

CRYSTAL STRUCTURES OF SOME HIGH-TEMPERATURE SUPERCONDUCTORS

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Abstract: An important fraction of the research on HTSC's was devoted to elucidating their structure. Knowledge of structure (the location of atoms) is a prerequisite for understanding the properties of the superconductor materials. We have shown in this paper some structural characteristics of YBCO and MgB_2 superconductor's compounds type. The YBCO have in common the presence of copper oxide layers, with superconductivity taking place between these layers. The more layers of CuO_2 , the higher are T_c . 123 compounds containing Cu-O planes and chains. The planes have an important role in the superconductivity mechanism and the chains are filled or empty "tanks of electrons", depending on the oxygen content or dopant. The crystal structure of a new binary intermetallic superconductor with a remarkably high superconducting transition temperature T_c is presented. It is a complex lattice with two layers of boron and magnesium.

Key words: superconducting ceramic materials, twinning, crystal structure

1. INTRODUCTION

After the first discovery of the superconducting ceramic system La-Ba-Cu-O with critical transition temperature between 30 – 40 K, other families of copper-oxide based ceramics have been synthesized with higher critical temperatures. These oxides include the Y-Ba-Cu-O series ($T_c \approx 90K$), the Bi-Sr-Ca-Cu-O series ($T_c \approx 80-115K$), the Tl-Ba-Ca-Cu-O group ($T_c \approx 85-125K$), and some others which do not form obvious classes (e.g., $Ba_{0.6}K_{0.4}BiO_3$), [1].

YBCO remains the best studied ceramic superconductor, although other ceramic oxide systems based on Bi/Sr/Ca/Cu/O or Tl/Ba/Ca/Cu/O have been prepared and found to have somewhat higher T_c 's than YBCO.

The basic structure of these compounds has been determined as a distorted, oxygen-deficient multi-layered perovskite structure. The properties of superconductors are strongly affected by subtle points of the structure; in particular the configurations of Cu-O seem to play an important role in superconducting mechanism.

The discovery of superconductivity with $T_c \approx 39K$ in magnesium diboride (MgB_2) was announced in January 2001, [2]. It caused excitement in the solid state physics

community because it introduced a new, simple (three atoms per unit cell) binary intermetallic superconductor with a record high (by nearly a factor of 2) superconducting transition temperature for a nonoxide and non-C60- based compound. The reported value of T_c seems to be either above or at the limit suggested theoretically several decades ago for BSC, phonon-mediated superconductivity. An immediate question raised by this discovery is whether this remarkably high T_c is due to some form of exotic coupling.

2. RESULTS AND DISCUSSION

The first superconductor found with $T_c > 77$ K is yttrium barium copper oxide ($Y_1Ba_2Cu_3O_{7-x}$), commonly termed “123”. Its structure appears in figure 1. It is related to the perovskite structure as follows: by tripling the perovskite (ABO_3) unit cell and substituting one yttrium atom for every third barium atom, the formula $Y_1Ba_2Cu_3O_9$ results. However, a little more than two oxygen vacancies are required for superconductivity. The formula can be thought of as $Y_1Ba_{3-1}Cu_3O_{9-2-x}$. The unit cell is orthorhombic, almost but not quite three cubes stacked upon one another.

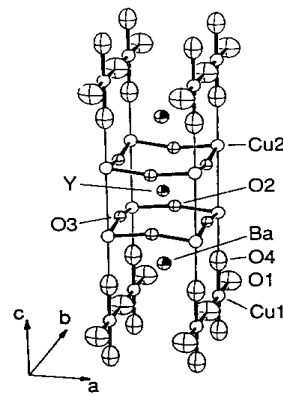


Fig. 1. - Structure of the double-layered $YBa_2Cu_3O_7$ compound

This drawing has at the exact center and Cu atoms on the four edges. Oxygen atoms play four different roles in this unit cell, depending on position; also, there are two different roles for copper atoms. The designations O1, ..., O4 and Cu1, Cu2 identify each type of atom.

There is another, entirely different way to draw these crystals, using polyhedrons of copper oxide. Six oxygens surrounding a copper atom form an 8-sided octagon, and these attach to various barium and yttrium atoms.

Figure 2 presents the YBCO unit cell in that form. Historically, the different types of drawings have been a matter of choice, with most geologists and chemists preferring the polyhedral method, whereas physicists prefer figure 1.

