CHAPTER 1
GENERAL INTRODUCTION

The advancements in materials science and technology have played an important role in human progress and civilization. We are in an era where the versatile potential of advanced materials has been unfolded and they have become an inevitable factor in almost every system of modern technology. Advanced materials are finding wide applications in electronic and microelectronic devices, transportation, industrial production, power engineering, communication, medicine and health care. The discovery and the expeditious growth of high temperature superconductivity in ceramic oxides during the last decade, in particular, has tremendously raised the potential of electronic ceramic materials for a wide range of applications. With the dawn of the new millennium, advanced ceramics are drawing the attention of researchers all over the world in the process of undergoing miniaturization from microtechnology to nanotechnology.

1.1 Ceramic Materials

The term ‘ceramics’ has originated from the Greek word ‘Keramos’, which means ‘object made from fired clay’. Ceramics are crystalline inorganic solid compounds of metal and/or nonmetals, formed by the application of heat, and some times heat and pressure. A large number of inorganic non-metallic and non water-soluble compounds including oxides, nitrides, borides, carbides and silicides of all metals and nonmetals come under the classification of ceramics. The bonding in ceramics is mostly ionic, but in some cases covalent or metallic bonding occurs. Ceramics, in general are brittle, hard, wear-resistant, prone to thermal shock, refractory, electrically and thermally insulative, intrinsically transparent, non-magnetic, chemically stable and oxidation resistant. However, a large number of ceramics are good electrical and thermal conductors and some are even superconducting. Though ceramics are generally nonmagnetic, high
field magnets were developed from ceramics and the magnetic properties of certain ceramics are such that they will find tremendous application in future.

Ceramic materials can be classified as traditional and advanced ceramics. Traditional ceramics are those derived from naturally occurring raw materials and include clay based products such as tableware and sanitaryware as well as structural claywares like bricks and pipes. Most of the traditional ceramics have a silicate-based structure with porous microstructures having coarse and nonuniform particles. Advanced or technical ceramics are developed through highly controlled chemical methods from naturally occurring materials that have been highly refined. They are characterised by very fine microstructure, greater homogeneity and less porosity. Based on the application, advanced ceramics can be further divided into functional and structural ceramics. Functional ceramics are used for performing special functions, viz. electrical, magnetic, optical etc in devices. Structural ceramics function as structural materials with high mechanical strength and stability at high temperature. Currently, ceramics are being applied for uses that were inconceivable two decades ago, like ceramic engines, electro-optic devices, laser materials, substrates in electronic circuits, electrodes in photoelectrochemical devices, etc. The conventional way of advanced ceramic preparation includes powder preparation, shaping and sintering. The technical properties of ceramic materials are not only determined by its chemical composition but also by the chemical homogeneity, crystal structure and the microstructure parameters like crystallite size, aggregate/aggglomerate structure of the ceramic powder. The microstructure of the final sintered product is controlled by the preparation conditions right from the raw material powder to the final heating of the ceramic compacts.

1.2 Perovskites

Majority of the electronic ceramic materials belong to a family of compounds by name perovskites, which has its origin from the specific mineral
called perovskite, CaTiO₃. Perovskite materials are of considerable technological importance particularly with regard to physical properties such as pyro and piezoelectricity, dielectric susceptibility, linear and non linear electro optic effects etc (1-2). The various compounds belonging to the perovskite family have a particular atomic arrangement. In their ideal form, perovskites are described by the general formula ABX₃ consisting of cubes where A, B and X are three distinct chemical elements in the ratio 1:1:3. Of the three elements, A and B are metallic cations and X is a non-metallic anion. The A cation, which is larger of the two types of metallic ions has a 12 fold co-ordination in the crystal and lies at the body centered position of the cube, the B cation has a 6 fold co-ordination and occupies all the eight corners of the cube and X anions lie at the midpoints of the 12 cube edges (3). In calcium titanate (CaTiO₃), the larger Ca occupies the A site, Ti the B position and oxygen fills the X site. A large number of elements of the periodic table combine to form hundreds of ideal or modified perovskites. Potassium, barium, strontium and rare earth elements can occupy the A position and more than half of the elements of the periodic table can adopt the B site. The X position can be occupied by any member of the halogen family of non metals like fluorine, chlorine or bromine in addition to oxygen. Figure 1.1(a) shows the ideal perovskite structure. The perovskite structure can also be visualised as a collection of polyhedron as shown, in Fig. 1.1(b). The X anions lie at the midpoint of the cubes twelve edges, giving corner shared strings of BX₆ octahedra, which extends infinitely in three dimensions. The BX₆ octahedra are perfect with 90° angles and with six equal B-X bonds. Each atom is surrounded by equidistant X anions. The ideal perovskite structure can also be regarded as a close packed structure in which the X and A atoms are stacked in cubic close packed layers along the cubic (111) direction. The resulting octahedral holes are occupied by B atoms.
Many members of the perovskite family are somewhat distorted because of the relative size of the A and B cations. This disparity causes the X atoms and in some cases also the B atoms to move out of position. Such “off centering” of positively charged cations can give perovskite crystals the electrical polarity, called spontaneous polarisation, one end being positively charged and the other end negatively charged. Moreover, the direction of the “off centering” can often be changed simply by subjecting the samples to an electric field. Materials that have a reversible spontaneous polarisation under the influence of an electric field are known as ferroelectrics and find wide applications in electronic devices. Perovskite materials run the whole range from insulators to semiconductors, superionic conductors, metal like conductors and at present the high temperature ceramic oxide superconductors. Both natural and synthetic perovskites exhibit an array of electrical properties, which arise from the tilting or distortion of the anion octahedra. Slight modifications of the ideal perovskite crystal structure results in extraordinary new features. There is no one to one correlation, a given modification does not automatically produce a particular degree of electrical conductivity. Yet an alteration of the ideal perovskite structure gives rise to new electrical properties. The octahedral deviations from the ideal structure and their relation to physical properties have been extensively studied in many articles (4-5).
There are a large number of compounds with the ideal perovskite structure (6-10). In the perovskite structure, the A and the B positions can be filled with two or more types of cations. Thus two or more cations randomly occupy either the 12 fold A position or the octahedral B position. There are many complex perovskites, which contain two or more octahedral cations. In some cases the different cations occupy the octahedral sites at random and in other cases an ordering takes place on the octahedral sites, with two different cations occupying the distinct crystallographic sites. In the case of two different cations, B and B', occupying the octahedral sites, the ordering of the two cations (B and B') at the octahedral sites leads to the formation of a superstructure or in other words the multiplying of the basic unit cell, which result in the cubic phase of A₂BB'O₆. The ordering of the B and B' cations strictly fill alternate octahedral positions in the entire structure. An ordered distribution of the B and B' cations is most probable when large differences exist in either their charges or ionic radii (11). The ordering of cations at the octahedral positions and the order disorder transitions in complex perovskite structure as a function of annealing conditions have been extensively studied and are found in literature (13-16). Similarly the ordering of the cations in the A site can also lead to the formation of superstructures in the AA'B₂O₆ compounds and they have been extensively studied by several groups (17-18).

