CHAPTER 4
SUPERCONDUCTIVITY AND FERROMAGNETIC STUDIES ON Mn DOPED BULK TEXTURED Bi-2212 CRYSTALS AND SINTERED CERAMICS BY MICROWAVE ABSORPTION

4.1 INTRODUCTION

Microwave absorption technique has become an important tool for the characterisation of high temperature superconductors (HTS) (Endo et al 1994 and Andreone et al 2002). It is well known that superconductors absorb microwave at low magnetic fields, and this absorption is called the non-resonant microwave absorption (NMA) (Sugawara et al 1999). The non-resonant microwave absorption (NMA) measurements provide accurate determination of applied and fundamental parameters of superconductivity, like superconductivity gap, penetration depth, pairing symmetry, vortex dynamics and pinning force constant (Haqim et al 2001). The principle of field modulated microwave absorption technique is to detect a change in microwave loss corresponding to a small change in the magnetic field, as a function of applied dc magnetic field (H_{dc}). It can be measured using an EPR spectrometer for various types of HTS. The main advantage of this technique is that there is no need for any contact leads on the sample for characterisation. In addition, it needs only an infinitesimally small specimen owing to its high sensitivity. A historical success of microwave absorption measurements was the first direct
experimental determination of the superconducting energy gap and anomalous skin effect (Hein et al 2002).

In general there are some features widely observed in the NMA signal which appears below $T_c$. It is highly sensitive to the variation of magnetic field, temperature and microwave power depending on the nature of the sample (Padam et al 1999). The characteristic signals of NMA in single crystals epitaxial crystalline thin films (Itoh et al 2001) and sintered bulks are different from each other. Saturation fields in NMA spectra for bulk polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) are only a few Gauss, while for thin films and single crystals the field values are of the order of kG. Moreover it has been reported that extrinsic grain boundaries dominate NMA signal behaviour in bulk ceramics, whereas the signals are dominated by intrinsic properties in single crystals and hence the difference in the line shape (Srinivasu et al 2001 and 2001a). For good quality thin films and single crystals the signal intensity ($S$) as a function of $H_a$ is almost flat. This implies that the change in microwave power absorption for a small change in the field is constant over a wide range of field values (Dulcic et al 1998). It is of great interest to study the microwave absorption in ‘Mn’ doped and undoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212), since it is highly anisotropic compared to YBCO. Therefore the study of NMA in Bi-2212, would become a fundamentally important factor concerning the anisotropy. It is noteworthy that there are no adequate reports on the microwave absorption in textured Bi-2212 crystals. Although many studies on microwave absorption have been performed on single crystalline materials of Bi-2212, it is essential to study on $c$-axis aligned samples, which will be useful for commercial applications.
In Bi-2212 system a variety of substitutional studies have been made as this system offers a wide range of isomorphic replacements (Gu et al 1994). The substitution by magnetic impurities provides valuable information on unusual normal state properties. Among 3d transition elements, Mn is an attractive dopant for its special magnetic properties. Hence in this work, attempt has been made on Mn-doped Bi-2212 textured crystals and sintered precursor bulk samples by microwave absorption technique at liquid nitrogen temperature.

It is of special interest to employ NMA technique on series of undoped and Mn doped Bi-2212 samples. The superconducting sample shows a peculiar NMA spectrum, whereas ferromagnetic samples have a particular microwave absorption signal arising from ferromagnetic resonance. If the sample is a mixture of superconducting and ferromagnetic phases, it should show the fundamental NMA signal, which is superimposed by the ferromagnetic resonance signal. In this case, the tuning of superconducting phase into the ferromagnetic phase can be studied by the same characterisation technique. This study must provide a new technology and physics for a variety of HTS materials in the future. The present work gives the first step of this explorative study.

4.2 MATERIAL SYNTHESIS

High purity chemicals of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, CuO and MnO$_2$ were mixed and calcined in air in the temperature range 750-800 °C for 30 h to ensure chemical homogeneity. The precursor powder was pressed in a hydraulic press to prepare feed rods of size 40 mm in length and 5 mm in diameter. The pelletized sample was sintered at 810-890 °C for 30-40 h depending on the
Mn concentration. After sintering the feed rod for 40 h, bulk textured crystals were grown at a growth rate of 1 mm/h using indigenously designed immersed heater floating zone system and a detailed experimental study is given in Chapter 2. The same procedure was employed for the growth of pure textured Bi-2212 bulk crystals. The as-grown crystals were subjected to non-microwave absorption measurements. Ferromagnetic resonance and the structural study has also been carried out by X-ray diffraction analysis.

