

CRYSTAL STRUCTURES OF CUPRATE BASED SUPERCONDUCTING MATERIALS

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Abstract

The high- T_c cuprate superconductors have their structure derived from ideal perovskite structure, either through an intergrowth phenomenon or by an ordered removal of oxygen atoms. The common features of the cuprate superconductors are their layered crystal structure consisting of one or more CuO_2 layers. The tetragonal cuprate superconductors shows small difference in lattice parameters a and b close to 0.38nm because of common structural features of the CuO_2 planes. In this paper, the crystal structures of cuprate based superconductors are discussed

Keywords: Cuprate based superconductors; Perovskite; Critical temperature; Lattice parameters.

1. Introduction

In September 1986, J.G. Bednorz and K.A. Muller [1] of IBM Zurich Research Laboratory, Switzerland, found critical temperature (T_c) near 30K in barium substituted LaCuO_4 . The phase responsible for superconductivity was identified to have nominal composition $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ ($x=0.2$) having K_2NiF_4 structure. Later on, it was confirmed by various groups [2-7] that replacement of Ba by Sr enhances T_c to 57 K by application of pressure. This discovery opened the way for all the subsequent work on high T_c superconductors. In 1987, Chu et al [8] at Houston synthesized the compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with a T_c few degrees above 90K. H. Maeda et al. [9] in 1988 first report the existence of a superconducting phase with a T_c of around 105K in BiSrCaCuO at the Tsukuba laboratories in Japan. It was quickly established that a new series of superconductors had the structural formula type $\text{Bi}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with T_c of 10, 85 and 110K for $n = 1, 2$ and 3 respectively [10-18]. Shortly afterwards, Z.Z. Sheng and A.M. Hermann [19] announced superconductivity above 100K in the TlBaCaCuO system. Again several groups established the structural formula for this system as $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with T_c of 80, 110 and 125 K for $n=1, 2$ and 3 respectively [20-23]. In 1993, Putilin et al. [24] and Shilling et al. [25] announced the discovery of superconductivity in HgBaCaCuO system with three CuO_2 layers per unit cell in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ and two CuO_2 layers per unit cell in $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+x}$ compound, the highest known T_c , over 135K. At 23.5 Gpa T_c onset for Hg 1223 was found to be 157K [26, 27] and an onset of 164K at 35 Gpa [28]. The key features, which govern the T_c of this compound, are the number of CuO layers in a unit cell. The T_c is found to increase with the increase in CuO_2 layers. The cuprates can be doped and their charge carrier concentration can be varied.

In this paper the crystal structure of the most commonly examined cuprate superconducting materials like $\text{La}_{2-x}\text{M}_x\text{CuO}_4$, $\text{M} = \text{Ba, Sr}$ ($T_c=37.5\text{K}$), $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 90-95\text{K}$), $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 85\text{K}$), $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 110\text{K}$), $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 110\text{K}$), $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 127\text{K}$) and $\text{HgBa}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ($T_c = 134\text{K}$) are discussed.

2. General Perovskite Structure

All cuprate superconductors have a general perovskite structure. Perovskites are ceramics described by generalized formula ABX_3 . They consist of cubes made up of three distinct chemical elements (A, B and X) that are present in ratio 1:1:3 as shown in figure1. The A and B atoms are non-metallic cations (positive) and X atoms are non-metallic anions (negative). An A cation – the largest of the two kinds of metals-lies at the centre of each cube, the B cations occupy all the eight corners and the X anions lies at the mid-points of cube edges.

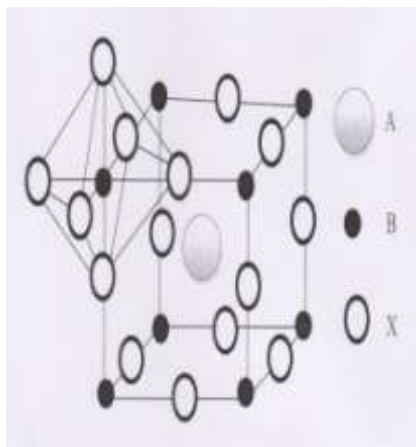


Figure 1. The perovskite structure ABX_3

3. Crystal Structures of Cuprate Based Oxide Superconductors

3.1 $La_{2-x}M_xCuO_4$ (M=Ca, Ba, Sr)