1.3 High Temperature Superconductivity

1.3.1 Superconductivity

The phenomenon of superconductivity was discovered by the Dutch physicist, H. Kammerlingh Onnes at the University of Leiden while he was investigating the behaviour of electrical resistance at liquid helium temperatures. He observed that the electrical resistance of a rod of frozen mercury suddenly dropped to an immeasurably small value as temperature was decreased to 4.2 K. Owing to this extraordinary property exhibited, Onnes named this state as the
superconductive state and compounds exhibiting superconductivity came to be called as superconductors. Superconductors possess four important characteristics (19) namely zero resistivity, Meissner effect, Josephson effect and quantization of magnetic field. Zero resistivity means, a material in its superconducting state offers no resistance to the flow of electric current. In other words a material in the superconducting state is a perfect electrical conductor. Meissner effect refers to the property of a superconductor in which a superconductor will expel magnetic flux from its interior by an internally induced magnetic field. Therefore a superconductor will act as a perfect diamagnet in a weak magnetic field. Josephson effect is the remarkable electrical property associated with the tunnelling of superconducting electron pairs from a superconductor through a thin layer of an insulator in to another superconductor. Quantization of magnetic field: the total magnetic flux that passes through a superconducting ring may assume only quantized value, integral multiples of the flux quantum \( \frac{hc}{q} \), where \( q = -2e \), the charge of an electron pair. The first two properties are related to electric power applications and the last two properties are related to microelectronic applications. Superconductors have three critical parameters namely; critical temperature \( (T_c) \), critical magnetic field \( (H_c) \) and critical current density \( (J_c) \). Critical temperature is defined as the temperature at which a material undergoes a transition from the normal state electrical resistivity to the superconducting state. Critical magnetic field is the value of the applied magnetic field that destroys superconductivity and is a function of temperature. The critical current density is the critical value of the current that the superconductor can support without destroying the superconducting property. Critical current density is a function of temperature and applied magnetic field. Until 1986 several hundred materials were found to exhibit the phenomenon of superconductivity at sufficiently low temperatures and required either liquid helium or liquid hydrogen as coolants. The evolution of superconductivity until the discovery of superconductivity in ceramic oxides is given in figure 1.2. The discovery of superconductivity above liquid nitrogen temperature in a ceramic
oxide of yttrium, barium and copper triggered a flurry of crystallographic research unprecedented in the history of materials science.

![Graph showing the evolution of superconductivity until the discovery of superconductivity in ceramic oxides](image)

**Fig 1.2** The evolution of superconductivity until the discovery of superconductivity in ceramic oxides

### 1.3.2 Evolution of High Temperature Superconductivity

In the year 1986, J. G. Bednorz and K. A. Muller, both from IBM laboratory in Zurich discovered superconductivity at 30 K in La$_{2-x}$Ba$_x$CuO$_4$, a mixed oxide of lanthanum, barium and copper (20). Even though the transition temperature of La$_{2-x}$Ba$_x$CuO$_4$ was not much higher than that was known for the best intermetallic superconductor (23 K), this compound was a totally different
type of material and paved the way for all the subsequent discoveries in the area of high temperature superconductivity. Several groups confirmed this discovery and La$_{2-x}$Ba$_x$CuO$_4$ was found to possess the layered K$_2$NiF$_4$ type crystal structure (21-22). It was soon discovered that the substitution of strontium for barium raised the $T_c$ to 40 K (23-24). Since the discovery of superconductivity in the cuprates having the K$_2$NiF$_4$ structure, many other cuprates with higher transition temperatures have been found and all of them possess two dimensional Cu-O sheets as an essential feature (25). In March 1987, M.K. Wu and co-workers (26) at the university of Alabama discovered that a compound consisting of yttrium, barium, copper and oxygen exhibits superconductivity above liquid nitrogen temperature at a temperature 92 K. Several groups confirmed this remarkable discovery (27-33) and the phase responsible for superconductivity above 77 K was identified as the orthorhombic YBa$_2$Cu$_3$O$_{7-8}$ (YBCO) phase with an oxygen deficient perovskite structure (34-36). All the research groups, who examined the structure of the superconducting Y-Ba-Cu-O compound recognised that the structure was based on a simple unit cell, composed of a stack of three perovskite like cubes (37). The neutron powder diffraction studies (38-42) resolved with certainty the details of the oxygen positions in the orthorhombic YBCO compound. Many other rare earth cuprates with the general formula LnBa$_2$Cu$_3$O$_7$ (Ln = rare earth) also having the orthorhombic structure are superconducting around 90 K, except for the rare earths Pr, Ce and Tb (43-45). In the year 1987 itself, Michel et al (46) substituted La by Bi in the original Bednorz and Muller formula and isolated a compound with the formula Bi$_2$Sr$_2$CuO$_{7-8}$ which has a transition temperature of 22 K. Following this discovery, the bismuth cuprates with the general formula Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$ were discovered in 1988 with superconducting transitions at 85 and 110 K respectively for $n = 2$ and $n = 3$ phase (47-48). The $n = 3$ phase has three sets of near by CuO$_2$ planes and has the highest transition temperature for this series of materials.
The replacement of Bi by Tl and Sr by Ba in Bi$_2$SrCa$_{n-1}$Cu$_n$O$_{2n+4}$ yields a similar set of compounds with general formula Tl$_2$Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$ with $T_c$ values of 80,110 and 125 K respectively for $n = 1, 2$ and $3$ (49-51). Sheng and Hermann (52) discovered superconductivity near 120 K in the Tl-Ba-Ca-Cu-O system. The thallium based compounds held the characteristic of a high transition temperature crossing the boiling point of liquified natural gas for quite some time. In 1993, Putlin and co-workers discovered the first mercury based superconductor HgBa$_2$CuO$_4$ with a $T_c = 94$ K (53). The mercury cuprate
superconductors HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n-3}$ have a structure derived from that of the thallium cuprites TlBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+3}$. The second member of this series with $n = 2$ has a $T_c$ of 120 K (54). The third member with $n = 3$ having a $T_c$ of 135 K (55) at ambient pressure is currently the highest superconducting transition temperature holder. The $T_c$ value of this compound reaches 164 K, when recorded under high pressure and is not too far from the lowest temperature recorded on earth (183 K). The details of some of the important superconductors their transition temperatures and crystal structure are summarized in Table 1. Figure 1.3 shows the evolution of high temperature superconductivity in ceramic oxides since its discovery in 1986 (25).

