PART B

OXIDE CERAMICS
CHAPTER VI

A man would do nothing if he waits until he could do it so well that no one would find fault with what he has done.

..... Cardinal Newman
Stages in the progress of human civilization have been characterized by the materials used. In Stone Age, Iron Age etc., ceramics represent one of the oldest materials employed both as objects of utility and beauty. Traditional or conventional ceramics have responded to basic human needs by providing building materials for shelter and pots for cooking and storage, besides refractories for high temperature furnaces, optical glass for spectacles, microscopes and telescopes, electrical and thermal insulation etc. These conventional ceramics are made from the minerals composed of elements like B, C, Al, Na, K, O, N and Si which of course are termed as ceramic raw materials. These are made from inexpensive materials such as clay, sand and other minerals which occur abundantly in nature and hence their applicability is widespread.

Among the three dominating technologies of the present age, the bio-technology, electronics and advanced materials, the third one is playing
significant role in the field of science and technology. Ceramics are drawn to the centre of this new technology. This is due to the steady progress in our scientific understanding of the structure-processing-property correlations in ceramics, often in quantitative terms. These advanced ceramics differ from that of conventional or traditional ceramics in processing, properties and applications. The basic differences between conventional and advanced ceramics are summarized in Table 6.1.

The discovery of ‘superconductivity’ in ceramics at unimaginably high temperatures (100 K) has been the most important achievement in decades of science as a whole and certainly in centuries in the field of ceramics. Room temperature superconducting ceramics appear to be around the corner? The fantastic range of applications, from loss-free power transmission, to levitated trains, computers etc., has already glorified the science and technology community and is sure to change the way of human life.

Ceramics are the best electric insulators. But it is now possible to confirm high electrical conductivity in these advanced ceramics where the charge carriers can by choice be electrons or ions. This most interesting and unusual property exhibited by ceramic metal oxides is known as ‘superconductivity’. So an attempt has been made to study this unique zero resistivity behaviour exhibited by these oxide ceramics.

HISTORICAL BACKGROUND AND THEORETICAL DEVELOPMENTS IN SUPERCONDUCTIVITY

A superconductor is a material which can carry an electric current without any measurable resistance. Superconductivity is an exceptional phenomena in the field of SOLID STATE PHYSICS and is a world in which Ohm’s law does not apply and in which the quantum properties of electrons lead to a ‘new order’. Large electrical currents flowing without losses and strong repulsive forces against magnets indicate some of the properties for future revolutionary applications in the area of energy usage. But these exotic properties were exhibited only at temperatures close to absolute zero, since a very low temperature minimizes the thermal vibrations within a material which could contribute to resistive losses. However this peculiar behaviour had been hidden for more than seventy years (after its discovery in 1911) in the depth of temperatures at and below 23 K, until, the now familiar cuprate oxide
<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Conventional</th>
<th>Advanced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>Natural minerals with little or no processing e.g. clay, sand</td>
<td>Processed materials e.g. Al₂O₃, ZrO₂, Si₃N₄, SiC, SiAlON</td>
</tr>
<tr>
<td>Processing</td>
<td>Pressing, extrusion, slip casting, drying, firing</td>
<td>Tape casting, hot isostatic pressing, injection moulding, CVD, in situ oxidation</td>
</tr>
<tr>
<td>Properties</td>
<td>Refractoriness, thermal and electrical insulation</td>
<td>Fracture toughness, electrical conductivity, electro-optics, dielectrics piezoelectrics, magnetics, superconductivity</td>
</tr>
<tr>
<td>Applications</td>
<td>Refractories, sanitaryware, sheet glass, building materials</td>
<td>Diesel engine, optical fibre, substrate, ferrites, capacitors, transducers</td>
</tr>
</tbody>
</table>
ceramic superconductors were discovered in 1986, since then the highest transition temperature has been steadily increasing and what was once only a dream in the world of cryogenics became a reality.

