There is no one on earth who does what is right all the time and never makes a mistake.

..... Bible (ECCL 7,20)
INTRODUCTION

The discovery of high temperature superconductivity in the La-Ba-Cu-O [1] and La-Sr-Cu-O [2] systems was soon followed by the discovery of superconductivity at 90 K in the Y-Ba-Cu-O system [3]. Michel [4] and Maeda et al [5] first reported the discovery of high $T_c$ superconductivity in the Bi-Sr-Ca-Cu-O system. Since then many superconducting phases with different transition temperatures have been unambiguously identified. Because of the existence of complex crystal structures and phases, great efforts were put in [6-12] to study the structural and electronic properties of these superconducting systems.
The lowest $T_c$-phase in this system was discovered [4] in 1987 with the composition $\text{Bi}_2\text{Sr}_2\text{CuO}_4+y$. The crystallographic structure consists essentially of a single $\text{CuO}_2$ layer intercalated between two layers of $\text{BiO}_2$. The critical temperature reported was only 10 K. A second phase with $T_c \sim 85$ K discovered in 1988 [5], has the chemical composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$. Here the structure consists of $\text{CuO}_2$-$\text{Ca}$-$\text{CuO}_2$ layer intercalated by the same $\text{BiO}_2$ layer. The third phase of BSCCO system was reported [13,14] to have the chemical composition $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{10+y}$ and has a $T_c$ of 110 K.

The three phases differ mainly in copper and calcium content and can be obtained by the same starting composition by solid state synthesis at different temperatures. These three phases can be identified with a general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with $n = 1, 2$ and $3$ [7]. Accordingly these three phases have been abbreviated as 2201, 2212 and 2223 for $n = 1, 2$ and $3$ respectively. Also, there are some reports on the identification of $n = 4$ member of the series [15-18], but these results have not been reproducible. Among the three phases, the $n = 2$ member was found to be more stable and can be prepared with a variety of nominal compositions [9,19-23].

The crystal chemistry and preparation techniques of BSCCO family differ from YBCO in several aspects. The YBCO compound has a single composition and definite cationic site occupancy because of the large size difference of Y, Ba and Cu ions. But in the case of BSCCO systems, the composition of different phases of BSCCO is much less definite, since the ions of Bi, Sr and Ca have rather similar radii and can exchange their crystal sites.

The preparation of superconducting bismuth cuprates is subject to various constraints which makes it difficult to obtain single phase compounds.

(i) The formation temperatures of the three phases are in the range of 1073-1143 K. This leads to the formation of more than one superconducting phase as impurity phase during the reaction.

(ii) It is difficult to avoid the partial reactions between various pairs of oxides because of the diverse nature of reactivity of the component oxides. This results in the formation of stable binary and ternary impurity phases which persist in the final product.
(iii) $\text{Bi}_2\text{O}_3$, one of the starting products, melts at about 1093 K; other known liquid phases also form at about the same temperature and tend to separate before they can react with other components, creating inhomogeneities in the resulting sample.

During the past four years several methods of syntheses were reported in the literature which include conventional solid state reactions, co-precipitation routes, synthesis from glassy precursors etc. Most of the studies reported suggest that it is easy to obtain a ceramic sample containing both low $T_c$ (2212) and high $T_c$ (2223) phases. The annealing time and temperature have been found to be crucial for the formation of high $T_c$ samples [24] with sharp transitions [25]. It is generally agreed that the oxide which forms most readily has the chemical composition of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (2212) and has a tetragonal structure with $a=0.54$ nm and $c=3.08$ nm with $T_c$ values varying from 70-85 K [26]. An increase in $T_c$ of Bi-2212 from 80 to 91 K was reported [27,28] by sudden quenching of the sample.

In the present investigation, an attempt has been made, to study the effect of sintering in air and the effect of subsequent annealing in flowing oxygen at various temperatures and annealing times, on the superconducting behaviour of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ single phase ceramic.

It is shown that the (2223)-phase invariably contains the presence of impurity phase inclusions [7,29,30] and this multiphase nature greatly complicates the structural determination and detailed structural features could not be analysed with certainty. So attempts are being made to produce single phase high-$T_c$ (110 K) superconducting phase with consistent $T_c$ values and also to produce highly homogeneous and dense samples. In the present investigation an attempt has also been made to study whether sintering conditions and times could bring changes in $T_c$-zero and to study the structural and electrical behaviour of Bi-(2223) compounds prepared under different conditions.

