

X-ray diffraction analysis and occurrence of multiple phases in Bi-Sr-Ca-Cu-O superconductors

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Abstract. Starting composition 1112 for Bi-Sr-Ca-Cu-oxide yields multiphase superconductors with the proportion of constituent phases depending sensitively on the annealing temperature. The R-T curves show zero resistivity and the transition corresponding to $T_c = 80$ K phase prominently. However, indexing of X-ray diffraction peaks reveals presence of 80 K (low T_c) as well as 108 K (high T_c) phase. The low T_c phase thus corresponds to the orthorhombic structure with a unit cell of $a = 5.4 \text{ \AA}$, $b = 27 \text{ \AA}$ and $c = 30.56 \text{ \AA}$. This is further understood to be composed of a pseudotetragonal cell of $a = b = 5.41 \text{ \AA}$. The high T_c phase similarly pertains to the orthorhombic structure with $c = 36 \text{ \AA}$.

Keywords. High temperature superconductivity; Bi-Sr-Ca-Cu-O; X-ray diffraction; multiple phase.

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1. Introduction

Bismuth-based high temperature superconductors are very attractive due to their rare earth free composition, inertness to moisture and possibility of incorporation of additional copper oxide layers (Bok 1988) in order to study effects on superconducting transition temperatures. Earlier work (Michel *et al* 1987; Akimitsu *et al* 1987) on BiSrCuO_x could find T_c in the range of 7–22 K. However, Maeda through his famous work (Maeda *et al* 1988) could attain T_c up to 110 K with zero resistivity observable at 80 K by merely adding calcium to the earlier system. This system with composition BiSrCaCu₂O_x (1112 hereafter) led to hectic research activity in this and other compositions. Some other groups (Hazen *et al* 1988; Subramanian *et al* 1988; Sunshine *et al* 1988; Tarascon *et al* 1988) not only confirmed the results but could even determine compositions and assign structures to the members of this exotic series.

Studies on Bi-Sr-Ca-Cu-O show superconducting properties to depend strongly on starting composition (Kajitani *et al* 1988), Sr/Ca ratio (Itoh *et al* 1988), processing (annealing/quenching) temperature (Yavari and Lejay 1988) and temperatures for oxygen treatment (Iguchi and Sugishita 1988).

In the present work we have synthesized Bi-Sr-Ca-Cu-O superconductor with starting composition 1112. Effects of annealing temperatures on structure of final compositions have been studied in a wide temperature range through R-T, X-ray diffraction (XRD) and microstructure studies.

2. Experimental procedure

The samples were prepared by the usual solid state reaction of well-mixed powders of Bi_2O_3 , SrCO_3 , CaCO_3 , CuO in the molar ratio of Bi: Sr: Ca: Cu: : 1: 1: 1: 2. Calcination was done at 750–820°C for about 16 hours. Grinding, pelletization and calcination were done repeatedly for homogenization. The pellets (12 mm dia, thickness 2–3 mm) were annealed (sintered) at a fixed temperature within the range 700–900°C and furnace-cooled subsequently. Individual pellets were cut in rectangular bar shape to attach four probes using air drying silver paint for resistivity measurements. The temperature was monitored below and above the liquid nitrogen temperatures with calibrated platinum resistance and germanium thermometers respectively. A suitable program was developed to record R-T plots using all Keithley-224 programmable current source, –181 nanovoltmeter and –195 Å digital multimeter linked to an HP computer (model 9126) through IEEE 488 bus. It was programmed to null thermo emf for each observation, besides averaging for forward and reverse biasings.

XRD studies were carried out on Siemen's diffractometer (model D-500) using CuK_α radiations. Microstructures were studied with a scanning electron microscope (JEOL JSM model 35 CF) and composition determined through EDX (model Kevex 7000–77) attachment.

3. Results and discussion

A large number of samples were prepared. The zero resistivity for these varied between 40 and 80 K depending on the magnitude of the annealing temperature. A few

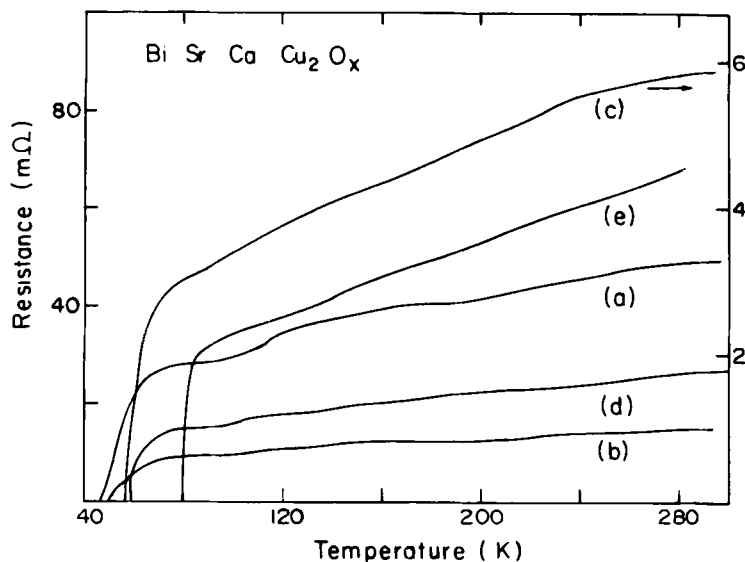


Figure 1. Representative R-T curves for Bi-Sr-Ca-Cu-O samples. The curves (a) to (c) are for those annealed for 16 h at 800, 820 and 840°C respectively, whereas curves (d) and (e) are for samples first premelted for four minutes at 880 and 900°C respectively before annealing them for 16 h at 860°C in each case.