1.3.2.1 Yttrium Barium Copper Oxide Superconductor

Superconductivity above liquid nitrogen temperature in a mixed oxide of yttrium, barium and copper was confirmed by several groups (27-33) soon after its discovery by Wu et al (26). The superconducting phase in the Y-Ba-Cu-O compound namely YBa$_2$Cu$_3$O$_{7-8}$ also commonly called as the 123 phase has an oxygen deficient perovskite crystal structure as established by powder x-ray (34-36) and neutron diffraction studies (38-42) as well as single crystal studies (56-59). In the YBa$_2$Cu$_3$O$_{7-8}$ structure the c-axis of the unit cell is tripled with two inequivalent Cu planes, labelled Cu1 and Cu2, sandwiched between Ba planes for Cu1 and Ba and Y planes for Cu2 (60). Thus the structure consists of triple layers of corner sharing polyhedra, parallel to (001) whose cohesion is provided by planes of yttrium cations (25, 60). Therefore the structure is often described as an association of Cu-O chains and pyramidal copper and oxygen layers. Besides the CuO$_2$ sheets, the superconducting phase contains Cu-O-Cu chains (or corner linked CuO$_4$ units) which are absent in the non superconducting samples (61-62). Figure 1.4 shows the structure of the superconducting YBCO compound with the copper oxygen layers and the Cu-O chains. It has been established beyond doubt that the 123 compound crystallizes as the tetragonal
phase at high temperatures but gets converted into the orthorhombic phase through oxygen absorption and ordering by annealing at lower temperatures for a long duration (63-64).

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (K)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{2-x}$Ba$<em>x$CuO$</em>{4+\delta}$</td>
<td>30</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>La$_{2-x}$Sr$<em>x$CuO$</em>{4+\delta}$</td>
<td>40</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{7-\delta}$</td>
<td>92</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>REBa$_2$Cu$<em>3$O$</em>{7-\delta}$ (RE = rare-earth except Ce, Pr and Tb)</td>
<td>~92</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>4$O$</em>{10}$</td>
<td>92</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CuO$_6$</td>
<td>17</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$CaCu$_2$O$_8$</td>
<td>85</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>110</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$CuO$_6$</td>
<td>20</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_x$</td>
<td>125</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>TlBa$_2$CaCu$<em>2$O$</em>{7+\delta}$</td>
<td>80</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>TlBa$_2$Ca$_2$Cu$<em>3$O$</em>{7+\delta}$</td>
<td>110</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>TlBa$_2$Ca$_3$Cu$<em>4$O$</em>{12+\delta}$</td>
<td>122</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$CaCu$<em>2$O$</em>{8+\delta}$</td>
<td>110</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$<em>2$O$</em>{10+\delta}$</td>
<td>125</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Ca$_3$Cu$<em>4$O$</em>{12+\delta}$</td>
<td>105</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$<em>2$CuO$</em>{5+\delta}$</td>
<td>94</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$_2$CaCu$<em>2$O$</em>{7+\delta}$</td>
<td>104</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_2$Cu$<em>3$O$</em>{9+\delta}$</td>
<td>135</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_3$Cu$<em>4$O$</em>{12+\delta}$</td>
<td>105</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_4$Cu$<em>5$O$</em>{8+\delta}$</td>
<td>105</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_5$Cu$_6$O$_x$</td>
<td>95</td>
<td>Tetragonal</td>
</tr>
</tbody>
</table>
Fig. 1.4 Structure of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound showing the position of the copper-oxygen planes and chains.

Fig. 1.5 Structure of the (a) orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound (b) tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound.