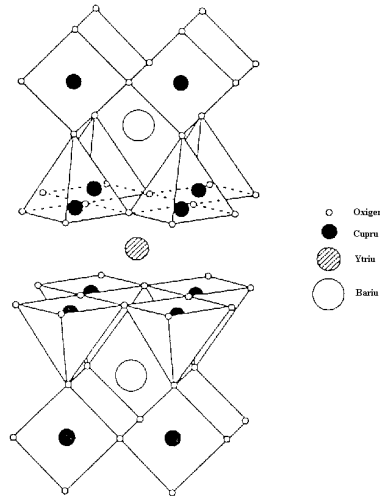


Fig. 2. - Alternative type of diagram of $\text{YBa}_2\text{Cu}_3\text{O}_7$, using polyhedrons to denote relationship of oxygen atoms to the metal atoms. In this form, the absence of oxygens on the yttrium plane out (some of the cooper atoms are hidden in this type of drawing)

Figure 3 shows the perovskit structure with the oxygen deficit for YBaCuO structure depending on the oxygen content, [3].

If the oxygen atoms numbers on elementary cells is decreasing to $6.7 - T_c$ value decreases up to $55 \text{ K} - 60 \text{ K}$ and below 6.41 the material is not superconductor. Oxygen vacations are carrying out beginning with it in the same chain, so that in the 123 cell appears ordered chains groups with oxygen deficit. For $\delta = 1$ Cu-O chains are disappearing.

After the separation of the occupied positions by Ba and Y, 123 elementary cells are re-arranging along the C axis (figure 1), with the values $a = b = 3.82 \text{ \AA}$, $c = 11.69 \text{ \AA}$. Depending on temperature and oxygen content, $y = 7 - \delta$, [3], are possible two polymorphous changes: tetragonal for $y \leq 6.5$ and orthorombic for the range $6.5 \leq y \leq 7$. The orthorombic phase is superconductor. The orthorombic deformation decreases direct proportional with oxygen content; for $y \sim 6.5$ the phase is tetragonal. By heating over 540°C temperature at 1 atm pressure, is beginning the oxygen loss and at $900^\circ\text{C} - 950^\circ\text{C}$ temperature, $y = 6$. Reversible structural transition is at 575°C . The coordination number of Cu2 is 5, pyramid (octagon) is oriented with the base to the OY plane and the coordination number of Cu1 ion is 4 or 2. For $0 \leq \delta \leq 1$ is forming a homologous compounds series with O compound alternating in the Cu-O chains forming in b direction, [4]. The CuO_2 and Y layers alternate.

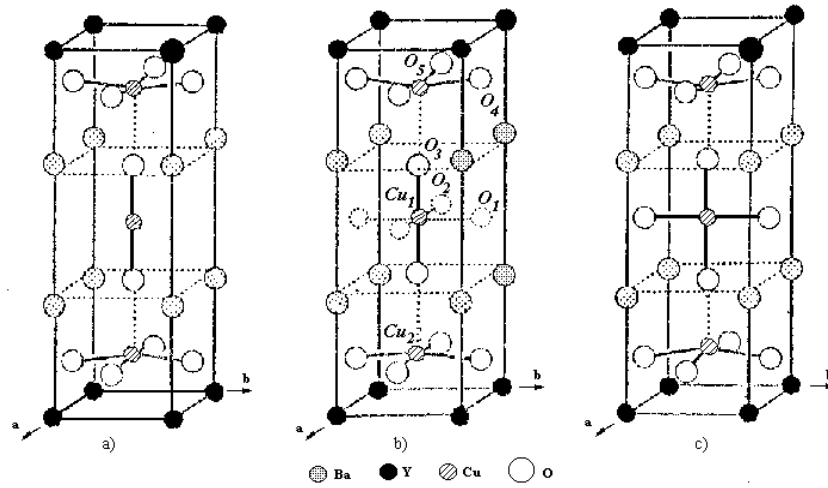


Fig. 3. - The oxygen deficient perovskite structures for YBaCuO system with oxygen content
 a) $\delta = 6$ b) $6 < \delta < 7$ c) $\delta = 7$

The deviation from the "O₇" stoichiometry conducting at general compound YBa₂Cu₃O_{7- δ} influence strongly the superconductor properties of this material. Different authors have presented that T_c decreases when δ increases from 0 to 1, figure 4, [5, 6].