This cuprate have structure derived from ideal perovskite structure [29, 30, 31] through an intergrowth phenomenon. The structure of $La_{2-x}M_xCuO_4$ (M=Ca, Sr, Ba) is as shown in figure 2. M is substituted on the La-site $La_{1.85}M_{0.15}CuO_4$ has a tetragonal K_2NiF_4 type of layered perovskite structure consisting of a stacking of single CuO_2 planes alternating with two LaO layers along c-axis. The structure can be viewed as stacking of $-CuO_2-LaO-LaO-CuO_2-LaO-LaO-CuO_2-$. The substitution of dopant M^{2+} for host La^{3+} in La_2CuO_4 induces hole carriers in the CuO_2 planes eventually, leading to superconductivity.

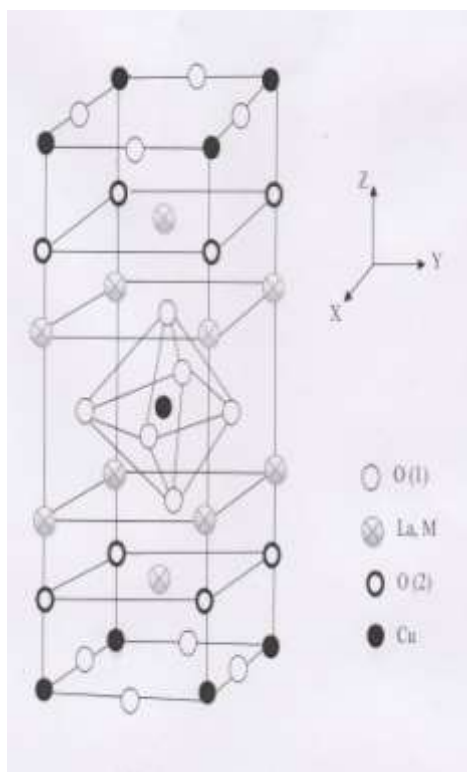


Figure 2. The crystal structure of $La_{2-x}M_xCuO_4$ (M=Ba or Sr)

The structure of the unit cell of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+x}$ has the body centering symmetry, it consists in two identical blocs, one above the other and shifted by a half a lattice constant in the x and y direction. Besides the four oxygen nearest neighbors in the CuO_2 plane, the Cu atom has also two apical oxygen atoms as nearest neighbors. The La atoms are located in a plane close to the one of the apical oxygen. In the corner of each octahedron, surrounding the Cu atom, an O atom is located. The O atoms in the upper and the lower corner are the apical oxygens. Above and below the CuO_2 planes, there are layers, consisting in a cation (La^{3+} in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+x}$) that forms an ionic bond with oxygen to which it transfers its valence electrons. These layers are called charge reservoir layers and are responsible for the doping with holes or electrons. The size of elementary cell is $a=b=0.378\text{nm}$, $c=1.32\text{nm}$. The highest T_c of this family achieved is 37.5K.

3.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (123)

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, popularly known as 123 is oxygen deficient perovskite; especially shortage of four oxygen in the Yttrium layer. The structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ oxide superconductors can be regarded as a quasi-two-dimensional superconducting CuO_2 sheet in the ab plane separated by a poorly conducting layer with Cu-O chains along the b-axis [32]. In the orthorhombic 123 compound there are two types of Cu sites; one in which Cu is fivefold coordinated by O (CuO_2 Plane) and one in which Cu is four fold coordinated (CuO chains). In the chain layer the presence of oxygen atoms along the b-crystallographic axis are essential for superconductivity. Every third Cu-O sheet of this layered structure is a sheet of CuO chains to create material with various oxygen contents. . Figure 3 shows the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