**Historical Back-Ground**

Kamerlingh Onnes of Leiden, The Netherlands discovered superconductivity in mercury when he held it at a temperature of 4 K, shortly after he succeeded in liquefying helium in 1911 [1]. He soon found similar behaviour in lead at 7.2 K and tin at a transition temperature $T_c$ (the temperature at which its electrical resistance, for all practical purposes, is zero and is denoted as $T_c$) of 3.7 K. Besides this dramatic behaviour of zero resistance; these superconductors also exhibit a few other unique characteristics which are not displayed by normal materials.

Walter Meissner and Robert Ochsenfeld, in Berlin found in 1933 [2] that superconductors expel magnetic fields and do not allow the magnetic flux to flow into the material which in turn act as a perfect diamagnetic material. This effect is known as 'Meissner effect'.

When a superconducting material is placed in a magnetic field and cooled below its transition temperature ($T_c$), the entire magnetic flux is expelled from the material. When the strength of the applied magnetic field is increased slowly, a value is reached where the magnetic lines of force begin to penetrate into the material and make it non-superconducting or normal. This particular value of the magnetic field above which the superconductivity is destroyed is called as the critical or threshold magnetic field ($H_c$) which is a function of temperature of the material and is given by the equation [3],

$$H_c \approx H_0 \left[1-(T/T_c)^2\right],$$

where $H_0 = H_c$ at $T = 0$ K. It is convenient to introduce the reduced coordinates, $t \equiv T/T_c$, and $h(t) \equiv H_c(T)/H_0$, in terms of which $h \approx 1-t^2$.

The actual temperature variation of $h$ is more accurately represented by a polynomial in which the coefficient of the $t^2$ term differs from unity by a few percent.

The perfect conductivity is necessary but not sufficient condition for the perfect diamagnetism, and so these two properties are to be regarded as distinct fundamental characteristics of a superconductor.
Type I and Type II Superconductors

Based on the Meissner effect, the superconducting materials were divided into two types, type I and type II superconductors.

A type I superconductor has the property of losing all its superconductivity when \( H_c \) (the critical magnetic field) is exceeded. A type II superconductor has two values of critical field. The first is \( H_{c1} \) below which all magnetic fields are expelled and above which the material begins to lose its superconductivity as the field is increased. In this mixed state the field penetrates into the superconductor. With further increase in the field, \( H_{c2} \) is reached above which the normal state exists. Hence, type I superconductors can exist only in one of the two states, superconducting or normal. But type II superconductors can be in one of the three states: superconducting, mixed or normal [4]. The phase diagrams of the two types are compared in Fig.6.1. The early materials, the metals and alloys, are type I, all of which had low values of \( H_c \). The modern high \( T_c \) materials are of type II in which \( H_c \) is high enough to enable their use in practical devices and applications reaching about 200 tesla, a factor of 10 greater than \( H_{c2} \) of low temperature superconductors (type I) and hence the applications of type I superconductors are limited.

Type I and type II superconductors are differentiated by the value of the Ginzburg-Landau (\( K \)) constant. The materials having the value of \( K < 0.71 \) are known as type I and materials with \( K > 0.71 \) come under type II. This constant \( K \) is defined as the ratio of the penetration depth \( \lambda \) to the coherence length \( \xi \) and is given by \( K = \lambda/\xi \). In type II superconductors, the larger the value of \( K \), the smaller will be \( H_{c1} \) but the larger will be \( H_{c2} \) relative to the critical field \( H_c \).

