Chapter 3

SAMPLE PREPARATION AND CHARACTERIZATION

This chapter deals with the preparation and characterization of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-z}\text{M}_z\text{Cu}_2\text{O}_y$ compounds, where $\text{M} = \text{Pr}, \text{Ce} \& \text{Tb}$.

The synthesized samples were characterized by X-ray diffraction (XRD) for phase purity and solubility limits of various dopants. The lattice parameters were estimated and their dependence on the nature and the content of the dopant is discussed. The superconducting transitions were measured by AC susceptibility and the results are presented in this chapter.

3.1 Sample Preparation

All the samples were prepared by solid state reaction method. Samples of nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-z}\text{M}_z\text{Cu}_2\text{O}_y$ ($\text{M} = \text{Pr}, \text{Ce} \& \text{Tb}$ and $0 < x < 1$) were synthesized using the oxides; $\text{Bi}_2\text{O}_3$ (99.99 %), CuO (99.99 %), $\text{Pr}_6\text{O}_{11}$ (99.9 %), $\text{CeO}_2$ (99.9 %) and $\text{Tb}_4\text{O}_7$ (99.9 %) and carbonates; $\text{SrCO}_3$ (99.9 %) and $\text{CaCO}_3$ (99.9 %) [1-3]. The chemicals were weighed out in the appropriate ratio and mixed thoroughly. The mixture was calcinated at $800^\circ\text{C}$ for 24 hours in a muffle furnace in air with several intermediate grindings. The reacted black powder was pressed into pellets of 13mm diameter and heat treated at $830^\circ\text{C}$ for 24 hours and quenched to room temperature. The pellets were again heat treated at $880^\circ\text{C}$ for 20-30 minutes (samples with higher dopant content required longer
heat treatment) and then quenched to room temperature. The pellets were given a final heat treatment at $830^\circ$C for 24 hours and then quenched to room temperature. The room temperature quenching is found to be useful in raising the $T_c$ values.

3.2 Structural studies

The samples were characterized by X-ray diffraction (XRD) in order to ascertain the phase purity and to estimate the lattice parameters from the observed reflections. The sample was taken in the form of powder and the X-ray diffractogram was recorded at room temperature using SIEFERT X-ray diffractometer with $CuK_\alpha$ radiation, whose characteristic wavelength is 1.5418 Å. For phase identification, the patterns were compared against standard patterns reported in the literature and indexed (assigning $h, k, l$ values). The lattice parameters were calculated by least square fitting assuming pseudo tetragonal symmetry.

3.2.1 Pr doped Series

Fig.3.1 shows the X-ray diffraction pattern obtained for Pr-doped series. The X-ray diffraction patterns reveal predominantly single phase formation in the substitution range $0<x<0.6$ [1]. Sumana Prabhu et al also reported solid solutions upto 60% replacement of Ca by Pr in Bi$_2$Sr$_2$CaCu$_2$O$_y$ (Bi-2212) system [4]. Whereas, Gao et al [5] and Xiaolong Chen et al [6] have obtained complete solid solubility of Pr in the same system. Awana et al could obtain solid solutions only upto 50% of the doping level [7]. The plots of a and c lattice parameter vs. Pr-concentration (x) are shown in Fig.3.4. The a-lattice parameter increases slightly with increasing Pr-content. Whereas, the c-lattice parameter decreases significantly with increasing x.
3.2.2 Ce-doped series

Fig. 3.2 shows the X-ray diffraction patterns obtained for Ce-doped series. The X-ray diffraction patterns reveal predominantly single phase formation in the substitution range 0<x<0.4 [2]. Awana et al [7], Jordan et al [8] and Wang et al [9] have also reported solid solution formation only up to 40% replacement of Ca by Ce in Bi-2212 system. Sawa et al [10], however could prepare solid solutions up to 50% dopant content in Ce-doped Bi-2212 system. The impurity phase started emerging for higher dopant concentration. The a & c lattice parameters are plotted against Ce-concentration (x) (Fig.3.4). As observed in the case of Pr-doped series, the a-lattice parameter increases marginally with increasing Ce-content. The c-lattice parameter shows a marked decrease with increasing x. The decrease in c-lattice parameter is faster compared to Pr-doped series.

3.2.3 Tb-doped series

Fig.3.3. shows the X-ray diffraction patterns obtained for Tb-doped series. The X-ray diffraction patterns reveal predominantly single phase formation in the substitution range 0<x<0.6 [3]. The impurity phase started emerging above this dopant concentration. The plots of a and c lattice parameters vs. Tb-concentration (x) are shown in Fig.3.4. As observed in the case of Pr and Ce doped series, the increase in a-lattice parameter is marginal with increasing Tb-content (x). The c-lattice parameter, however, decreases significantly with increasing x. The decrease in c-lattice parameter is comparable with the depression rate observed for Pr-doped series.

Small increase in a-lattice parameter with increase in x is observed in all the three series of samples [1-3]. Similar changes in a-lattice parameter value have been reported in other rare-earth substituted Bi-2212 systems and Tl-based systems [4-13]. The elongation of the a-axis is attributed to the decrease in Cu-valence. The dopant ion introduces
Fig. 3.1 XRD patterns for the samples $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Pr}_x\text{Cu}_2\text{O}_y$ where $x = 0, 0.2, 0.4$ and 0.6
Fig. 3.2 XRD patterns for the samples $\text{(Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_y)}$ where $x = 0, 0.2$ and 0.4
Fig. 3.3 XRD patterns for the samples $\text{Bi}_2\text{Sr}_3\text{Ca}_{1-x}\text{TB}_x\text{Cu}_2\text{O}_y$ where $x = 0, 0.2, 0.4$ and 0.6.
Fig. 3.4 Variation of $a$ and $c$ lattice parameters as function of dopant concentration ($x$)
extra electrons in the lattice. The extra extra electrons reduce the Cu valence and thus lead to an increase in Cu-0 bond length, reflected as an increase in the a-lattice parameter.

