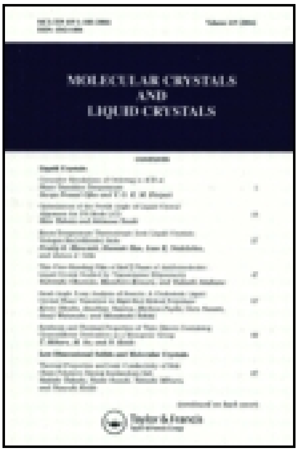

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# Structural Characteristics of High Tc Superconducting Oxide in (Bi,Pb)-Sr-Ca-Cu-O System

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# STRUCTURAL CHARACTERISTICS OF HIGH Tc SUPERCONDUCTING OXIDE IN (Bi,Pb)-Sr-Ca-Cu-O SYSTEM

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Abstract The various phases, which is responsible for variant maximum d-value including 18.5Å, 15.4Å, 12.2Å, 6.2Å and 3.2Å respectively, observed in high Tc superconducting oxide of (Bi,Pb)-Sr-Ca-Cu-O system is reported in this paper according to the result of X-ray diffractions on platelets. The phase of tetragonal system with c=3.21Å, a=3.86Å is possible parent structural unit and it is of great significance to the structure consititution of various phases with large lattice parameter c and structural characteristics of superconducting oxide.
In view of the above, a model of two-dimension stack-up which causes to stack in variant styles along c-axis and constitute various phases with different lattice parameter c is proposed and discussed.

## INTRODUCTION

Since the discovery of new high Tc superconductivity in Bi-Sr-Ca-Cu-O system by Michel[1] and Maeda[2] et al, much work[3-8] has been made to study the crystal structures of the superconductors. It has been confirmed in Bi-base system (with the general formula $A_2B_2Ca_{n-1}Cu_nO_{4+2n}$ that the ortherhombic unit cell structures differ in number of $CuO_2$ plane(n) along the c-axis, which are separated by $[ABO_2]_n$ unit with NaCl structure. It is notable that zero resistant temperature (Tce) increases with n(table 1)[8-17]. Recently, the parent structure with composition $(Ca_{0.86}Sr_{0.14})CuO_2$ (a=3.865Å, c=3.214Å) has been reported[13] It is of great significance to the structure consititution of various phases with large lattice constant c and hance assists the formation of new materials.

The structures of superconductors has been extensively investigated using high resolution electron microscopy.[8,14-17] In another point of of view, we study structures of (Bi,Pb)-Sr-Ca-Cu-O by means of X-ray diffraction and a model of two-dimension stacking is proposed.

TABLE 1 Relation of Tc and number of $CuO_2$-plane

| Nominal Composition | $CuO_2$-plane (n) | The length of c axis (Å) | Tc (K) |
|---|---|---|---|
| $Bi_2Sr_2CuO_y$ | 1 | 24 | 20 |
| $Bi_2Sr_2CaCu_2O_y$ | 2 | 30.7 | 85 |
| $Bi_2Sr_2Ca_2Cu_3O_y$ | 3 | 38 | 110 |

## EXPERIMENT

### Preparation of platelets

Powders of $Bi_2O_3$(AR), $SrCO_3$(AR), $CaCO_3$(AR) and CuO(99.9%) with an atomic ratio of Bi:Ca:Sr:Cu=1:1:1:3 were thoroughly mixed, preheaded in air at 820$^\circ$C for 24 hours. The mixture was reground, fired at 980$^\circ$C for long time, then cooled slowly down to room temperature in furnace. Many platelets with dimension of 0.5x0.5x0.01--3x3x0.05 $mm^3$ were chosen from the cooled molten. These platelets with good natural plane show uniform thickness and a matellic lustre. The platelets of Bi-Pb-Sr-Ca-Cu-O system are prepared by the same method described above with the molar ratio of Bi:Pb:Sr:Ca:Cu=1.5:0.5:1.5:1.5:2.

### X-ray diffraction

X-ray multi-reflections are carried out with Japan Rigaku D/MAX-$\gamma A^2$ X-ray diffractometer using monochromate high-intensity CuK$\alpha$ radiation ($\lambda$=1.5418A), 40KV, 100mA, attached pulse-height analyser. The platelet were adhered parallel to monocrystalline silicon carrier with rosin ethanol solution. After adjusting $\theta$-2$\theta$ location, employed $\theta$-2$\theta$ scan technique.