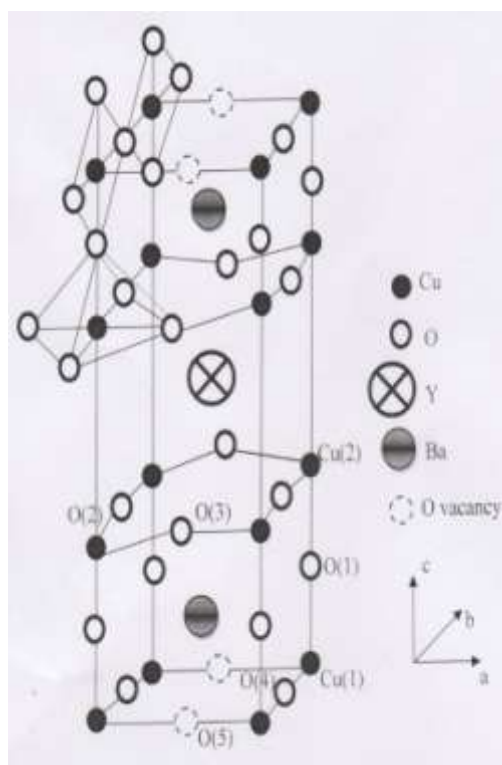


Figure 3. The crystal structure of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, seven atom of oxygen are crucial for the occurrence of superconductivity. The seven atoms of oxygen require fourteen electrons to fill their outermost shells to achieve state of minimum energy. The three electrons are provided by Yttrium atoms, four electrons by barium atoms and the remaining seven electrons are provided by three copper atoms belonging to sheets and chains of CuO planes.

The structure of these materials depends on the oxygen content. This non-stoichiometry is denoted by the x in the chemical formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. When $x = 1$, the O(1) sites in the Cu(1) layer are vacant and the structure is tetragonal. The tetragonal form of YBCO is insulating and does

not superconduct. Increasing the oxygen content slightly causes more of the O(1) sites to become occupied. For $x < 0.65$, Cu-O chains along the b axis of the crystal are formed. The presence of the CuO chains introduces elongation of the b axis, which in turn changes the structure to orthorhombic, with lattice parameters of $a = 0.382$ nm, $b = 0.389$ nm, and $c = 1.168$ nm [33]. Optimum superconducting properties occur when $x \sim 0.07$, i.e., almost all of the O(1) sites are occupied, with few vacancies. The stacking sequence of the (ab) planes is Y-CuO-BaO-CuO₂-BaO-CuO₂-Y. The stacking sequence of YBCO layers along c-axis of the crystal goes as follows: CuO-BaO-CuO₂-Y-CuO₂-BaO-CuO [34]. All corner sites of the unit cell are occupied by Cu, which has two different coordinations, Cu(1) and Cu(2), with respect to oxygen. There are four possible crystallographic sites [35] for oxygen: O(1), O(2), O(3) and O(4). The coordination polyhedra of Y and Ba with respect to oxygen are different.

The crystal structure of YBa₂Cu₃O_{7-x} is tetragonal for $x=1$ and orthorhombic for $x=0$. In a fully oxygenated YBa₂Cu₃O_{7-x} structure, the chain acts as an electron reservoir for electron transfer from the planes to the chains. As oxygen is removed, the structural effect is to fragment the square chains by removing the connecting oxygens, creating Cu-O dumb-bell intermittently. As more and more oxygen is removed (for $x=0.7$) the chain fragments get shorter and shorter and eventually the strain energy which stabilized the single direction of the chains is lost; the chain fragments can then easily align along the b or a axes. These axes then become equivalent on averaging over long length scales and the overall symmetry become tetragonal. The orthorhombic to tetragonal transition is an order-disorder transition in the orientations of chain fragments. The lattice constants changes from $a=0.3865$ nm, $c=1.1852$ nm for $x=1$ to $a=0.382$ nm, $b=0.388$ nm, $c=1.1676$ nm for $x=0$ [36]. In an insulating YBa₂Cu₃O_{7-x} structure ($x=1$), the lack of oxygen atoms at the chains isolates the CuO₂ planes from the chains, rendering the sample nonsuperconducting.

3.3 BiSrCaCuO

This material has three superconducting phases: Bi₂Sr₂CuO₆ (2201), Bi₂Sr₂CaCu₂O₈ (2212) and Bi₂Sr₂Ca₂Cu₃O₁₀ (2223) with T_c of 10, 85 and 110K respectively [37].