representative R-T curves are shown in figure 1. Samples (a) to (c) were annealed for 16 hours at 800, 820 and 840°C respectively, whereas samples (d) and (e) were first pre-melted at 880° and 900°C respectively for approximately four minutes and later annealed for 16 hours at 860°C. Values of low T_c on-set and off-set temperatures as a function of annealing temperatures are shown in figure 2. In partial melting range there is a larger growth of high T_c phase, although at the cost of the low T_c phase material. The latter serves as a precursor.

In figure 3 the microstructure shows presence of needle-shaped crystallite showing growth of one superconducting phase with a nodule-like structure representing the growth of the other phase. Inhomogeneity and possible connectivity problems are associated with the high T_c phase. AC susceptibility studies (Maeda *et al* 1988) have shown that the high T_c phase is hardly 10% in a typical sample. Additional incorporation of Pb (Sunshine *et al* 1988; Green *et al* 1988) not only gave further higher T_c (108 K) in 2223 phase (Statt *et al* 1988; Zandbergen *et al* 1988) by providing necessary connectivity to the particles of high T_c phase, it also stabilized the structure by partial substitution of Pb for Bi (Cava *et al* 1988; Statt *et al* 1988). High T_c phase is understood to have the composition 2223, while the low T_c phase has 2212. The ideal composition for high T_c phase is considered to be 2443 (Ono *et al* 1988; Matsui *et al* 1988).

The sample calcined above 850°C show deficiency of Bi showing immiscibility of Bi-Cu compounds in the molten state. Complete melting of the mixtures renders the sample an amorphous phase, which is a high resistivity non-superconducting phase as can be seen in figure 2. Similarly annealing below 700°C renders the sample in

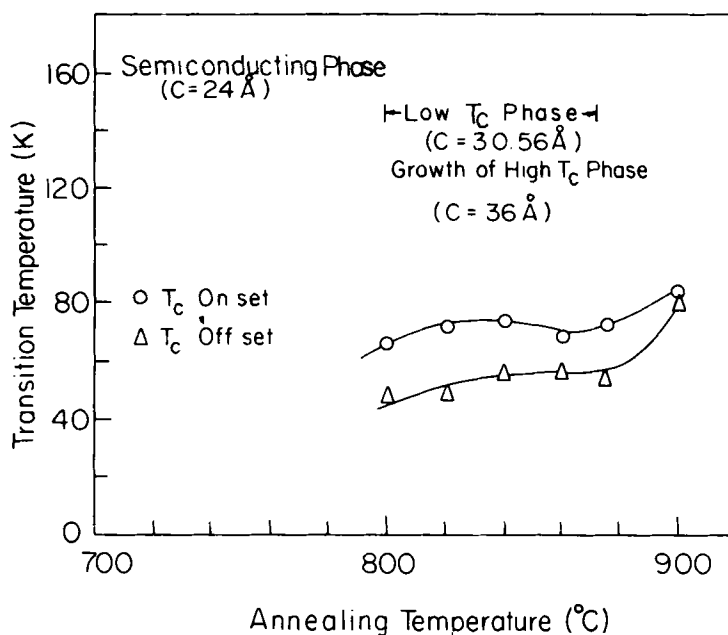


Figure 2. Superconducting transition temperature (T_c) as a function of annealing temperature. The low T_c phase on-set and off-set temperatures show maxima around 820°C. High T_c phase is ~ 108 K for annealing beyond this temperature.