Superconductivity in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound is extremely sensitive to oxygen stoichiometry. The compound is orthorhombic if $\delta < 0.15$, and becomes tetragonal as $\delta > 0.5$. The structures of the orthorhombic and tetragonal phases differ considerably and it is shown in fig 1.5. Oxygen gets
readily intercalated in the $\delta > 0.5$ sample and the stoichiometry reaches close to YBa$_2$Cu$_3$O$_7$ on intercalation. The variation of the transition temperature of YBCO with oxygen stoichiometry is shown in figure 1.6. The $T_c$ is maximised by reducing $\delta$ to 0.1 and obtaining a fully orthorhombic phase. In both the orthorhombic and tetragonal phases, oxygen sites in the Y plane are vacant, leaving Cu2 five fold co-ordinated. In the ideal orthorhombic phase, in the Cu1 plane, the O4 and O5 sites are occupied differently. As $\delta \rightarrow 0$ the O4 sites are occupied along the b-axis and the similar O5 sites are vacant along the a-axis, giving b-axis Cu1-04 chains. In the tetragonal YBa$_2$Cu$_3$O$_6$ phase both O4 and O5 sites are vacant. Several groups have reported the structural transformations and the associated superconducting properties depending on the oxygen content of YBCO (65-68). Superconductivity of the YBCO samples is greatly degraded by the interaction of water and humid air (69-70). The lattice parameters of the orthorhombic YBCO phase are $a = 3.8231$ Å, $b = 3.8864$ Å and $c = 11.6807$ Å and these values depend on the annealing conditions (71). Some of the important characteristics of the YBCO superconductor have been summarized in table 2.

![Figure 1.6](attachment:figure16.png)

**Fig. 1.6** Variation of the transition temperature of YBa$_2$Cu$_3$O$_{7-\delta}$ with oxygen stoichiometry
Table 2  
Physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7.4}$ superconductor

<table>
<thead>
<tr>
<th>Structure</th>
<th>Orthorhombic perovskite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters ($\text{Å}$)</td>
<td>$a = 3.8231$, $b = 3.8864$, $c = 11.6807$</td>
</tr>
<tr>
<td>Theoretical density ($\text{g/cc}$)</td>
<td>6.374</td>
</tr>
<tr>
<td>Thermal expansivity ($\text{K}^{-1}$)</td>
<td>$11.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Specific Heat Capacity ($\text{JK}^{-1}\text{K}^{-1}$)</td>
<td>431</td>
</tr>
<tr>
<td>Thermal Conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)</td>
<td>$2.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>Hall carrier density ($\text{cm}^{-3}$)</td>
<td>$4 \times 10^{21}$ (for a sample with resistivity 400 mohms just above $T_c$)</td>
</tr>
<tr>
<td>Less coherence length (nm)</td>
<td>1.4</td>
</tr>
<tr>
<td>London penetration depth (nm)</td>
<td>200</td>
</tr>
<tr>
<td>Mean free path (nm)</td>
<td>1.2</td>
</tr>
<tr>
<td>$T_c$ (0) (K)</td>
<td>92</td>
</tr>
<tr>
<td>$H_c1$ (0) (T)</td>
<td>1</td>
</tr>
<tr>
<td>$H_c2$ (0) (T)</td>
<td>120</td>
</tr>
<tr>
<td>Absolute thermo electric power ($\mu\text{VK}^{-1}$)</td>
<td>3</td>
</tr>
<tr>
<td>$J_c$ at 77 K and zero field (bulk)</td>
<td>$10^3 - 10^4 \text{ A/cm}^2$</td>
</tr>
<tr>
<td>$J_c$ at 77 K and zero field (epitaxial thin film)</td>
<td>$10^6 - 10^7 \text{ A/cm}^2$</td>
</tr>
</tbody>
</table>

Numerous studies have been carried out on the substitution of different ions for all the four ions in the YBCO superconductor. As already mentioned the substitution of $Y$ by any rare earth other than those of Ce, Pr and
Tb show no remarkable variation in the $T_c$ (43-45). But there are reports that thin films of PrBa$_2$Cu$_3$O$_7$ pseudomorphically grown on single crystals of YBCO are superconducting with $T_c \sim 90$ K (72-73). A decrease in $T_c$ is observed when barium is partially substituted by strontium or calcium (74-75). The Cu atom in the YBCO compound has been partly replaced by Zn, Fe, Ni, Co, Zr, etc., which resulted in a drastic decrease in the transition temperature (76-80). Partial substitution of oxygen by sulphur showed no variation in the transition temperature but resulted in a sharp transition (81). Meanwhile, partial substitution of oxygen by chlorine showed a depression in the $T_c$ (81). Though it has been reported that the partial substitution of oxygen by fluorine (82-83) enhanced the $T_c$ ($\sim$150 K) there has been no confirmation of this result. The discovery of the superconducting orthorhombic phase in the Y-Ba-Cu-O system was followed by the synthesis of different new superconducting rare-earth cuprates having a close structural relationship to the 1-2-3 compound. They include the YBa$_2$Cu$_4$O$_8$ (84), Y$_2$Ba$_4$Cu$_7$O$_{15}$ (85) and Y$_2$BaCuO$_5$ (86) compounds all of which have transition temperatures less than 92 K.

1.3.2.2 Bismuth Strontium Calcium Copper Oxide Superconductor

In 1987, Michel et al (46) substituted Bi for La in the La-Sr-Cu-O system and isolated a compound with the formula Bi$_2$Sr$_2$CuO$_{7+\delta}$ with a transition temperature of 22 K. However, this discovery did not gain much attention at that time due to its low value of transition temperature. In 1988 the addition of Ca to the above system led to the discovery of the bismuth cuprates with general formula Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ with $n = 1$, 2 and 3 (87-88). A transition temperature of 85 K and 110 K were obtained for the $n = 2$ and $n = 3$ phases respectively. The first member of this series Bi$_2$Sr$_2$Cu$_1$O$_4$(Bi-2201) has a $T_c$ between 7 and 22 K depending on the Bi-Sr ratio. It has an orthorhombic structure with $a = 5.32$ Å, $b = 26.6$ Å and $c = 48.8$ Å. The crystal structure of Bi-2201 is shown in Fig. 1.7 (a).
The second member of the series with $n = 2$, $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ ($\text{Bi-2212}$) has $T_c$ of 85 K. The single phase $\text{Bi-2212}$ compound is obtained easily by firing a mixture of oxides and carbonates in the nominal composition of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ at 850°C for two days (89). Liu et al. (90) reported the synthesis of the $n = 2$ phase by rapid calcination and post annealing. In this method, homogeneous semiconducting $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ precursor was obtained by heating at 1200°C under argon atmosphere for 10 seconds and the subsequent annealing at 860°C for 16 h transformed it into the superconducting $\text{Bi}_2\text{Sr}_2\text{CuCu}_2\text{O}_x$ compound. Tallon et al. (91) reported an increase in $T_c$ of $\text{Bi-2212}$ from 80 K to 91 K by the quenching process and this was confirmed by Almond et al. (92). The crystal structure of the $\text{Bi-2212}$ compound was elucidated from single crystals using high-resolution lattice imaging as well as x-ray and neutron diffraction techniques (93-95). Figure 1.7(b) shows the crystal structure of $\text{Bi-2212}$. The structure was elucidated as an orthorhombic cell with lattice parameters $a = 5.411$
\( \text{Å, b = 5.418 Å and c = 30.89 Å having Fmm symmetry (96).} \) The crystal structure of Bi-2212 consists of intergrowths with perovskite-like units containing two CuO$_2$ planes sandwiched between Bi-O bilayers. This perovskite unit is similar to the 123 compound. The Ca and Sr cations play the same role as the Y and Ba cations in the 123 compound. The linear chains in the 123 compound are replaced by the Bi-O layer. The weak bonding between the Bi-O layers results in easy cleavage with in the Bi-2212 structure (97).