In 1956 Cooper of University of Illinois found that superconductor current is carried by electron pairs created by phonon interaction with the lattice (which causes them to have equal and opposite moments). These electrons are now called 'Cooper Pairs'. In 1957, a successful microscopic theory of the mechanism of superconductivity was developed by Bardeen, Cooper and Schrieffer of the University of Illinois and usually it is known as BCS theory [5]. The BCS theory has two parts. First one has the concept of pairing mechanism leading to an instability in the normal metal towards the formation of bound pairs of electrons. The second part consists of a description of entire system, through a wave function, as made up of several pairs, in a coherent fashion. The second part is presumably common to any
Fig. 6.1. Phase diagrams of type-I and type-II superconductors.
theory of superconductivity, so the search is now on for a suitable pairing mechanism that can support a high $T_c$. The BCS theory essentially explains how an electron-phonon (lattice vibrations) interactions can lead to an electron-electron attraction to form a Cooper pair and hence superconductivity. According to this theory, an electron moving through the lattice momentarily distorts the lattice and gets scattered. It will create a concentration of positive charge around the region. A second electron is attracted to this positively charged region. Thus the two electrons can form a "bound pair" (Cooper pair) possessing an opposite spin (and also momentum) and with a binding energy which is the characteristic of the material. However the attractive force is very weak, as evidenced by the fact that superconductivity exists only at low temperatures where the thermal effects are small. At higher temperature there is sufficient thermal energy to disrupt the pairs. The condensation of electrons into Cooper pairs opens up an energy gap (superconducting energy gap, $2\Delta$) at the Fermi level at and below $T_c$. Below $T_c$ eventhough the electron pairs get scattered by the phonons continuously, the net electron momentum transfered to the lattice is zero. This is because the total momentum of the pair is always constant. Thus materials exhibiting this superconductivity offer no resistance when the electric field is applied below the transition temperature ($T_c$). The existence of these Cooper pairs below $T_c$ can successfully explain many typical properties of superconductors like zero resistance, Meissner effect, anomaly in the heat capacity ($C_P$) and vanishing of Seebeck coefficient ($\alpha$). The prediction of the energy gap ($2\Delta$) and explanation of the isotope effect [6] ($T_c \propto M^{1/2}$ where $M$ is the isotopic mass of the material) are some of the other consequences of BCS pairing mechanism.

According to the BCS theory,

$$T_c = 1.14\theta_0 \exp(-1/N(0)V),$$

where $\theta_0$ is the Debye temperature, which is related to the average resonance frequency of the lattice. $N(0)$ is the density of states at the Fermi level per spin and $V$ is net pairing potential for the electron-phonon interaction.

Although the BCS theory has been successful in explaining the many of the properties of superconductivity state, the theory makes no restriction on how large the $T_c$ can be. General consideration of interactions in solids have been invoked by
some theorists to argue that no material can be a superconductor at temperatures anywhere near room temperature. McMillan has argued [7] that the softening of the lattice may establish an upper limit to the $T_c$ of superconductivity. Taking into consideration the inherent Coulombic repulsion between the electrons, he extended the BCS theory and gave an expression for $T_c$ as:

$$T_c = \frac{\theta_0}{1.45} \exp\left\{\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right\},$$

where $\lambda$ is the attractive electron-phonon coupling constant and $\mu^*$ is the coulombic repulsion between the electrons (a constant with a value $\approx 0.1$ in most cases). This model predicts optimum $T_c$ values for several superconductors. When $\lambda < 1$, we have the weak coupling limit and when $\lambda > 1$, the strong coupling limit. McMillan's theory was able to account for the failure over many years to find any substance with critical temperature higher than that of Nb$_3$Ge alloy ($T_c = 23K$) until the recent discoveries in oxide ceramic superconductors.

In 1962, Josephson, at Cambridge University predicted the tunnelling of superconducting electrons (Cooper pairs) through a very thin dielectric material sandwiched between the two superconductor strips with no voltage across the sandwich. This effect is known as 'Josephson effect' which led to the development of the Josephson junction, a key element in devices that find applications in SQUIDS and in certain kinds of logic circuits. An observation of the effect was made by Anderson and Rowell in 1964 [8].