## RESULTS AND DISCUSSION

### Results of X-ray diffraction of (Bi,Pb)-Sr-Ca-Cu-O platelets

All samples with nominal composition of $Bi_4Sr_3Ca_3Cu_4O_y$ have good superconductivity in measuring AC magnetic susceptibility (Tc=80K), but in measuring resistance, their performance are different, some of them are good superconductors, some have metallic electric conductivity, few of them show large surface resistance.

X-ray multi-reflections on (001) plane of planelets indicate that almost all the specimens consist of two or three phases with different cell parameters c. Figure 1 is the X-ray multi-reflections of a typical platelet in which existed three phases(I: c=12.2Å, II: c=15.4Å, III: c=3.2Å). These phases own (001)plane in common and arrange parallel to each other along the direction perpendicular to the c-axis which is conformed by X-ray multi-reflections of the obverse and the reverse sides of a platelet (Figure 2). Due to absorption, the relative intensity of the three phase is different on the two sides, it shows variant phases arrange in order along c-axis direction in one platelet.

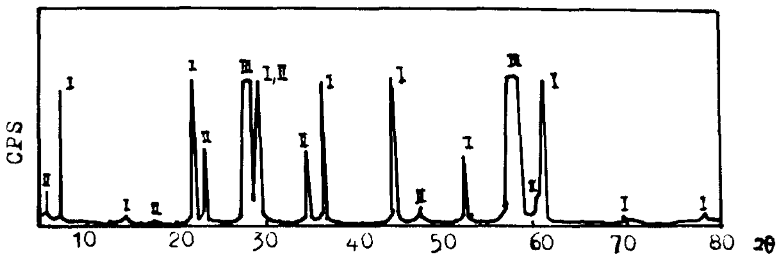


FIGURE 1 X-ray multi-reflections on (001) plane of platelet (c=12Å of phase I , c=15Å of phase II , c=3Å of phase III )

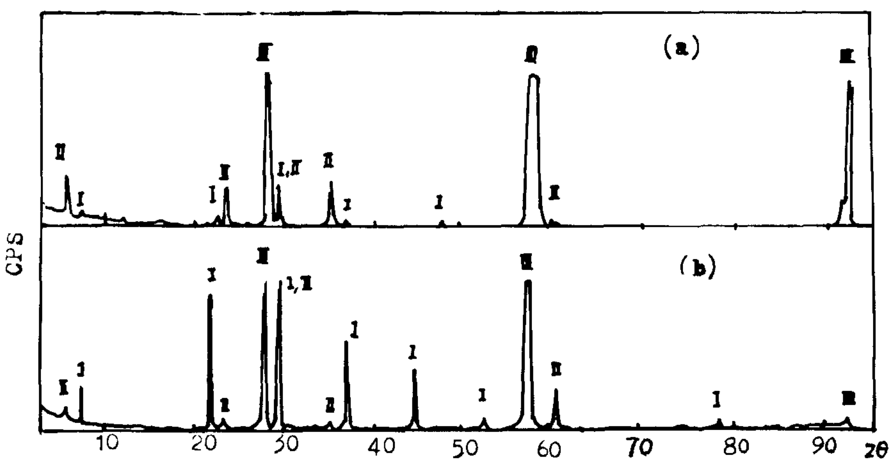


FIGURE 2 X-ray multi-reflections on (001) plane of two sides of a planelet(a,b represent the obverse and the reverse sides respectivily)

TABLE 2 X-ray diffraction data of the three phases

| Phases in this paper | | | | Superconducting phase in ref.19 | |
|---|---|---|---|---|---|
| d value(Å) | HKL I | HKL II | HKL III | d value(Å) | HKL |
| 15.014 | | 001 | | 15.66 | 002 |
| 12.013 | 001 | | | | |
| 6.043 | 002 | | | | |
| 5.105 | | 003 | | | |
| 4.039 | 003 | | | | |
| 3.824 | | 004 | | 3.857 | 008 |
| 3.217 | | | 001 | 3.257 | 115 |
| 3.054 | 004 | 005 | | 3.085 | 0010 |
| 2.558 | | 006 | | 2.556 | 0012 |
| 2.432 | 005 | | | 2.413 | 211 |
| 2.029 | 006 | | | 2.033 | 2010 |
| 1.923 | | 008 | | 1.915 | 220 |
| 1.741 | 007 | | | | |
| 1.610 | | | 002 | 1.595 | 317 |
| 1.538 | | 0010 | | | |
| 1.524 | 008 | | | 1.531 | 319 |
| 1.355 | 009 | | | | |
| 1.220 | 0010 | | | | |
| 1.071 | | | 003 | | |

Table 2 gives the X-ray data of the three phases, compared with d value of the phase reported in ref. 19, it is clear that the second phase(c=15.4Å) is in consistent with the superconducting phase.