4.3 MICROWAVE ABSORPTION STUDIES

The block diagram of NMA measurement system is shown in Figure 4.1. For NMA measurements, a commercial EPR spectrometer was used and the microcavity was operated in the TE\textsubscript{102} mode. Figure 4.2 shows the microwave magnetic flux distribution in the TE\textsubscript{102} mode. In the cavity the sample was placed at the maximal position of microwave magnetic field (H\textsubscript{w}). Helmholtz coils were employed to nullify the remnant field due to the electromagnet of the spectrometer. To enhance the sensitivity of detection of microwave absorption, field modulation and phase sensitive detectors were used. A thermocouple was fixed to the sample directly to measure the temperature.

Superconductivity related NMA is more sensitive near zero field, and hence NMA was measured at low fields with the microwave power of 0.1mW liquid nitrogen temperature by sweeping dc field (H\textsubscript{d}) up and down from -100 to +300 G. The measurements were carried out with a sweep rate of Rs=1.67 G/s. Usually a ferromagnetic sample shows ferromagnetic resonant (FMR) microwave absorption at high fields. Hence high field sweep (-100 to 9900 G) microwave absorption measurements were done at a sweep rate of Rs = 41.6 G/s in order to investigate the ferromagnetic property of the samples.
Figure 4.1 Block diagram of NMA system
Figure 4.2  Microwave magnetic flux distribution in TE$_{102}$ Mode
4.3.1 Low field microwave absorption

The microwave absorption (NMA) signal at low fields for Mn-doped Bi-2212 textured crystals with an applied field \( H_a \) perpendicular to the \( ab \)-plane is shown in Figure 4.3. It is important to note that in this configuration, there is no hysteresis for upward and downward field sweeps. The absence of hysteresis may be attributed to the signal corresponds to the surface current but not due to the inner flux profiles of the critical state and hence the same signal strength for upward and downward sweeps. Further the Meissner surface current will be the same even though the flux profiles are different (Endo et al 1995). The NMA signal for the textured crystals shows pronounced hysteresis with an applied field \( H_a \) parallel to \( ab \)-plane as shown in Figure 4.4. This hysteresis behaviour is attributed to the anisotropic pinning effects. Figure 4.5 shows the NMA line shape for the sintered samples and it reveals that there is no signal corresponding to the superconducting property except for 0.2 Mn concentration.

4.3.2 Ferromagnetic resonance study

For the ferromagnetic resonance (FMR) microwave absorption, the sample was placed in the cavity and cooled to 79 K as shown in Figure 4.6. Magnetic field \( H_a \) was applied perpendicular to the sample. Modulated magnetic field \( H_m = 5 \text{ G} \) was superimposed on \( H_a \) at 100 kHz. \( H_a \) was swept from 100 Gauss to 1000 Gauss up and down. The modulated FMR signal was directly recorded on a chart. Ferromagnetic resonance signals obtained for the sintered samples are shown in Figure 4.7. The 0.4 Mn sintered sample shows a doublet peak and it might be probably due to the presence of two kinds of
Figure 4.3 Microwave absorption signal for Mn-doped Bi-2212 with applied field $H_a$ perpendicular to ‘ab’ plane.
Figure 4.4 Microwave absorption signal for $H_a$ parallel to $ab$ plane
Figure 4.5 NMA signal for sintered sample
Figure 4.6  Block diagram of FMR measurement with an applied field perpendicular to the sample
Figure 4.7  FMR signal for sintered sample
ferromagnetic phases. It is evident from signals of sintered samples with Mn concentration of 0.3 and 0.4 that the appearance of characteristic peak can be attributed to the ferromagnetic property. For higher order magnetic substitution FMR signal intensity increases and this behavior is attributed to the strengthening of magnetic phase by increase in the magnetic moment upon Mn doping.

It is well known that the inhomogeneity of the samples depends on the doping level and preparation conditions. In particular there are two main types of inhomogeneity sources such as extrinsic and intrinsic. Extrinsic sources are due to various preparation techniques. This source leads to chemical composition inhomogeneity and structural inhomogeneity. Intrinsic sources are caused by thermodynamical factors and can lead to phase separation on two phases with different concentration of the charge carriers. In the present study the inhomogeneity effect is minimal at the doping level ($x = 0.2$) but significant at higher doping level. From the aforesaid, it might be assumed that sintered bulk is magnetically inhomogeneous in the range $0.3 \geq x \geq 0.4$. It is suggested that this inhomogeneous state should appear as, so called magnetic cluster phase as shown in Figure 4.8.

The cluster glass is some set of clusters formed due to short range ferromagnetic ordering. Due to the randomly distributed ferromagnetic clusters there should be magnetic disorder in sintered sample. As a contrary when the sample underwent a textured growth the orientation of random ferromagnetic clusters are forced to align uniformly, so that the magnetic disorder is reduced and hence the absence of ferromagnetic phase as shown in Figure 4.9 and Figure 4.10 for parallel and perpendicular configurations. Also there have been
some explanations that in the presence of magnetic impurities, electron spins of a superconducting state may be partially polarized to gain exchange energy leading to the co-existence of ferromagnetism and superconductivity. Further experiments are needed to get more insight on the tuning of ferromagnetism for the sintered samples of higher order substitution.