Superconducting Materials

The unique zero resistance property of the superconducting materials have made the scientists from different groups and fields to search for the materials with higher transition temperature.

The basic elements in the periodic table exhibiting this property were studied by many scientists and these superconducting ceramics are shown in Fig.6.2 [9]. As observed from the figure one can say that nearly twenty six elements exhibit the superconductivity property at low temperatures directly and most of the metals are purely from d block especially the transition metals. Among these, the element niobium has the highest $T_c$ of 9.5 K. Semiconducting materials like silicon and germanium will become superconducting materials only under high pressure or in
Fig. 6.2. Superconducting Elements.
thin film form. It is really worth noting that the pure conducting materials like Cu, Ag and Au are not at all superconducting even though they are metallic in nature.

Alloys and Compounds

The quest for high $T_c$ superconductors made many groups of researchers to divert the path towards alloys and compounds. In 1960's they used the empirical rules and stayed within the standard classes of metallic alloys and compounds. Among them niobium has become the favourite element and $A_{15}$ structure was considered to be ideal for high $T_c$ superconductors. Empirical rules such as electron-to-atom ratio ($e/A$) [10], atomic volume [11] and atomic mass correlations [12,13] etc. identified Nb$_2$Ge and Nb$_2$Si as candidates to raise $T_c$ above 20 K. But the stoichiometric equilibrium differs from that of $A_{15}$ phase. To overcome this difficulty and to make metastable phases of desired compounds, special techniques like rapid cooling were employed and in 1971, a record high $T_c$ of 23 K was discovered in Nb$_3$Ge [14]. Later Nb$_2$Si was also prepared which was purported to have a $T_c$ near 30 K. Nb$_2$Si with $A_{15}$ structure was prepared by high pressure and film growth techniques in 1979, but it showed a low $T_c$ at 20 K [15,16].

Some metal oxides were also found to exhibit superconductivity. The first oxides were TiO and NbO [17]. Later the system SrTiO$_{3-x}$ ($T_c \sim$ 1 K) was prepared with a perovskite structure [18] and little later alkali tungsten bronzes were prepared which showed a $T_c \sim$ 6 K [19]. Most of the empirical rules developed for binary systems became invalid for ternaries and synthesis became more sophisticated. The search for new superconductors led to the discovery of superconductivity in LiTi$_2$O$_4$ by Johnston et al [20] at temperature as high as 13.7 K in 1972. In 1975 Sleight et al [21] discovered superconductivity at 13 K in BaPb$_{1-x}$Bi$_x$O$_3$ a compound with perovskite structure not containing any transition metal.

Advanced Ceramic Oxide Superconductors

At room temperature ceramics are nonconductors. But the recent discoveries found a new class of ceramics (metal oxides) that superconduct at temperatures much higher than near absolute zero. Hence, they are termed as high $T_c$ oxide superconductors. No discovery in solid state science has created as much excitement as that of high temperature superconductivity in cuprates.

In 1986, Bednorz and Muller of IBM, Zurich laboratories, Switzerland, found a new class of ceramic oxide superconductors that exhibit superconductivity well
above the previously achieved transition temperatures. In April 1986, they reported
the observation of superconductivity in oxygen deficient perovskite compounds in
the La-Ba-Cu-O system with nominal composition \( \text{La}_{x}\text{Ba}_{y}\text{Cu}_{z}\text{O}_{3\gamma} \) at temperatures
as high as 35 K [22]. The underlying single-phase compound responsible for
superconductivity was later identified as \( \text{La}_{2-x}\text{Ba}_{x}\text{CuO}_{4+d} \) \((x = 0.2)\) [23-25] with
K\(_2\)NiF\(_4\) structure. Subsequently Chu et al [26] enhanced the \( T_c \) of the same
compound to 52.5 K by applying pressure.