The highest transition temperature in the Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ series was obtained for the \( n = 3 \) phase, Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2223) having a \( T_c \) of 110 K. Earlier it was extremely difficult to prepare the Bi-2223 phase in its pure form. The initial efforts to synthesise Bi-2223 by heating nominal stoichiometric mixtures of oxides and carbonates at 850°C led to the formation of Bi-2212 as the major phase and only a small fraction of Bi-2223 (98). Later the volume fraction of Bi-2223 was increased by heating the reaction mixture at 880°C, which is just below the melting temperature suggesting that the kinetics of the formation of the Bi-2223 phase is closely related to the melting characteristics of the multicomponent mixture. But later Takano et al (99) showed that the partial substitution of bismuth by lead around its ideal composition drastically promoted and stabilized the formation of the Bi-2223 phase. Since then several reports were made which proved that the incorporation of Pb in the Bi-Sr-Ca-Cu-O system coupled with a prolonged sintering for nearly 200 h increased the volume fraction of the Bi-2223 phase in the final product (100-104). All the single phase Bi-2223 samples reported so far have been synthesized by the partial substitution of Bi by Pb which appears to enhance the long range diffusion of Ca and Cu, since the addition of Pb lowers the melting point of the mixture, thus accelerating the formation of the Bi-2223 phase. The Bi-2223 superconductor has an orthorhombic structure with \( a = 5.420 \, \text{Å}, \, b = 5.411 \, \text{Å} \) and \( c = 37.290 \, \text{Å} \). Figure 1.7(c) shows the crystal structure of the Bi-2223 superconductor.
1.3.2.3 Thallium Barium Calcium Copper Oxide Superconductor

Superconductivity in the Tl-Ba-Cu-O system with a transition temperature above 77 K was first discovered by Sheng and Hermann (52). They raised the \( T_c \) further by adding Ca to the same system and obtained a \( T_c \) with onset at about 120 K (53). Two superconducting phases were identified by Hazen et al (41) in the new samples synthesized by Sheng and Hermann as Tl<sub>2</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>8+δ</sub> and Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10+δ</sub>. Later, Parkin et al (105) changed the processing conditions to greatly increase the amount of Tl-2223 and produced a \( T_c \) of 125 K. Later different superconducting compounds in the family TlBa<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4</sub> were discovered.

![Crystal structure diagram of thallium superconductors](image)

**Fig. 1.8** Crystal structure diagram of thallium superconductors (a) Tl<sub>1</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, (b) Tl<sub>1</sub>Ca<sub>1</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>7</sub>, (c) Tl<sub>1</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>6</sub>, (d) Tl<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, (e) Tl<sub>2</sub>Ca<sub>1</sub>Ba<sub>2</sub>Cu<sub>2</sub>O<sub>8</sub> and (f) Tl<sub>2</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>
The replacement of bismuth by thallium and strontium by barium in the bismuth system yielded a similar set of compounds which are superconducting. In the case of thallium compounds in the series Tl\(_2\)Ba\(_2\)Ca\(_{n-1}\)Cu\(_n\)O\(_{2n+4+\delta}\), the structure consists of perovskite like units containing one, two or three CuO\(_2\) planes separated by Tl-O bilayers (95). Whereas, the thallium compound of the series with the formula TlBa\(_2\)Ca\(_{n-1}\)Cu\(_n\)O\(_{2n+3+\delta}\), are made up of perovskite like units containing one, two or three CuO\(_2\) planes separated by Tl-O monolayers respectively and have no bismuth analogs. All the thallium compounds have tetragonal structure at room temperature. The thallium compounds with Tl-O monolayers have primitive tetragonal cells whereas the oxides with Tl-O bilayers have body centered tetragonal cells. The crystal structure diagrams of all the six compounds in the Tl-Ca-Ba-Cu-O system are shown in figure 1.8.

### 1.3.2.4 Mercury Barium Calcium Copper Oxide Superconductor

In 1993 Putilin et al (106) reported the existence of superconductivity in HgBa\(_2\)CuO\(_{4+\delta}\) with a \(T_c\) of 94 K. Later the presence of the superconducting phenomenon above 130 K was reported in a multiphase compound of Hg-Ba-Ca-Cu-O system (55). Subsequently single phase HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+\delta}\) was synthesized and it was observed to be superconducting at a temperature of 135 K (107). Owing to the high volatility and toxicity of the mercury compounds, the synthesis of single phase Hg based superconductors was difficult in the initial days of its discovery. This was overcome by using the high pressure technique (108). Hirabayashi et al (109) have reported the synthesis of single phase Hg-1223 by a reaction sintering under high pressure and temperature. In this technique, a precursor with the required composition of Ba, Ca and Cu was calcined and an appropriate amount of HgO is added to it. This is then sealed in an Au capsule for the high pressure synthesis and heated under pressure of ~ 5 GPa. At present, HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_7\) has the highest transition temperature of 135 K.
under ambient pressures and the transition temperature reaches 164 K when measured at high pressures.