The platelets which only possess the third phase are insulator whose composition is nearly $(Ca_{0.86}Sr_{0.14})CuO_2$ including little amount of Bi. Figure 3 is the X-ray multi-reflections of this platelet(c=3.2Å) In the Bi contained system of superconductor, some other phases which c=6Å, 9Å, 18Å et al are also observed. Figure 4 is the X-ray multi-reflections of the phase of c=6Å.

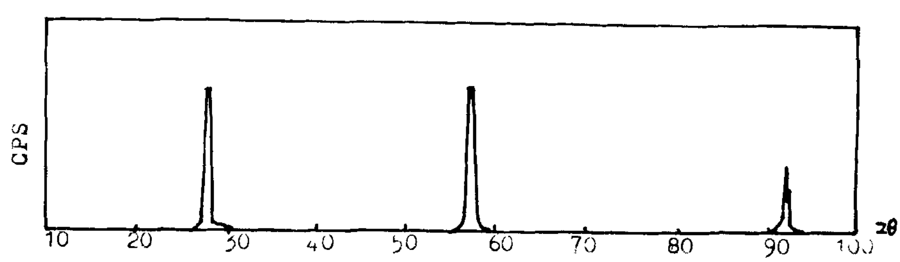


FIGURE 3 X-ray diffraction pattern of the phase of c=3.2Å

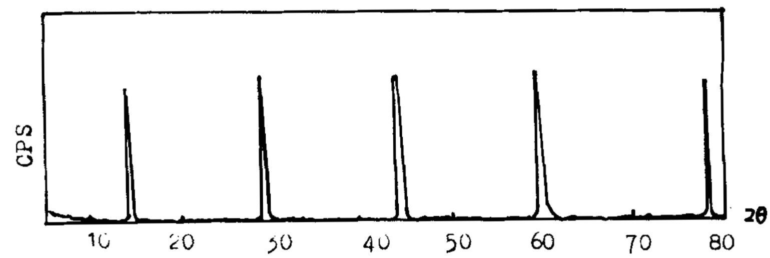


FIGURE 4 X-ray multi-reflections on (001) plane of planelet of c=6Å

The planelets in Pb doped Bi system have also revealed that there are variant phases existed in one platelet. Figure 5 and figure 6 are two examples of X-ray multi-reflections of the Bi-Pb-Sr-Ca-Cu-O platelets.

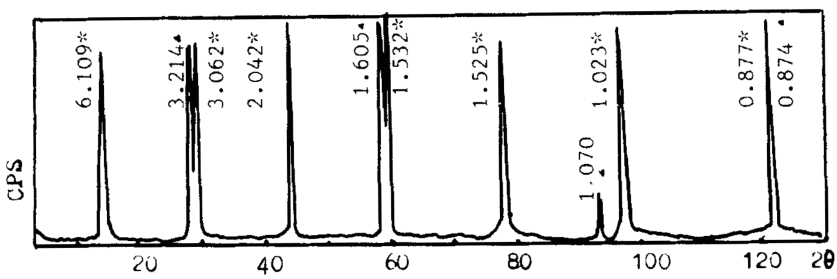


FIGURE 5 X-ray multi-reflections on (001) plane of planelet of Bi-Pb-Sr-Ca-Cu-O which consists of two phase (*.▲)

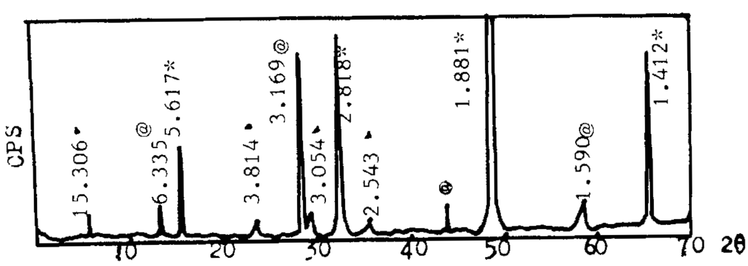


FIGURE 6 X-ray multi-reflections on (001) plane of planelet of Bi-Pb-Sr-Ca-Cu-O which consists of three phase (▲.*.@)

## The model of two-dimension stacking

According to the results of X-ray diffraction of (Bi,Pb)-Sr-Ca-Cu-O superconducting system, variant phases with different cell parameters c arrange sequece and parallel in crystals. It is difficult to interpret with the layer Perovskite structure, so a model of two-dimension atomic layer stacking is proposed.