In 1987, a group of researchers at the University of Houston, under Chu
substituted yttrium for the lanthanum and observed a \( T_c \)-zero at 90 K [27]. The
underlying single phase compound responsible for 90 K in this Y-Ba-Cu-O system
was identified as an orthorhombic \( Y_1\text{Ba}_{2}\text{Cu}_{3}\text{O}_{7\gamma} \) by Cava et al [28], Rao et al [29]
and several others independently. Since the composition of YBCO is in the ratio of 1:2:3;
the system is often termed as 123 superconductor.

In 1988, Maeda et al [30] discovered superconductivity above 100 K in the
rare earth free Bi-Sr-Ca-Cu-O system. A little later Sheng and Herman [31]
developed a new system Tl-Ca-Ba-Cu-O which superconducts at still higher
temperatures of 125 K. These two materials are abbreviated as BSCCO and TBCCO.
These two systems were followed by discoveries of superconductivity in several other
Cu-based ceramic oxides [32-36]. All these superconductors discovered so far are
p-type (majority carriers are holes) except for the \( \text{Nd}_{2-x}\text{Ce}_{x}\text{CuO}_{4} \) superconductors
[37] which are n-type (majority carriers are electrons). The historical record of the
increase in the superconductivity transition temperatures \( (T_c \text{ value}) \) from the
discovery of superconductivity in mercury (Hg) to today's high \( T_c \) superconductors is
shown in Fig.6.3 [38]. The remarkable and unexpected jump in superconductive
critical temperatures (as shown in figure) i.e. from low temperatures to high
temperatures led to the evolution of the new class of compounds named as high \( T_c \)
ceramic oxide superconductors. The three compounds YBCO, BSCCO and TBCCO,
along with the related compounds made up of the same constituents (Cu-O planes)
with different proportions, are the focus on all the current activity in high
temperature superconductivity. Table 6.2 lists all the superconductivity systems with
the corresponding phases and their \( T_c \) values, discovered in the last four years.
Fig. 6.3. Historical record of the increase in the superconductivity transition temperatures from the discovery of superconductivity in mercury to today’s high $T_c$ superconductors.
<table>
<thead>
<tr>
<th>System</th>
<th>Composition</th>
<th>Acronym</th>
<th>$T_c$(K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-M-Cu-O</td>
<td>La$_2$M$_2$CuO$_4$</td>
<td>La-214</td>
<td>25-40</td>
<td>22-25</td>
</tr>
<tr>
<td>(M = Ba, Sr, Ca)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-Ba-Cu-O</td>
<td>R$_2$Ba$_2$Cu$_3$O$_7$</td>
<td>123</td>
<td>90</td>
<td>27-29</td>
</tr>
<tr>
<td>(R = all rare earths except Ce, Pr, Tb)</td>