1.4 High Temperature Superconducting Films

The immediate applications of high temperature superconducting (HTSC) materials are in the form of thick and thin films in various microelectronic devices like low loss microwave resonators and filters, bolometers, delay lines, flux transformers, magnetic shields, dc and rf superconducting quantum interference devices, and various other superconducting two and three terminal devices (110-112). High critical current density values which are attainable in good quality films are essential for practical applications. The selection of suitable substrates and optimisation of the processing conditions are crucial to obtain high quality films of superconducting materials (113-114).

High temperature superconducting films are also potentially suited to give an insight into the fundamental mechanisms governing high temperature superconductivity. It is difficult to produce high quality films of these materials because of the sheer complexity, high anisotropic nature, close tolerance of the composition required and the high processing temperature which make the chemical compatibility requirement of the substrate with the film more severe. Also the oxygen atmosphere required in the case of in situ growth of YBCO thin films imposes additional constraints for the preparation of films, as oxygen is incompatible with many aspects of traditional thin film growth methods, especially the substrate heating necessary for producing superconducting film. Another difficulty arising is the complex structure of most of the high temperature superconductors. Most of the HTSC compounds are composed of a minimum of four elements that must be deposited in the correct ratio in order to obtain optimised and high quality films. Each high $T_c$ material contains oxygen, an element that is incompatible with many aspects of thin film growth methods, especially the substrate heating is necessary for in situ annealed films, which
reacts with hot filaments for evaporators. The role of oxygen is also critical in
determining the properties of various film imperfections such as grain
boundaries. Most of the materials are highly reactive, leading to unwanted
chemical reactions that makes severe deviations from chemical purity in the
films. Hence, the selection of a suitable substrate is a crucial factor that offers
particular challenges in the field of high temperature superconducting materials.

1.4.1 Superconducting thick films

The term thick film does not relate to the thickness of the film but to
the method of deposition of the film (115). Thick films are very complex non-
equilibrium systems having physical properties that are intimately related to their
microstructure, which in turn is determined by the combination of material
properties and processing conditions. Thick film technology involves two main
steps, (a) the deposition of the film of the required material in the desired pattern
on to a substrate by common coating methods such as screen printing, spin
coating, dip coating, spray pyrolysis, paint-on method etc and (b) the subsequent
drying followed by firing at a higher temperature to produce films of about 3 to
50 microns thick. The final electrical properties of the films depend on the
material properties of the ink ingredients (homogeneous mixture consisting of the
material to be coated with suitable solvents and polymers) and the substrate as
well as the deposition process and time-temperature-atmosphere conditions
during firing (115). Most of the ink contain some active ingredients (the material
to be printed), a binder and a screening agent. The primary function of the
screening agent is to establish proper rheology for the ink. The thick film inks
must have a high viscosity to retain the particles in suspension and the blending
of the organic and inorganic constituents of the ink is required. In addition to
providing suitable rheology, the other major requirement for the organic
constituent in the ink is that they are removed completely during the heating
process and they should also not affect the chemistry of the inorganic
constituents before removal. In order to achieve good adherence, partial melting of the high temperature superconducting materials is almost essential. The processing based on thick film technology offers many advantages over thin films in certain applications (116-118). First, the preparation of thick film is inexpensive when compared with thin films which requires expensive and sophisticated instrumentation for their deposition. Secondly, they can cover large areas as well as curved surfaces. Also thick film methods are simple, less costly and easy to apply. Thick films of HTSC materials are of interest for many practical applications such as high Q resonators, substrate wiring and magnetic shielding (119-120).

Thick films of high temperature superconducting materials have been fabricated using different methods such as screen printing, dip-coating, spray pyrolysis, spin-coating, paint-on method etc. In all these cases sufficient adhesion and post heat treatment are essential. In the case of screen printing, the ink is prepared by thoroughly mixing fine HTSC powder with an appropriate amount of organic vehicle. This is then printed on a desired substrate through a screen of suitable mesh size. The printed film is then dried and subjected to controlled heat treatment for obtaining a superconducting thick film (121-122). For spray pyrolysis, an aqueous solution of the different metal nitrates are prepared in the desired stoichiometric ratio. This desired stoichiometric solution is then sprayed on to a heated substrate placed at a suitable distance from the aerosol nozzle using a carrier gas (123-124). In the case of spin coating the substrate is attached to a spinning rotor and the thick film paste is allowed to fall on the spinning substrate drop by drop (125-126). In the dip-coating process of thick films, the substrate is dipped in the thick film suspension to obtain a thick film coating of the desired material (127-128). In the paint-on method, the ink is applied on the substrate by means of a fine brush (129-130). In all the above cases, the dried film is subjected to heat treatment for obtaining the final adherent superconducting film.
A survey of literature shows that attempts were carried out in the preparation of YBCO, Bi-2223 and Bi-2212 thick films. In the case of YBCO films developed on Si, SiO₂, and Al₂O₃ yielded poor quality films with low \( T_C \) and \( J_C \) values. The YBCO thick films developed on MgO had low \( T_C \) values of ~80 K but was better than the films on Si, SiO₂, Al₂O₃ etc (131-132). Bi-2223 and Bi-2212 thick films developed on Si, SiO₂, and Al₂O₃ showed interdiffusion of ions in the film and the substrate. The Bi-2223 films developed on MgO substrate always contained both low \( T_C \) and high \( T_C \) phases (138-140). The deterioration of superconducting properties of the commonly used conventional superconductors is due to the chemical reactivity between the substrate and the film at the partial melting temperature. Owing to its complexity and increased demand for better quality, substrate development continues to be an area of active research.