**Figure 4.8** A model of magnetic cluster phase
Figure 4.9 FMR line shape for $H_a$ parallel to ab plane
Figure 4.10 FMR line shape for $H_a$ perpendicular to ab plane
4.4 X-RAY DIFFRACTION ANALYSIS

In order to substantiate the phase transition in sintered samples, X-ray diffraction analysis was performed on the Bi-2212 with 0.3 and 0.4 Mn concentration. The XRD patterns shown in Figure 4.11 confirm the presence of impurity phases in the sintered samples. This impurity phases disappear on melting and solidification of the sample during textured crystals growth. Further, the X-ray diffractogram shows some split in the peaks, which suggests a phase transition. The origin of this phase separation may be due to the co-existence of different structures within the same sample, which is responsible for the ferromagnetic phase. This is in agreement with the FMR results.

4.5 EVOLUTION OF REENTRANT PHASE IN BULK TEXTURED Bi-2212: POWER DEPENDENCE

Since the tunable microwave filters possess a high possibility to be used under magnetic fields, it is essential to study the fundamental microwave loss properties under the magnetic field. Hence the non-resonant microwave absorption signal (S) of textured Bi-2212 as a function of field (Hjc) in the configuration of the applied field perpendicular to the ab-plane at various microwave powers at 9.32 GHz at 77 K have been measured. The particular interest of this configuration is that the non-resonant microwave absorption signal is higher for the field applied in the c direction than that in the b direction. This is because when field is applied along c direction the shielding currents are flowing in the copper-oxygen plane, which is larger, compared to the out of plane shielding currents. Hence NMA signal is much stronger for the applied field parallel to the c direction.
Figure 4.11 XRD for the sintered Mn doped 2212 (x = 0.3, 0.4)
It is well known that the phase diagram of high temperature superconductors is complicated due to the co-existence different phases. The theoretically proposed phase diagram for the 2-dimensionality nature has not been confirmed experimentally (Kale et al 2002). The existence of reentrant phase has been confirmed by the microwave absorption studies on Bi-2212 textured crystals.

In this study non-resonant microwave absorption measurements were carried out on the Bi-2212 textured samples by employing "cavity perturbation method". The sample in a cryostat was put in a dc magnetic field (H_d) and a modulation field was superimposed on the dc field with an amplitude of 5 G at 100 kHz. The microwave absorption signals were measured on the samples at liquid nitrogen temperature (T) as a function of H_d. The microwave power (P_w) was varied in a range of 0.1-10 mW. The dc field (H_d) was applied on the sample along its c-axis direction (H_d//c). The second peak was clearly observed in textured Bi-2212 crystal.

The microwave absorption spectra measured at various microwave powers (P_w) at 77 K is shown in Figure 4.12. The microwave absorption spectrum reveals a first peak, followed by a broad second peak P_2. This broad peak is a remarkable feature it is not observed regularly in the non-resonant microwave absorption measurements. Further they manifested that the presence of second peak is attributed due to the presence of second superconductivity phase. The structure of microwave absorption spectra composed of three characteristics parts, which resembles the reentrant phase diagram reported by Rastogi et al (1996). This confirms the existence of reentrant phase in the textured crystal.
Textured Bi-2212 Crystal; $H_{dc}$ Lab-plane

Figure 4.12 NMA signals of textured Bi-2212 for different microwave powers

Figure 4.12 NMA signals of textured Bi-2212 for different microwave powers
The first peak and the broad second peak expose the Meissner state and solid phase respectively. The dip reflects the reentrant liquid phase ($L_1$), which lies between the Meissner state and solid phase as shown in Figure 4.13. The same features have been observed for the Bi-2212 single crystal (Kale et al 2002). Hence the bulk textured Bi-2212 crystals have the same characteristics similar to that of single crystals grown by flux technique.

Figure 4.13 A model of for reentrant phase diagram
A systematic study on non-resonant microwave absorption has been made Mn doped Bi-2212 bulk textured crystals and sintered samples for various Mn concentrations. Among the different compositions studied, only the sintered samples of Mn concentration 0.3 and 0.4 exhibit the desired properties of ferromagnetism. From the ferromagnetic resonance measurements of sintered samples, it has been found that the FMR intensity increases with Mn concentration and this behaviour is assigned to the increase of magnetic moment, upon doping. The absence of such behaviour in the textured samples is due to the annihilation of ferromagnetic phase on heating and melting of the sample during the growth. Further study is necessary to reveal this behaviour, which would lead to the better understanding of this phenomenon. Reentrant phase has been observed for the textured Bi-2212 similar to the flux grown Bi-2212 crystals. Hence the quality of the textured crystals grown by IHFZ technique is found to be comparable to the single crystals.