<td>R$_2$Ba$_2$Cu$_4$O$_8$</td>
<td>124</td>
<td>80</td>
<td>39-45</td>
</tr>
<tr>
<td></td>
<td>R$_2$Ba$_4$Cu$<em>7$O$</em>{15}$</td>
<td>247</td>
<td>40</td>
<td>42,43</td>
</tr>
<tr>
<td>Bi-Sr-Ca-Cu-O</td>
<td>Bi$_2$Sr$_2$CuO$_6$</td>
<td>Bi-2201</td>
<td>10</td>
<td>44,46</td>
</tr>
<tr>
<td></td>
<td>Bi$_2$Sr$_2$CaCu$_2$O$_3$</td>
<td>Bi-2212</td>
<td>85</td>
<td>30, 46,48</td>
</tr>
<tr>
<td></td>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_10$</td>
<td>Bi-2223</td>
<td>110</td>
<td>46,48</td>
</tr>
<tr>
<td></td>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$_4$O$_10$</td>
<td>Bi-2234</td>
<td>90</td>
<td>48,49</td>
</tr>
<tr>
<td>Tl-Ca-Ba-Cu-O</td>
<td>Tl$_2$Ba$_2$CuO$_6$</td>
<td>Tl-2021</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$CaBa$_2$Cu$_2$O$_6$</td>
<td>Tl-2122</td>
<td>108</td>
<td>50,51</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_9$</td>
<td>Tl-2223</td>
<td>125</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$<em>4$O$</em>{12}$</td>
<td>Tl-2324</td>
<td>90</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ba$_2$Cu$_4$O$_6$</td>
<td>Tl-1021</td>
<td>10</td>
<td>53-64</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$_6$O$_7$</td>
<td>Tl-1122</td>
<td>90</td>
<td>33, 55, 56</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_9$</td>
<td>Tl-1223</td>
<td>110</td>
<td>66,67</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$<em>4$O$</em>{11}$</td>
<td>Tl-1324</td>
<td>122</td>
<td>56,57</td>
</tr>
<tr>
<td></td>
<td>Tl$_2$Ca$_2$Ba$_2$Cu$<em>5$O$</em>{13}$</td>
<td>Tl-1425</td>
<td>115</td>
<td>56,57</td>
</tr>
<tr>
<td>(Tl,Pb)-Ca-Sr-Cu-O</td>
<td>(Tl,Pb)$_2$Sr$_2$Cu$_3$O$_6$</td>
<td>(Tl,Pb)-1021</td>
<td>50</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>(Tl,Pb)$_2$Sr$_2$Cu$_2$O$_7$</td>
<td>(Tl,Pb)-1122</td>
<td>90</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>(Tl,Pb)$_2$Ca$_2$Sr$_2$Cu$_3$O$_9$</td>
<td>(Tl,Pb)-1223</td>
<td>122</td>
<td>34</td>
</tr>
<tr>
<td>Pb-Sr-(Ca/R)-Cu-O</td>
<td>Pb$_2$Sr$_2$(Ca,R)$_1$Cu$_3$O$_y$</td>
<td>2213</td>
<td>50</td>
<td>32</td>
</tr>
<tr>
<td>(R = rare earth)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-Sr(Th)-Cu-O</td>
<td>R$_2$-xCe$_x$CuO$_4$</td>
<td>214</td>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td>Ba-K-Cu-O</td>
<td>Ba$_{1+x}K_x$CuO$_3$</td>
<td>--</td>
<td>30</td>
<td>59</td>
</tr>
<tr>
<td>Sr-Nd-Cu-O</td>
<td>Sr$<em>{x}$Nd$</em>{y}$CuO$_2$</td>
<td>--</td>
<td>40</td>
<td>59</td>
</tr>
<tr>
<td>La-Sr-Ca-Cu-O</td>
<td>La$_{2-x}$Sr$_x$Ca$_1$Cu$_2$O$_8$</td>
<td>--</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>
Applications of Superconductors