SYNTHESES OF BI-(2212) AND (2223) SUPERCONDUCTORS

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ samples were prepared by the standard solid state reaction method. It has been reported [19,31] that the single phase 2212 compound is not formed easily when the constituent oxides/carbonates are reacted in the
stoichiometric ratio. The method employed to obtain a single phase compound in the present study is as follows: SrCO$_3$ and CaCO$_3$ powders were mixed in the molar ratio 2:1, ball-milled to promote thorough mixing and calcined at 1273 K for 10 h and at 1673 K for 5 h. This high temperature calcination of SrCO$_3$ and CaCO$_3$ mixtures at 1673 K resulted in complete decomposition. The reacted powder was cooled and ground well. To this material Bi$_2$O$_3$ and CuO powders were added in stoichiometric proportion, mixed, milled and heated at 1198 K in air for about 5 min till the mixture turned black. The reacted powder was slowly cooled and ground well. The mixture was calcined for 24 h in air at 1100 K and allowed to cool to room temperature in the furnace. The resulting materials were subjected to a second calcination for 12 h in air at 1135 K and allowed to cool to room temperature. The doubly calcined powder was ground to a particle size of 100 μm and pressed (4.5 kbar) into pellets. The pellets were sintered in air at various temperatures ranging from 1073-1173 K for various periods (10-30 h) and slowly furnace cooled to room temperature. The sintered samples were annealed in flowing oxygen atmosphere at various pressures (0.01 to 100 bar), temperatures (873-1073 K) and heating periods (4-24 h).

The specimens of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ were prepared by the standard solid state reaction method. The powders of 4N pure Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO, were mixed in the atomic ratio of 2:2:2:3. The mixture was taken in silica crucible, heated in air at 1118 K for 100 h with intermittent grinding for every 25 h and was finally quenched in air. The air quenched sample was ground to a particle size of 100 μm and pressed to form pellets of 12 mm dia and 1.5 mm thick. The pellets were sintered at different temperatures (1098-1148 K) for different periods of time (100-300 h) and then furnace cooled to room temperature. The samples were black in colour and stable towards exposure to atmosphere.

X-ray diffraction patterns were recorded using Philips X-ray diffractometer at room temperature with CuKα radiation using Ni-filter. Electrical transport measurements were carried out on pellets sintered under different conditions, using the standard four-probe technique in the temperature range 303-70 K. The temperature dependence (303-70 K) of ac susceptibility was studied at 317 Hz and an ac field of 0.05 Oe. The temperature of the samples was determined with a calibrated copper-constantan thermocouple.
RESULTS AND DISCUSSION

\textbf{Bi}_2\textbf{Sr}_2\textbf{CaCu}_2\textbf{O}_8 \textbf{High } T_c \textbf{ Ceramic Oxide System}

The X-ray diffraction pattern of the sample is shown in Fig.9.1. The observed reflections were characteristic of a tetragonal structure with lattice parameters, \(a = 0.5398 \text{ nm}\) and \(c = 3.0620 \text{ nm}\), which are consistent with those previously reported [26].

The influence of sintering temperature and time on the superconducting characteristics of \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\) is shown in Fig.9.2. It is seen from the figure 9.2(a) that to achieve the highest \(T_c\), the samples must be sintered in air at 1138 K for 24 h and slowly cooled to room temperature. \(T_c\) increases almost linearly with increasing sintering temperature up to 1138 K and then decreases. This decrease may be due to the fact that thermal treatment near or above the melting point degrades the superconducting properties as well as the structure. During slow furnace cooling, the high-\(T_c\) phase, even if present, decomposes while the low-\(T_c\) phase is retained. Figure 9.2(b) reveals that a sintering time of at least 24 h is necessary to have the highest \(T_c\) in the samples. There is no systematic change in \(T_c\) beyond 24 h. Long-term sintering followed by slow cooling to room temperature appears to improve the bulk superconducting properties.

\(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\) samples sintered at 1138 K in air for 24 h and slow cooled to room temperature showed a resistivity of the order of 5-10 milliohm-cm. The temperature dependence of resistivity of \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\) is shown in Fig.9.3. The behaviour is metallic between 303 and 100 K and the onset of superconducting transition sets in at about 100 K followed by zero resistive transition temperature at 88 K. The transition width (\(\Delta T_c\)) and temperature dependence of resistivity above \(T_c\) strongly depend on the sintering temperature and time. The sharp transition observed implies that the samples are homogeneous and single-phase and that the major phase must be superconducting.

The temperature dependence of ac susceptibility was determined by monitoring the mutual inductance of two coils when the sample is kept in one of the coils. The ac susceptibility measured at different temperatures on a sample is shown in Fig.9.4. At room temperature the specimen is Pauli-paramagnetic and on cooling,
Fig. 9.1. X-ray diffraction pattern of Bi$_2$Sr$_2$Ca$_4$Cu$_2$O$_{8+}$ sintered at 1138 K for 24 h.
Fig. 9.2. Superconducting characteristics of Bi$_2$Sr$_2$Ca$_1$Cu$_2$O$_8$ as a function of (a) sintering temperature and (b) sintering time.
Fig. 9.3. Temperature dependence of electrical resistivity of \( \text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8 \) sintered at 1138 K for 24 h.
Fig. 9.4. Temperature dependence of ac susceptibility of Bi₂Sr₂Ca₂Cu₃O₈ sintered at 1138 K for 24 h.
changes to diamagnetic state with a diamagnetic temperature at 100 K. A large change in inductance signal followed by saturation below 90 K suggests the bulk nature of superconductivity and this Pauli-paramagnetic to diamagnetic transition with a single drop in the $\chi$-T curve suggests that the sample is single-phase and homogeneous.