Define Ca-O, Cu-O, Sr-O, Bi-O,...... atomic layers as A, B, C, D ...... layers respectively (FIGURE 7), Ca and Sr often can substitute for each other. These atomic layers should be able to stack in variant styles along c-axis. Generally speaking, cell parameters c can be calculated in order, and variant styles can have the same value of c.

For example, stacking with A,B,C layers:

| | |
|---|---|
| ABA | About 3Å |
| ABCBA | About 6Å |
| ABCBCBA | About 9Å |
| ABABCBABA | About 12Å |
| ABCBABCBCBA | About 15Å |
| ABABABCBABABA | About 18Å |

... ...

Many factors such as A,C plane sliping $\frac{1}{2}(\vec{a}+\vec{b})$, two identical plane sliping $\frac{1}{2}(\vec{a}+\vec{b})$, D layer replacing A or C layer et al. cause stacking styles varied, yield long-period stacking, maybe no period or disorder stacking.

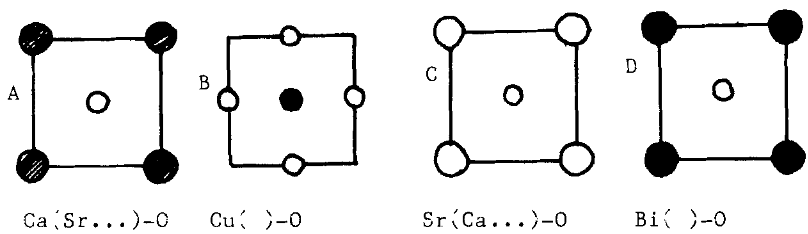


FIGURE 7 The schematic diagramme of layers (small white circle is oxygen atom)

Figure 8 is the schematic diagramme of forming three stacking styles with different c. Real cell parameter c in crystal is determined by specific stacking styles, metal atoms position, oxygen deficent et al. Stacking also can form variant transition situation. Meanwhile, the serious lattice distortion in a,b direction can be emerged due to the varied defects which nearly continuous distribution. The variety of structures, phases and defects may occur when the order phases of stacking and the disorder phases of stacking overlap each other.

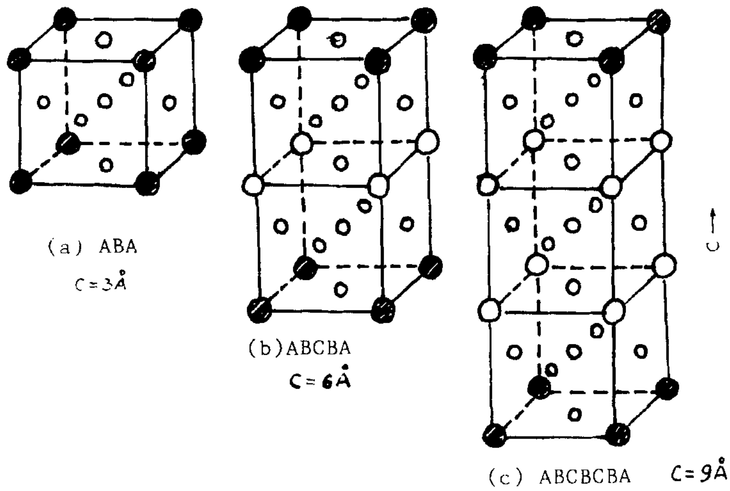


FIGURE 8 The schematic diagramme of forming three c cell parameters

## CONCLUSION

In general, the structures of superconductors are stackings of relative atomic layers existing as variant transition styles between the perovskites structure and disorder stackings.
Sliping, substitution, deficence and lattice distortion make stacking styles complicated. Variant phases are often growth in one crystal, this made it difficult to growth large sizes single crystals without twins and defects. Experiment results also indicate that the single crystals without twins and defects may be not a good superconductor.

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