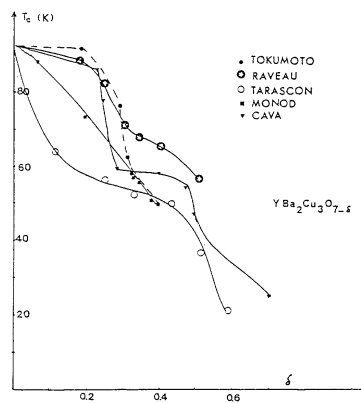


Fig. 4 - Dependence T_c from oxygen stoichiometry

The crystal structure of YBCO indicates that there are oxygen vacancies in a Cu layer. The value of T_c was found to depend on the oxygen content and it is usually recommended to anneal the prepared compound in an oxygen atmosphere.

123 presents sometimes a twinning structure which appears accidental and produce a small change in the orientation direction, [7]. The twinning appears in the crystalline structure if the axis length a and b differs very little between them and, in the time of crystalline increasing, when the unit cell is continuously repeating, this axis can be invert.

Initially presumed as essential role in the superconductivity mechanism, the role was denied later on of compounds discovery with Bi and Tl without twinning (with T_c more higher than 123), as the obtaining of 123 monocrystals with superconductor properties in the absence of twinning, [4]. The twinning is produce in the plane (110), but only in the superconductor phase.

The crystal structure of a unit cell of one superconducting member (i.e., the 123 phase) is well established [1], as shown in figure 5.

We first neglect the oxygen deficiency in the diagram. We can consider $YBa_2Cu_3O_{7-d}$ to be composed of a block of $YBaCu_2O_{5-d}$ (112) and another block $BaCuO_2$ which we believe to be again a semiconductor:



The idea that the Y-112 phase may be the basic building block of the Y-family was first put forward by Wong. Recently, Fei [1] discovered that both the single-phase composition $Ca_{0,9}Bi_{0,1}SrCu_2O_{5-\delta}$ (112) and $Ca_{0,9}Bi_{0,1}Sr_2Cu_3O_{7-\delta}$ (123) are superconductors with $T_c \cong 80$ K and the doped Ca-123 structure can be considered to be made up of the doped Ca-112 structure plus $SrCuO_2$; the same group is searching for the single phase structure of $YBaCu_2O_{5-\delta}$.

As $BaCuO_2$ is a semiconductor [1, 7], we expect $BaCuO_2$ to be a semiconductor also. If the YBCO-112 structure does exist and is superconducting, again we might have a superconductor-semiconductor array for the YBCO-123 crystal.

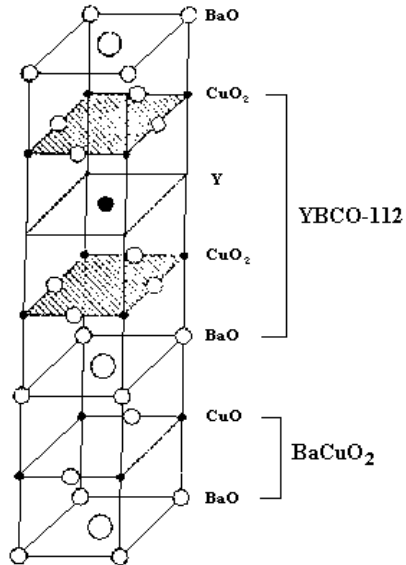


Fig. 5 -The unit cell structure $\text{YBa}_2\text{Cu}_3\text{O}_7$ deduced from neutron diffraction

In the researches it was studied the YBCO compound obtained by the reaction method in the solid state. X-ray diffractions indicated the presence of 4-5 individual crystallographic phases. Between 20°C and 70°C there were identified about 17 lines which corresponded of a perovskite zone, figure 6. The other phases present volume fractions in low proportions. It is obvious that besides the superconductor phase also other 3-4 existed phases can be superconductors, which explains the tight transition interval. In the greatest part, the powder is in orthorhombic phase with high T_c , the better correspondence being obtained according to ASTM files, with $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound or $\text{YBa}_2\text{Cu}_3\text{O}_{6,8}$ compounds from which we can not distinguish the precision of the analysis.