Sintered $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ samples were annealed in flowing oxygen at various pressures, temperatures and times. The sample resistivity decreases indicating the disappearance of intermediary phases formed, if any, during calcination and sintering in flowing oxygen which is also reflected in the XRD pattern taken on these samples. In addition, the zero resistivity temperature was reduced significantly with increase in oxygen partial pressure. The effect of annealing conditions on the superconducting properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is shown in Table 9.1. It is seen that with increasing $\text{O}_2$ pressure, $T_c$ decreases progressively to a lower temperature. This may be due to the fact that the added oxygen ions lower the Fermi level thereby reducing the metallic conductivity of Bi-O layers and hence lowers $T_c$ [32]. With increase in oxygen content, the transitions are broadened. With increase in annealing time beyond 24 h, no systematic change in $T_c$ is found, indicating that the treatment time of 24 h is optimum. Also, increasing the sintering temperature from 873 to 1073 K had little effect on zero resistivity temperature ($T_c$ zero). However, increasing the treatment temperature from 873 to 973 K resulted in 25% reduction in ac susceptibility signal at 70 K; and sintering at 1073 K resulted in a further 50% reduction. It is therefore clear that if the samples are annealed in oxygen in a partial pressure of $\pm0.01$ bar at 873 K for at least 24 h and then cooled slowly, it is possible to achieve the highest $T_c$ of 85K.

$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ High $T_c$ Ceramic Oxide System

The sintered samples showed room temperature resistivity of the order of 10-15 milliohm-cm. The effect of sintering conditions on the temperature dependence of resistivity was studied on all the samples. The sintering conditions are given in Table 9.2 along with the corresponding zero resistance transition temperatures.

A look at the table reveals that $T_c$-zero increases with increase in sintering temperature and sintering period. It is of interest to note that the sintering temperature of 1148 K with sintering time of at least 200 h is an optimum condition to obtain a maximum $T_c$-zero of 100 K.
TABLE 9.1: Effect of annealing conditions on the superconductivity of Bi$_2$Sr$_2$CaCu$_2$O$_8$.

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>$T_c$ Onset (K)</th>
<th>$T_c$ Offset (K)</th>
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<tr>
<td>Temperature (K)</td>
<td>Time (h)</td>
<td>O$_2$ Pressure (bar)</td>
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<tr>
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</table>
TABLE 9.2: Effect of sintering temperature and time on $T_c$-zero of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10-\delta}$ ceramics.

<table>
<thead>
<tr>
<th>Sintering temperature (K)</th>
<th>Sintering period (h)</th>
<th>$T_c$-zero (K)</th>
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The X-ray diffraction pattern of the sample sintered at 1148 K for 300 h is shown in Fig. 9.5. The majority of the observed reflections were characteristic of tetragonal structure with lattice parameters $a = 0.3813$ nm and $c = 3.6873$ nm which are consistent with that previously reported [33]. From the XRD pattern it is also seen that majority of the sample contains the high-$T_c$ (2223)-phase with minor presence of (2212)- and (2201)-phases.

The temperature dependence of resistivity for the sample sintered at 1148 K for 300 h is shown in Fig. 9.6. The behaviour is metallic between 303 and 110 K and the resistivity starts dropping at about 110 K and becomes zero at 100 K. Wang et al [34] reported a $T_c$-zero of 85 K for Bi-based (2223) samples prepared by solid state reaction method. For the (2223) samples, Shi et al [35] found only very small amounts of the 110 K phase and $T_c$-zero of 85 K, whereas Gogia et al [36] reported a transition temperature of 80 K only with a small transition step at a temperature close to 100 K.

Temperature dependence of ac susceptibility (Fig. 9.7) of the sample sintered at 1148 K for 300 h, revealed that at room temperature the specimen was Pauli-paramagnetic and on cooling changes to diamagnetic state at 110 K. The diamagnetic signal saturated at 100 K.

SUMMARY AND CONCLUSIONS

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ceramics sintered at 1138 K for 24 h in air and slowly furnace cooled to room temperature are single-phase, exhibit tetragonal structure with lattice parameters $a = 0.5398$ nm and $c = 3.0620$ nm, and had the highest zero resistivity temperature of 88 K. $T_c(0)$ values obtained from resistivity measurements agree well with that of susceptibility measurements. $T_c$ gets lowered with increased oxygen concentration in the case of Bi-2212.

The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{10+x}$ compounds sintered at 1148 K for 300 h in air exhibited tetragonal structure with lattice parameters $a = 0.3813$ nm and $c = 3.687$ nm and had the zero resistivity transition temperature of 100 K. The majority of the sample contained (2223) high-$T_c$ phase and as minor components, the (2212)- and (2201)-phases were present.
Fig 9.5. X-ray diffraction pattern of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$. 
Fig. 9.6. Temperature dependence of electrical resistivity for Bi$_2$Sr$_2$Cu$_2$O$_{10+δ}$. 
Fig. 9.7. Temperature dependence of ac susceptibility for $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_8+\delta$. 
REFERENCES