The basic properties of superconductors such as zero electrical resistance, Meissner effect and Josephson effect etc. have been successfully exploited for their practical applications. The three fundamental parameters that determine the economic feasibility for the applications are: (i) critical temperature \( T_c \), (ii) critical current \( J_c \) and (iii) the critical magnetic field \( H_{c2} \). The higher the \( T_c \), \( J_c \) and \( H_{c2} \) values for a superconductor, the better the material for practical applications. Hence, the race is on world wide to find out higher \( T_c \), high \( H_{c2} \) and high \( J_c \) superconducting materials. Due to the high cost of liquid Helium, the progress made in this direction has been rather slow, but with the advent of high \( T_c \) superconductors, an economic feasibility now exists for the realization of many of these practical applications. Table 6.3 summarizes the practical applications of superconductivity materials.

STRUCTURE OF HIGH \( T_c \) OXIDE CERAMICS

The understanding of superconducting mechanism in the newly discovered oxide superconductors is closely connected to the knowledge of the structural properties displayed by these materials. Besides it is more significant to explore possible connections between structural and superconducting properties and to establish general structural principles which can guide the researchers for new compounds.

The copper containing ceramic oxides exhibiting superconductivity properties are: (i) \( \text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_2\text{O}_4 \) \( (T_c = 37 \text{ K}) \); (ii) \( \text{LnBa}_2\text{Cu}_3\text{O}_7 \) \( (T_c = 91 \text{ K}) \); \( \text{Ln} = \text{Rare Earth} \); (iii) \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y \) \( (T_c = 80 \text{ K}) \); (iv) \( \text{Bi(Pb)}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_y \) \( (T_c = 110 \text{ K}) \) and (v) \( \text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_y \) \( (T_c = 125 \text{ K}) \). The latter four compounds exhibit the superconductivity behaviour well above liquid nitrogen temperature and possesses different complex crystal structures and some show oxygen deficiency. Polycrystalline samples of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7.4} \) show twin-domains, stacking faults, while single crystals are always almost 'twinned'. But the Bi and Tl compounds form twin-free crystals.

Structure of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7.4} \) (YBCO)

The crystal structure of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7.4} \) (YBCO) has been investigated and well characterized by many workers [28, 61-71]. The room temperature structure of YBCO samples with critical temperature \( T_c = 92 \text{ K} \) was found to be orthorhombic with the space group as \( \text{Pnmm} \). The unit cell of YBCO system is shown in Fig.6.4. It
<table>
<thead>
<tr>
<th>Based on Zero resistance</th>
<th>Based on Meissner effect</th>
<th>Based on Josephson effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power transmission</td>
<td>Magnetic shielding</td>
<td>* SQUIDS</td>
</tr>
<tr>
<td>Superconducting magnets</td>
<td></td>
<td>* high speed computer</td>
</tr>
<tr>
<td>(large volume and homogeneity) required for NMR, research on magnetic materials and MRI (medical diagnosis)</td>
<td></td>
<td>switches and memory</td>
</tr>
<tr>
<td>DC motor</td>
<td></td>
<td>* Magnetic cardiogram</td>
</tr>
<tr>
<td>AC Generator</td>
<td></td>
<td>* Mineral Prospecting</td>
</tr>
<tr>
<td>Power storage</td>
<td></td>
<td>* Radiation detectors</td>
</tr>
<tr>
<td>Particle accelerators</td>
<td></td>
<td>* Earthquake warning</td>
</tr>
<tr>
<td>Fusion research (energy research)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6.4. The Unit cell of YBCO.
consists of three oxygen deficient perovskite blocks with barium and yttrium in the centres of the blocks in the order Ba-Y-Ba and Cu at the corners. Compared with the ideal perovskite formula, two oxygen atoms are lacking in the unit cell. Oxygen is completely absent in the Y-containing plane perpendicular to c-axis, whereas only the oxygen positions along the b-axis in the basal plane are filled, which is obviously connected with the fact that the unit cell is slightly orthorhombic. There are two crystallographically different Cu-sites. The basal plane of Cu is coordinated by four oxygen atoms in a planar configuration so that infinite chains of corner sharing CuO₄ rhombs are present along the b-axis. The other copper ions are coordinated by five oxygens in a bell-shaped configuration. One of the oxygens is at a much larger distance than the other four, which also coordinate the copper ions in a planar configuration, but in this case infinite CuO₂ planes of corner sharing CuO₄ rhombs are present perpendicular to c-axis. The orthorhombic distortion is caused by the ordering of oxygen ions in the basal plane; the oxygen sites at (0,1/2,0) (hereafter 0(0)) are almost completely filled while those at (1/2,0,0) (hereafter 0(2)) are empty. Such distribution of oxygen ions gives rise to one dimensional Cu-O in the b-direction. The decrease of the oxygen content per atomic formula unit (a.f.u) was found to give rise to an increase of the lattice parameter 'c' according to the formula [72],

\[ 7 - \delta = 70.512 - 5.45\epsilon. \]

Furthermore, the decrease in oxygen content results in a decrease of orthorhombic distortion and finally (for an oxygen content of about 6.5 per a.f.u) in a crystallographic phase transition from an orthorhombic to a tetragonal structure (space group P4/mmm). By decreasing the oxygen content an increasing number of oxygen vacancies occurs at the 0(1) sites while at the same time, the oxygen occupancy of the 0(2) sites slightly increases. Finally at the structural transition from orthorhombic to tetragonal the 0(1) and 0(2) sites become equivalent with an occupancy of 0.25.