1.5 Substrates for High Temperature Superconducting Films

Substrates play a very important role in determining the properties and quality of a superconducting film. A varied number of properties are critical in the selection of a material as a substrate for a high temperature superconducting film and they are been discussed in detail. The most vital and basic requirement for the selection of any material as a substrate for a superconductor is the chemical non-reactivity between the substrate and the superconductor at the processing temperature. This constraint is especially critical for high temperature superconductors because they react with most of the substrates at the processing temperature which are otherwise good candidates. The overriding importance of chemical compatibility over other substrate requirements in determining the suitability as substrate for HTSC film growth have been highlighted in many review articles (133-134). Therefore, if the chemical compatibility fails, a good match of other substrate requirements becomes irrelevant.

Another important criterion for the determination of a material as substrate for superconducting epitaxial films is the matching of the lattice
constant values and the thermal vibration. The epitaxial growth requires a misfit
\( \varepsilon, (\varepsilon = \frac{b-a}{a}, \) where 'a' and 'b' are the interplane lattice constant of the substrate
and the overgrown materials respectively) of not greater than 15% (135). It is
necessary to minimise the lattice mismatch to obtain highly oriented epitaxial
films. Along with a close lattice match between the substrate and the film, it is
also necessary that there exists a reasonable number of coincidence sites between
the substrate material and the film. Coincidence sites are atomic positions,
preferably with same or similar atomic sizes and values that coincide on either
side of the interface. Hence, for good epitaxy, both the superconducting material
and the substrate should have the same crystal structure. As the epitaxial growth
of films take place at high temperatures, the difference between the thermal
expansion coefficient of the substrate and the film should be a minimum. Since
all the high temperature superconducting materials are brittle being ceramic in
nature, cracking of the films occur if the thermal mismatch is high. This will lead
to a decrease in the value of \( T_c \) and \( J_c \) for substrate applications (136).

The quality of the substrate surface is another important property to be
considered to obtain high quality films as interaction occurs between the
substrate material and the superconducting film. A flat surface is necessary to
grow a uniform and homogeneous film. A number of factors like crystal defects,
cracks, non-uniform sinterability of the substrate, scratches, secondary phases,
surface warp etc., affect the surface properties of the substrate. Surface
smoothness is also equally important to obtain defined microstructure and well-
oriented superconducting films. Therefore an ideal substrate surface should be
flat, dense and free of twins and inhomogenities. The substrate material should be
thermodynamically stable within the temperature range required to grow and
process the film. A phase transition within this range will have significant effects
on the surface quality of the substrates which leads to film cracks and
deterioration of superconducting properties of the film. If at all a phase transition
occurs it should be as minor as possible, i.e., a second order one with no discontinuous volume change and minimal structural change (133-134).

Low dielectric constant and loss factor are basic requirements for device applications of high temperature superconducting films in the microwave frequency region. The desired value of the dielectric constant is related to the length of the electromagnetic wave in the substrate material and the microwave circuit fabrication tolerances. In order to avoid destruction of the electromagnetic stability of the circuit, the substrate thickness as well as the width of the coplanar lines should be sufficiently less than the wavelength (136). By increasing the operating frequency, one reduces the maximum of the allowed substrate thickness and line width. However, the thickness cannot be reduced to less than 0.3 to 0.5 mm without compromising much on its mechanical strength. This imposes restriction on the values of dielectric constant of the substrate material and extremely high value of dielectric constant and loss factor rule out their application as substrate for microwave applications (136). Also for microwave applications the presence of twinning in the processing temperature range is undesirable as it precludes device-modelling (137). Large area single crystal substrates are required for most of the device applications.

Most of the commercially available substrates such as Si, SiO₂, Al₂O₃, GeO, MgO, LaAlO₃ etc, react with both YBCO and BSCCO superconductors at the processing temperatures thereby degrading the transition temperature of the film drastically (138-140). Even though Al₂O₃ possess outstanding dielectric properties, high mechanical strength and commercial availability in twin free large diameter single crystals, the reaction between Al₂O₃ restricts its use as a substrate for YBCO and BSCCO superconductors (140-142). MgO, the widely used commercial substrate for YBCO and Bi-2223 films, has modest dielectric properties and are readily available as large area single crystals (133-134). However, in the case of YBCO, MgO forms an interlayer of barium salt at the
YBCO-MgO interface if the processing temperature is greater than 700°C and reduces the superconducting transition temperature of the film drastically (140-143). The superconducting Bi-2223 film developed on MgO always contained both the low $T_c$ Bi-2212 and high $T_c$ Bi-2223 phases (144-145). LaAlO$_3$, a chemically compatible substrate, has a phase transition in the film processing regime (800 K) and its dielectric constant varies from point to point in a manner that cannot be controlled or predicted (133-134). SrTiO$_3$ is another substrate material used for both YBCO and BSCCO superconductors. However, its high dielectric constant restricts its use in microwave applications in addition to its unavailability in reasonable sizes (133-134, 146). LaGaO$_3$ was identified as a potential substrate material with its good lattice and thermal expansion match and attractive dielectric properties ($\varepsilon' = 25$). However, it has a serious drawback with a first order phase transition at 420 K (133-134, 146). In the recent years a new group of complex perovskite ceramic oxides with the general formula Ba$_2$REM$_6$ (RE = rare earth, M = Sn, Sb, Nb, Zr, Ta and Hf) have been synthesized and characterized for their potential use as substrates for YBCO and BSCCO superconductors (147-152). A considerable amount of work is going on with regard to their development as single crystals for substrate applications.