The c-lattice parameter, however, decreases with increase in x. Among the three series of samples studied, the c-lattice parameter falls sharply for Ce-doped samples in comparison to the other two series. Decrease in c-lattice parameter is also reported in other rare-earth doped Bi-2212 systems [4-13]. In the case of other rare-earth substitutions like Y [5] and Gd [13], this change can be attributed to the smaller radius of the substituent ion. In the case of present samples also, one can attribute the same reason to the present systems, provided the substituent ion exists either in +4 state or between +3 and +4 states. It is likely that the rare earth ions may be distributed between the Ca and Sr sites, as in the case of Y-doped Bi-2212 system reported by Almeras et al [14] from photocmission spectroscopy studies. From the comparison of ionic radii of Sr$^{+2}$ (1.13), Ca$^{+2}$ (0.99), Ce$^{+3}$ (1.11), Ce$^{+4}$ (1.01), Pr$^{+3}$ (1.09), Pr$^{+4}$ (0.92), Tb$^{+3}$ (1.0), Tb$^{+4}$ (0.90), it is likely that larger trivalent rare-earth ion may substitute Sr site in preference to Ca site, and thus lead to the decrease in c-lattice parameter. However, detailed analysis is necessary to resolve this issue.

There can be, however, another explanation for the decrease in c-lattice parameter. The substitution of rare-earth ion at Ca site introduces excess oxygen in between the Bi-0 double layers [11, 12, 15-17], which consequently decreases the metalliclicity and the superconducting transition temperature [18]. This excess oxygen reduces the net positive charge and thus repulsion between the Bi-0 double layers leading to a decrease in c-lattice parameter [2.15]. The observed decrease in c-lattice parameter, therefore, can be ascribed to the excess oxygen between the Bi-0 double layers. This effect is likely to be more pronounced, if Ce exists as Ce$^{+4}$ ion and thus the faster decrease in c-lattice...
parameter of Ce-doped Bi-2212 system in comparison to other rare-earth dopants can be explained [2]. This is consistent with the faster depression rate in superconducting transition temperature in the case of Ce-doped Bi-2212 system [2].

3.3 AC susceptibility

AC susceptibility study gives information about the superconducting transition temperature, volume fraction of the superconducting phase, microstructure etc [19,20]. The complex AC susceptibility (x) is defined as $\chi = \chi' + i\chi''$, where $\chi'$, the in-phase (inductive) component describes the dispersive response to the diamagnetic transition and $\chi''$ the out-of-phase (resistive) component describes energy dissipation. AC susceptibility measurements were carried out on these series of samples at a field of 0.3 Oe and a frequency of 33 Hz. The samples were cooled in zero field. The $\chi'$ and $\chi''$ as a function of temperature for Pr, Ce and Tb doped Bi-2212 samples are shown in Fig. 3.5, 3.6 and 3.7 respectively.

The sintered high $T_c$ materials exhibit double drop behavior in $\chi'$-T curve. The drop at high temperatures is intrinsic to the grains of the superconductor ($T_c(\text{gran})$) and the other drop at low temperatures is characteristic of the coupling between grains, which determines the bulk superconducting properties of the compound ($T_c(\text{bulk})$) [21-24]. Both these critical temperatures are field dependent [22, 25]. Multiphase compounds also exhibit this type of double drop behavior of $\chi'$-T plots. Measurements were carried out on powders of these samples which contained only isolated grains. A single drop in $\chi'$-T plot was observed, which is due to the grains. This observation and the fact that the XRD studies indicate no impurity phases, confirm that the double drop behavior observed in $\chi'$-T plot is characteristic of the granular nature of the present samples. With increasing $x$, decrease in the diamagnetic onset temperatures ($T_c(\text{bulk})$ and $T_c(\text{gran})$) is observed.
Fig. 3.5 Plot of $\chi'$ vs. $T$ for Bi$_2$Sr$_2$Ca$_{1-x}$Pr$_x$Cu$_2$O$_y$ samples
($\chi''$-$T$ plot shown as an inset)
Fig. 3.6 Plot of $\chi'$ vs. $T$ for $\text{Bi}_2\text{Sr}_2\text{Ca}_{3-x}\text{Ce}_x\text{Cu}_2\text{O}_y$ samples

($\chi''-T$ plot shown as an inset)
Fig. 3.7 Plot of $\chi'$ vs. $T$ for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{ Tb}_x\text{Cu}_2\text{O}_8$ samples
($\chi''$-$T$ plot shown as an inset).
$\chi''$-$T$ plots show a peak, whose width depends on the connectivity between the grains [19]. The broadening of this peak is seen with increase in $x$ and its absence for higher dopant concentrations may be due to the reduction in volume fraction of superconducting phase with increase in $x$. The parameters ($T_c(\text{gran})$, $T_c(\text{bulk})$ and $\chi''(T)$ peak temperature) obtained from the measurements are listed in Table-3.1 for all the three series of samples.
Table-3.1

peak temperature, $T_c^{\text{(gran)}}$ and $T_c^{\text{(bulk)}}$ for various superconducting samples

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<th>$x$</th>
<th>$\chi''$ peak temperature (K)</th>
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<th>$T_c^{\text{(bulk)}}$ (K)</th>
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3.4 References

10. Akihito Sawa, Tae-Su Han, Takayuki Iwamatsu, Hiromoto UWE, Tunetaro Sakudo, *Physica* B165&166, 1553 (1990)