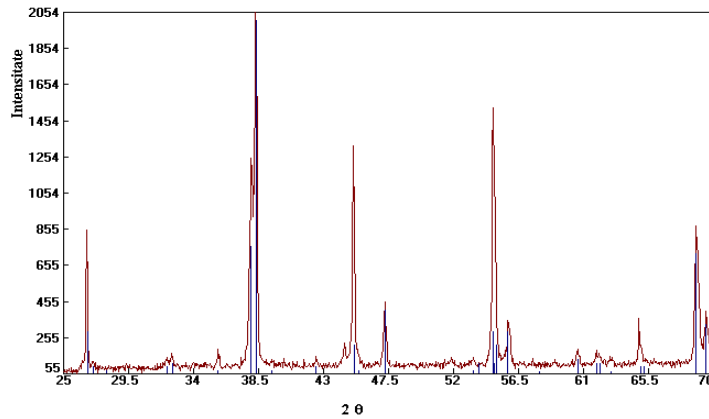


Fig. 6 - X-ray diffraction spectra of YBCO powder

The other superconductor, MgB_2 crystallizes in the hexagonal AlB_2 type structure, which consists of alternating hexagonal layers of Mg atoms and graphitelike honeycomb layers of B atoms. This material, along with other 3d-5d transition metal diborides, has been studied for several decades, mainly as a promising technological material, [2].

Figure 7 shows a typical diffraction pattern of MgB_2 taken at room temperature, [8]. All these peaks can be indexed assuming an hexagonal unit cell, with $a = 3.086 \text{ \AA}$ and $c = 3.524 \text{ \AA}$.

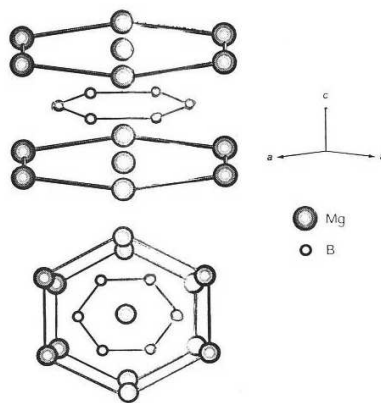


Fig. 7- X-ray diffraction pattern of MgB_2 at room temperature

It shows in the figure 7, the boron atoms are arranged in layers, with the atoms Mg interleaved between them. The structure of each boron atom is the same as that of a layer in

the graphite structure: each atom is here equidistant from three other boron atoms. The material MgB_2 is composed of two layers of boron and magnesium and the a and c axis in the hexagonal lattice.

Figure 8 shows the crystal structure for MgB_2 , of which the space group is $P6/mmm$.

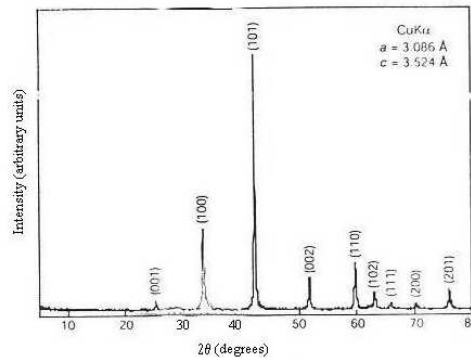


Fig. 8 - Crystal structure of MgB_2

3. CONCLUSIONS

We presented drawings of the unit cells of several different ceramic oxides. The unit cells are not perfectly symmetric, which has important consequences for superconductivity. In particular, the modest anisotropy of the crystal lattice is magnified many times into a severe anisotropy of the electronic properties; superconductivity is virtually two-dimensional in the HTSC's. The building up of ceramic superconductors by layers or blocks are not new.

The YBCO have in common the presence of copper oxide layers, with superconductivity taking place between these layers. The more layers of CuO_2 , the higher is T_c . The presence of CuO_2 layers in the crystal structure is necessary for superconductivity above 77 K.

123 compounds containing Cu-O planes and chains. The planes have an important role in the superconductivity mechanism and the chains are filled or empty "tanks of electrons", depending on the oxygen content or dopant.

Critical temperatures depend on the chemical compositions, cations substitutions and oxygen content.

The crystal structure of a new binary intermetallic superconductor with a remarkably high superconducting transition temperature T_c is presented. It is a complex lattice with two layers of boron and magnesium.

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