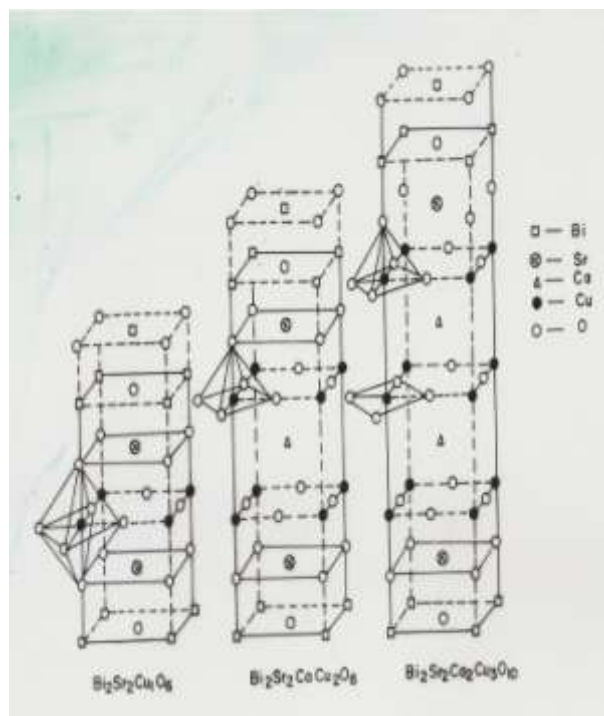


Figure 4 Crystal structure of Bi₂Sr₂Ca_{n-1}Cu_nO_{2n+4} compound for n=1, 2, 3

Each copper atom has one or two additional oxygen atoms positioned above or below the CuO₂ sheet to form axially elongated octahedra in Bi₂Sr₂CuO₆ [38] and square pyramids in

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The lattice compound contains calcium between the CuO_2 sheets in eight-fold coordination with oxygen. Strontium cations reside just above and below the single and double CuO sheets. A material containing three copper oxygen sheets with ideal formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ can also be made. There is no CuO chain in this structure. Figure 4 show the crystal structures of the three superconducting phases of BiSrCaCuO compound. The two phases have a tetragonal structure which consists of two sheared crystallographic unit cells. The unit cell of these phases has double Bi-O planes which are stacked in a way that the Bi atom of one plane sits below the oxygen atom of the next consecutive plane. The Ca atom forms a layer within the interior of the CuO_2 layers in both Bi-2212 and Bi-2223; there is no Ca layer in the Bi-2201 phase. The three phases differ with each other in the number of CuO_2 planes; Bi-2201, Bi-2212 and Bi-2223 phases have one, two and three CuO_2 planes, respectively. The c axis lattice constant of these phases increases with the number of CuO_2 planes. The coordination of the Cu atom is different in the three phases. The Cu atom forms an octahedral coordination with respect to oxygen atoms in the 2201 phase, whereas in 2212, the Cu atom is surrounded by five oxygen atoms in a pyramidal arrangement. In the 2223 structure, Cu has two coordinations with respect to oxygen: one Cu atom is bonded with four oxygen atoms in square planar configuration and another Cu atom is coordinated with five oxygen atoms in a pyramidal arrangement [39]. For $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212), the stacking sequence is Bi-Sr-Cu-Ca-Cu-Sr-Bi. In $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223), the layer sequence is Bi-Sr-Cu-Ca-Cu-Ca-Cu-Sr-Bi.

3.4 TlBaCaCuO

The first series of the Tl-based superconductor containing one Tl-O layer has the general formula $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ [40], whereas the second series containing two Tl-O layers has a formula of $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with $n = 1, 2$ and 3 . In the structure of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (Tl-2201), there is one CuO_2 layer with the stacking sequence (Tl-O) (Tl-O) (Ba-O) (Cu-O) (Ba-O) (Tl-O) (Tl-O). In $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Tl-2212), there are two Cu-O layers with a Ca layer in between. Similar to the $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ structure, Tl-O layers are present outside the Ba-O layers. In $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Tl-2223), there are three CuO_2 layers enclosing Ca layers between each of these. In Tl-based superconductors, T_c is found to increase with the increase in CuO_2 layers. However, the value of T_c decreases after four CuO_2 layers in $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$, and in the $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ compounds, it decreases after three CuO_2 layers [41]. Figure 5 shows the crystal structures of three superconducting phases of TlBaCaCuO . The Ca containing 2223 phase $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and 2212 phase $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ were first identified by Hazen et al [42]. There is a series of Tl based superconducting phases with double Tl_2O_2 layer with a general formula of $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n=1, 2, 3\dots$) [43, 44, 45]. Each next member is found by adding a Ca layer and a CuO layer into the previous one. The superconductivity in the thallium cuprates with the double block layer structure is promoted by the supply of electrons from CuO_2 layer to the empty 6s orbital of thallium [46]. Another series of Tl based superconducting phases have single TlO layer $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ ($n=1, 2, 3\dots$), two CuO_2 layers per unit cell and $T_c \sim 85\text{K}$ [47].