1.6 Nanostructured Materials

The early research work carried out in the field of materials science established that the microstructure of a solid is one of the crucial parameters in determining the properties of a material. As the particle size of a material is reduced to a considerably smaller scale, while maintaining the chemical composition and arrangement of atoms, the properties of the material vary dramatically. Nanostructured or nanocrystalline materials are materials with a microstructure having particles of characteristic length of the order of nanometers (152-155). Such nanocrystalline materials containing particles in the nanometer range exhibit a host of unique and attractive properties that are much superior.
from their corresponding coarse grained particles. They include increased strength / hardness (161-162), enhanced diffusivity (163-164), improved ductility/toughness (156), reduced elastic modulus (165-166), higher electric resistivity (167-168), increased specific heat (169-170), higher thermal expansion coefficient (156, 160), lower thermal conductivity (156), superior magnetic properties (171-172) and enhanced sinterability (173-174). This deviation in the properties of nanostructured materials results from the reduced size and dimensionality of the nanometer sized particles as well as from the numerous interfaces between adjacent crystallites. The synthesis of materials and/or devices with new properties by controlling the microstructure on the atomic level has become one of the most active and rapidly progressing interdisciplinary areas of research based on solid state physics, chemistry, biology and materials science. The potential importance of these new generation materials in industry is cited in many recent review articles (153-154, 156-160).

The nanostructured materials are often classified in to the following three categories (153). The first category comprises materials with reduced dimensions in the form of nanometer sized particles, thin wires or thin films that are isolated, substrate supported or embedded. Chemical Vapour deposition (CVD), Physical Vapour Deposition (PVD), inert gas condensation, various aerosol techniques, precipitation from the vapour appear to be the techniques most frequently used to generate this type of microstructure. Well known examples of technological application of materials whose properties depends on this type of microstructure are catalysts and semiconductor devices utilizing single or multilayer quantum well structures (153). The second category comprises materials in which the nanometer sized microstructure is limited to a thin nanometer sized surface region of a bulk material. PVD, CVD, ion implantation and laser beam treatments are the most widely applied procedure to modify the chemical composition or atomic structure of solid surface on a nanometer scale. Surfaces with enhanced corrosion resistance, hardness, wear
resistance or protective coatings are examples in which the properties of thin surface layer are improved by means of creating a nanometer sized microstructure in a thin surface region. An important subgroup of this category is materials, the surface of which is structured laterally on a nanometer scale by developing a nanometer sized structural pattern on the free surface. Patterns of this type may be synthesized by lithography, means of local probes and surface precipitation processes. Patterns in the form of an array of nanometer sized islands (e.g. quantum dots) connected by nanometer sized wires are examples of this type of microstructure. Processes and devices of this type are expected to play a key role in the production of the next generation of electronic devices such as highly integrated electronic circuits, terabit memories, single electron transistor, quantum computers, etc.

The third category comprises of bulk solids with a nanometer sized microstructure and are assembled of nanometer sized building blocks-mostly crystallites. These building blocks may differ in their atomic structure, their crystallographic orientation or chemical composition. In other words, materials assembled of nanometer sized building blocks are microstructurally heterogeneous consisting of crystallites and grain boundaries. Bulk materials with a nanometer sized microstructure are called nanostructured materials. The synthesis, characterization and processing of such nanostructured materials are the part of an emerging and rapidly growing field referred to as nanotechnology. Research and development in this field emphasizes scientific discoveries in generation of materials with controlled microstructural characteristics, research on their processing into bulk materials with engineered properties and technological functions, and introduction of new devices, concepts and manufacturing methods.

The physics and chemistry of nanoscale systems has advanced rapidly over the last years and there are real prospects of translating these exciting scientific developments into a new generation of high technology products and
processes. Since nanotechnology is a generic technology, it also has the potential to impact on a wide range of industrial sectors, from chemicals to electronics, from sensors to advanced materials. In our present study we have focussed our attention on the synthesis of a new group of cubic perovskite ceramic oxides, with the general formula, $\text{Ba}_2\text{REHfO}_{5.5}$ ($\text{RE} = \text{Rare earth}$) as nanoparticles by a modified combustion process for better phase purity, homogeneity and sintering behaviour.

### 1.7 Origin of the Present Work

In the course of our study on the effect of oxide additives in the YBCO superconductor (175-178), it was observed that the addition of $\text{HfO}_2$ in YBCO did not show any effect on its superconducting transition (179). It was observed that $\text{HfO}_2$ addition in the YBCO system tremendously enhanced the oxygen absorption ability, thereby making it possible to obtain superconductivity even by directly quenching in air to room temperature from a sintering temperature of $950^\circ\text{C}$. This method of obtaining superconducting samples by rapid quenching eliminates the need of slow cooling ($2^\circ\text{C/min}$) or annealing at $550^\circ\text{C}$ for several hours, after high temperature sintering for oxygenation in the processing of YBCO. X-ray diffraction studies of the quenched samples showed the presence of a second phase in the system which did not have any effect on the structure or superconducting properties of YBCO (200). This new secondary phase present in the YBCO-$\text{HfO}_2$ system was identified as $\text{YBa}_2\text{HfO}_{5.5}$ (YBHO) and our studies showed that $\text{YBa}_2\text{HfO}_{5.5}$ could be used as a suitable substrate for YBCO superconducting films (180). $\text{YBa}_2\text{HfO}_{5.5}$ was synthesized as a single phase material through the solid state reaction method. However, to get a sintered $\text{YBa}_2\text{HfO}_{5.5}$ specimen, it was necessary to introduce the liquid phase sintering by the addition of small impurities (0.2 wt % of CuO) in the calcined powder. This impurity addition is undesirable for substrate application because it adversely affects the chemical homogeneity and dielectric properties of the material. In this
context, we made attempts to synthesize other materials by substituting rare earth elements for the yttrium atom. A new class of complex perovskite ceramic oxides with the general formula Ba$_2$REHfO$_{5.5}$ (RE = La, Pr, Nd and Eu) were synthesized by the solid state reaction method. These materials were found to be non-reacting with HTSC materials even at the extreme processing conditions and has favourable dielectric properties for microwave applications. These materials were thermodynamically stable and melt congruently making single crystal growth from melt possible. The suitability of the Ba$_2$REHfO$_{5.5}$ materials as substrates for HTSC films was confirmed by developing thick films with excellent superconducting characteristics. The newly developed ceramic materials were also synthesised as nanoparticles by a modified combustion process. The implications of the studies carried out are presented in the following sections of this thesis.
REFERENCES


**Further References**


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