns using X'pert high score software, it has been found that these peaks correspond to that of CeO_2 [34-0394], as referred in the database. The absence of any Ce containing phase up to $x = 0.4$ shows that the solubility limit of Ce in (Bi,Pb)-2212 system is around, $x = 0.4$.

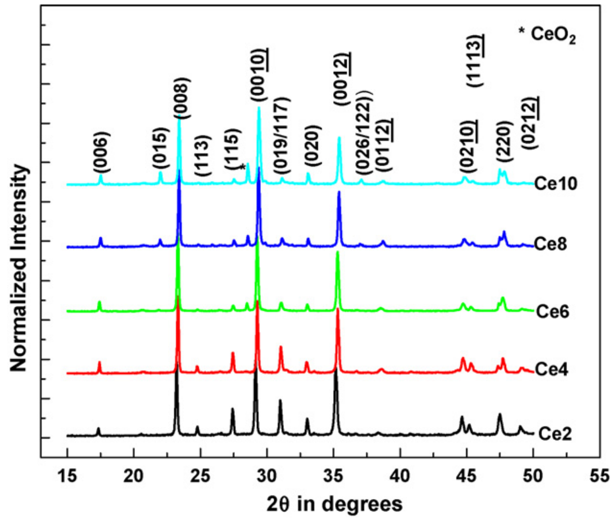

Fig. 1. XRD pattern of samples after final stage sintering process.

The SEM micrographs of the fractured samples after the last stage sintering process are shown in Fig. 2. It is found that the grain morphology is not much affected by the substitution of Ce. All the samples contain long and flaky grains that characterize the (Bi,Pb)-2212 system. But with the increase in Ce content, presence of small, rounded secondary phase is also observed in samples with $x > 0.6$. The secondary phase and (Bi,Pb)-2212 grains were analyzed through EDAX and Fig. 3 shows the EDAX spectra of (Bi,Pb)-2212 grains of the pure and a typical Ce substituted (Bi,Pb)-2212 [Ce10] samples. Presence of Ce is detected in the (Bi,Pb)-2212 grains of Ce substituted samples with a corresponding reduction in Sr. This indicates that the Ce atoms are successfully substituted in place of Sr site of the (Bi,Pb)-2212 system. The relative concentration of Ce and Sr are evaluated as a function of the nominal doping value x and the results are shown in Table 1. From the EDAX analysis, it is identified that the rounded phase which is observed between the flaky grains of (Bi,Pb)-2212 system in the SEM micrographs corresponds to the CeO_2. This indicates that beyond the solubility limit, CeO_2 remains as such in the system and this was already confirmed from the XRD pattern of the Ce10 sample.

From the XRD patterns, the lattice parameters are calculated using the d values and $(h\,k\,l)$ parameters by assuming an orthorhombic symmetry for (Bi,Pb)-2212. The variation of lattice parameters against actual Ce concentration is shown in Fig. 4 with an accuracy of (±0.002). The c axis length decreases with the dopant concentration. This decrease in c lattice parameter can arise due to (i) the increase in oxygen content of the system, (ii) the substitution of higher valence cation Ce^{4+} with an ionic radius smaller than that

Table 1
Quantitative EDX results of cation stoichiometry of Ce substituted (Bi,Pb)-2212 grains (standardized with respect to Ca).

Sample	Stoichiometry	(Bi,Pb)	Sr	Cu	Ce
Ce2	Initial	2.10	1.80	2.10	0.20
	From EDX	2.00	1.78	2.00	0.19
Ce4	Initial	2.10	1.60	2.10	0.40
	From EDX	1.99	1.59	1.99	0.38
Ce6	Initial	2.10	1.40	2.10	0.60
	From EDX	2.00	1.38	2.00	0.56
Ce8	Initial	2.10	1.20	2.10	0.80
	From EDX	1.98	1.16	2.00	0.72
Ce10	Initial	2.10	1.00	2.10	1.00
	From EDX	1.99	0.97	2.00	0.85