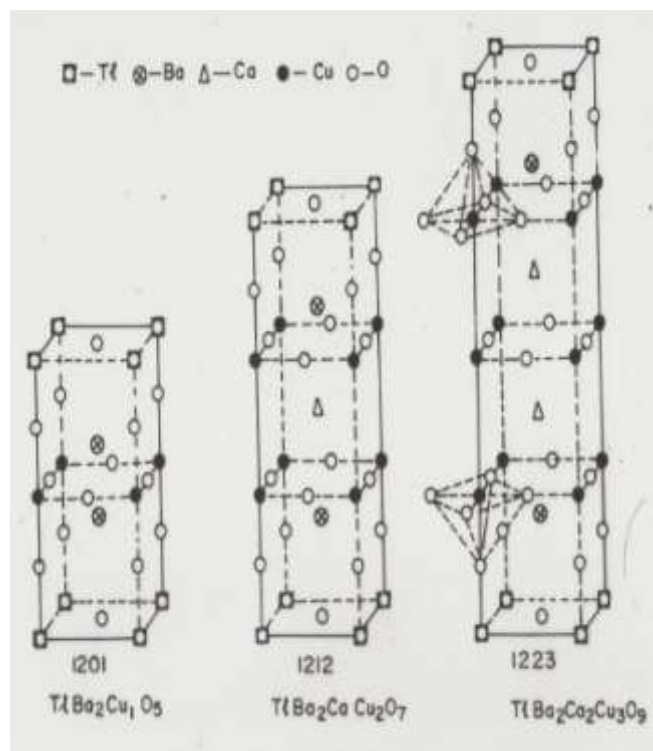


Figure 5 Crystal structures of three superconducting phases of TlBaCaCuO.

It is generally accepted that superconductivity in the thallium oxide superconductor is dominated by two dimensional CuO_2 conduction planes separated by Tl-O blocking layers that acts as charge reservoirs and thus moderate the charge on the superconducting CuO_2 planes by the transfer of holes or electrons.

3.5 HgBaCaCuO

The mercury-based superconductors contain a single layer of HgO and varying layers of CuO_2 planes. The first mercury cuprate to be synthesized was the $\text{HgBa}_2\text{CaCu}_2\text{O}_8$ compound prepared by solid state reaction in an evacuated silica tube. T_c in bulk samples of Hg1212 was reported to be 126K [48]. The crystal structure of Hg1212 was tetragonal and lattice parameters were $a=0.38556\text{nm}$ [49] and $c= 1.2652\text{nm}$. In HgBaCaCuO system, there are three CuO_2 layers per unit cell in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ and two CuO_2 layers per unit cell in $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+x}$ compound. There is large increase of T_c observed under high pressure. For example, at 23.5 Gpa T_c onset for Hg1223 was found to be 157K and an onset of 164K at 35Gpa. Figure 6 shows the crystal structure of three superconducting phases of HgBaCaCuO compound. The crystal structure of $\text{HgBa}_2\text{CuO}_4$ (Hg-1201), $\text{HgBa}_2\text{CaCu}_2\text{O}_6$ (Hg-1212) and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ (Hg-1223) is similar to that of Tl-1201, Tl-1212 and Tl-1223, with Hg in place of Tl. The T_c of the Hg compound (Hg-1201) containing one CuO_2 layer is much larger as compared to the one- CuO_2 -layer compound of thallium (Tl-1201). In the Hg-based superconductor, T_c is also found to increase as the CuO_2 layer increases. For Hg-1201, Hg-1212 and Hg-1223, the values of T_c are 94, 128 and the record value at ambient pressure 134 K, respectively. The observation that the T_c of Hg-1223 increases to 153 K under high pressure indicates that the T_c of this compound is very sensitive to the structure of the compound.