Structure of Bi-Sr-Ca-Cu-O (BSSCO)

The structural difference between the Bi-based compounds and the rare earth (123) compounds offered an incomparable opportunity to test the relative importance of some structural features in both types of systems. The crystallographic structure of both Tl and Bi based systems is same whereas the 1:2:3 compounds
presented subtle differences. The Tl and Bi compounds have only one type of Cu-O configuration, the Cu-O$_2$ planes, while in 1:2:3 compounds two Cu-O configurations exist, the Cu-O$_2$ planes and Cu-O chains.

The structural determination of Bi-Sr-Ca-Cu-O systems has become complicated because many samples contain mixtures of various phases. Even microscopic single crystals often contain synitic intergrowths (i.e. stacking errors along x-axis) of more than one phase. It was reported [46] that there were three superconducting phases with one, two or three consecutive CuO$_2$ layers and are represented by the general formula Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2(n+4)}$ (n = 1, 2 and 3). These three phases represented as 2201, 2212 and 2223, have $T_c$ values of $\sim 10$ K, $\sim 85$ K and $\sim 110$ K respectively. The structures of these three phases are made up of oxygen deficient perovskite type blocks sandwiched between the BiO double layers [47]. The n = 1 phase (2201), which crystallizes in an orthorhombic subcell, can be viewed as a stacking along c-axis of two Bi$_2$Sr$_2$CuO$_y$ slabs, with each slab having a CuO$_2$ layer at its centre and surrounded on each side first by a SrO layer and then by a Bi-O layer. Here the lattice parameters are about $\sqrt{2}$ times that of the perovskite slab ($c = 2.46$ nm). Insertion of one or two CaCuO$_2$ slabs between the CuO$_2$ layer and one of the Sr-O layers in the n = 1 phase produces the n = 2 ($c = 3.06$ nm) and n = 3 ($c = 3.71$ nm) phases, respectively. The structures of these three phases are shown in Fig.6.5. The important features in those structures are due to the presence of two Bi-O layers separated by a rather large distance of 0.32 nm and shifted with respect to each other (crystallographic shear) along the diagonal direction of the perovskite sub-cell, in going from one slab to the next.

The structure of 2212 phase was investigated by a large number of groups [46,47,73-75] using different techniques. The broad structural features reported by different groups are in good agreement with each other. But the conflict between them was regarding the position of oxygen in the Bi-O layers. Recent neutron diffraction studies [76,77] revealed that oxygen is within the Bi-O layers and the space group is a subgroup of Fmmn i.e., Amaa or Azan.

The present thesis is aimed to study the sintering effects on $T_c$ (zero) of the high $T_c$ materials. Attempt has been made to prepare YBCO, BSCCO bulk samples by solid state reaction method and their sintering conditions were optimized. Resistivity and ac susceptibility measurements were also carried out to study the
Fig. 6.5. The crystal substructures of the Bi-phases of general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+4)}$ with $n = 1, 2$ and 3.
variation of $T_c$ with respect to the preparation condition. Work has also been made to study the doping effects of Pb as substituent to Bi in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ system and the concentration of Pb was also optimized to get high $T_c$ single phase superconductivity material.

Because of the enormous number of publications that appeared in the literature on high $T_c$ ceramic oxide superconductors, it is not possible to refer all of them. However, all original and important papers that are relevant to the present study have been referred.
REFERENCES


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