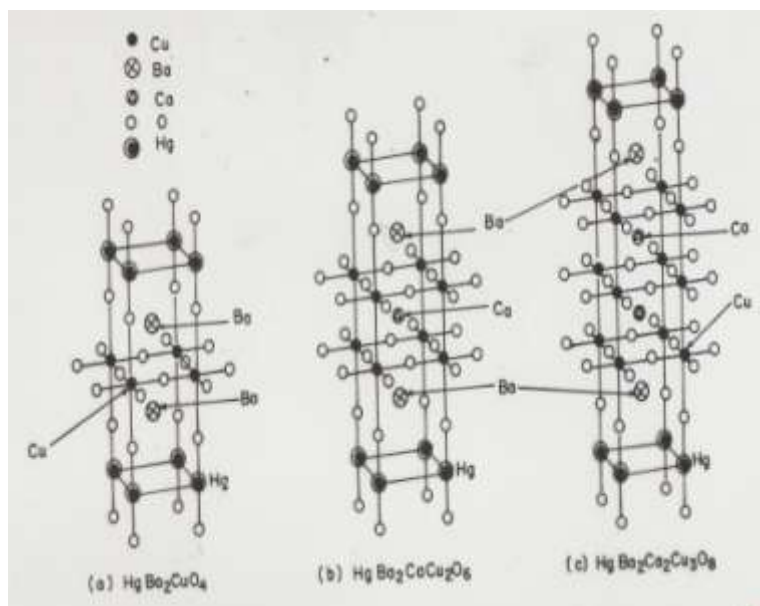


Figure 6 Crystal structures of three superconducting phases of HgBaCaCuO compound.

Most of the cuprate superconductors crystallize with an orthorhombic or tetragonal crystal structure. The difference between the lattice parameter a and b is very small. Because of the common structural features of the CuO_2 planes, the lattice parameter a and b are both close to 0.38nm serves as good candidate for high- T_c superconductors. The crystal structure and lattice parameters of cuprate based superconductors are summarized in table 1.

Material	Crystal system	T_c (K)	Lattice constants (nm)
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (La-Sr-214)	Tetragonal	37.5	$a=b=0.378$, $c=1.32$
$\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123)	Orthorhombic	92	$a=0.38227$, $b=0.38872$, $c=1.16802$
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201)	Tetragonal	10	$a=b=0.544$, $c=2.46$
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212)	Tetragonal	85	$a=b=0.5410$, $c=3.07$
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223)	Tetragonal	110	$a=b=0.541$, $c=3.71$
$\text{TlBa}_2\text{Ca}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ (Tl-1223)	Tetragonal	120	$a=b=0.3853$, $c=1.5913$
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (Tl-2201)	Tetragonal	80	$a=b=0.3866$, $c=2.312$
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ (Tl-2212)	Tetragonal	108	$a=b=0.3855$, $c=2.9259$
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Tl-2223)	Tetragonal	125	$a=b=0.385$, $c=3.588$
$\text{HgBa}_2\text{CuO}_4$ (Hg-1201)	Tetragonal	94	$a=b=0.3875$, $c=0.9513$
$\text{HgBa}_2\text{CaCu}_2\text{O}_6$ (Hg-1212)	Tetragonal	120	$a=b=0.3855$, $c=1.266$
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ (Hg-1223)	Tetragonal	134	$a=b=0.3850$, $c=1.578$
$\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10}$ (Hg-1234)	Tetragonal	127	$a=b=0.3850$, $c=1.9$

Table 1. Crystal structure and lattice parameters of cuprate based superconductors

4. Conclusions

All cuprate superconductors have a layered perovskite structure that consists of alternating conducting CuO_2 layers and insulating blocking layers that provide charge carriers to the CuO_2 layers. The number of CuO_2 layers is different in different cuprate families. Superconductivity occurs in only CuO_2 planes. The T_c is found to increase with the increase in CuO_2 layers. The crystal structure of Bi-, Tl- and Hg-based high- T_c superconductors are very similar. However, unlike YBCO, Cu-O chains are not present in these superconductors. In YBCO, there are CuO chains along the b -axis. The presence of oxygen atoms in these chains is essential for superconductivity. The YBCO superconductor has an orthorhombic structure, whereas the other high- T_c superconductors have a tetragonal structure. Among the cuprates, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+x}$, has one

of the simplest unit cells and the distance between copper atom and its apical oxygen is smaller than in all the other cuprate superconductors. The Bi- based high- T_c superconductors are superior to the YBCO in respect of higher T_c , compositional stability and humidity resistant. Its Bi-O layers being Vanderwaal bonded, so successfully utilized for tape casting.

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