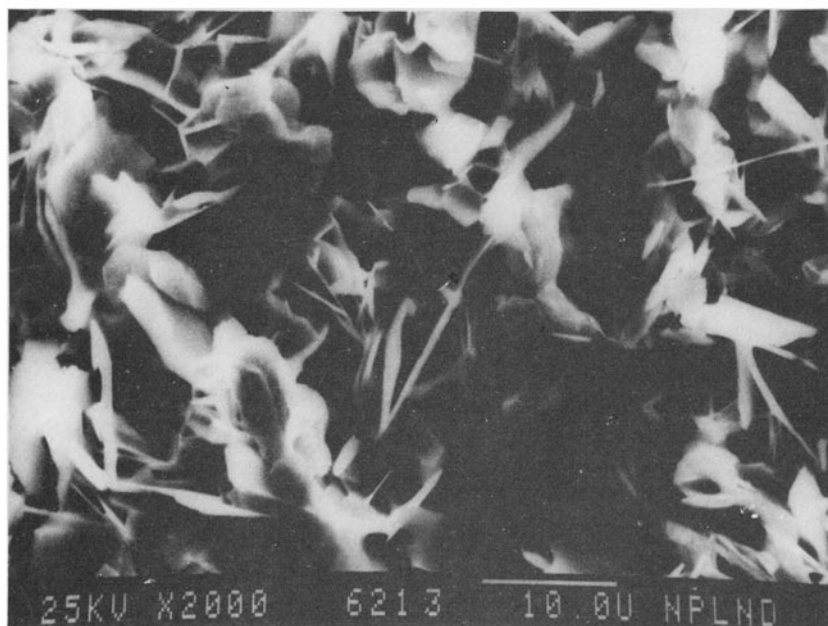


Figure 3. Micrograph for Bi-Sr-Ca-Cu-O sample as revealed by scanning electron microscope. The typical fractured sample shows long needle-shaped crystallites with nodule region often rich in copper contents.

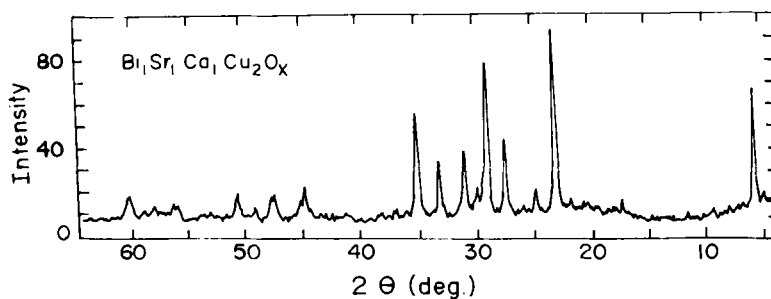


Figure 4. A representative X-ray powder diffraction pattern for Bi-Sr-Ca-Cu-O superconductor obtained from 1112 starting composition.

crystalline phase but still semiconducting. The semiconducting phase is now understood (Takayama-Muromachi *et al* 1988) to be similar in structure to $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ superconductor with $T_c = 7$ K (Akimitsu *et al* 1987; Sawa *et al* 1988). The experiments thus clearly indicate that crystallinity is an essential prerequisite.

In the present work we have made XRD studies for several samples; however a representative 2θ -intensity spectrum is given in figure 4. All possible values of lattice parameters are used to determine values of lattice spacing (d) and Miller indices (hkl) for every observable peak. Corresponding to $a = 5.4$ Å and $b = 27$ Å, we have taken $c = 18, 24, 30$ and 36 Å to see fitting to possible orthorhombic structures. The reasonable fits for indexing of XRD peaks correspond to $c = 30.56$ Å and 36 Å showing the low T_c

(80 K) and the high T_c (110 K) phase respectively. The 002 reflections has been seen predominantly at $2\theta = 4.9$ and 5.7 degrees corroborating the presence of the two structures. This finding is similar to other reports (Nobumasa *et al* 1988). The 4.9 degree peak is weaker and broader than the 5.7 peak indicating that the 110 K phase does not crystallize properly. This phase has slow thermodynamic kinetics. Besides, this confirms the presence of low and high T_c phases with double and triple layers of CuO_2 sheets. The peak at 7.25 \AA is expected to be associated with a single CuO_2 layer structure with $c = 24 \text{ \AA}$. However, our fittings unequivocally deny the presence of such a phase in our samples.

Crystal structure of 80 K phase has been assigned by several workers earlier (Tarascon *et al* 1988; Subramanian *et al* 1988; Syono *et al* 1988 and references therein). In recent work (Kugimiya *et al* 1988) on electron diffraction of single phase material of 80 K, it is established that low T_c phase has an orthorhombic structure with unit cell of $a = 5.407 \text{ \AA}$, $b = 27.011 \text{ \AA}$ and $c = 30.588 \text{ \AA}$. This can be approximated to a pseudo-tetragonal (body-centered) structure with lattice parameters $a = b = 5.4 \text{ \AA}$. The value of c increases on the presence of one, two or three CuO_2 layers. The actual structure has incommensurate superlattice ($\sim 4.8b$) within the basal plane for $a = b$ with Bi-O double layers. This structure is closely related to the so-called Aurivillius phases (Aurivillius 1949). (Bi_2O_2) layers exert pressure on the two-dimensional layer (sheet) arrangement causing superlattice effect. However, superconductivity confines to copper oxide sheets.

The high T_c phase is very similar in structure to the low T_c phase except that in the former case the c -axis is longer. We can thus attribute the low T_c phase with $c = 30.56 \text{ \AA}$, double copper oxide layers and is laid with the composition 2212. For a similar c value there are several divergent reports on other possible compositions, for example 4324 (Matsui 1988), 2332 (Ono *et al* 1988 and references therein) and 2 (1.7) (1.2) 2 (Michel *et al* 1987).

The high T_c phase thus corresponds to $n = 3$ layered structure with $c = 36 \text{ \AA}$. The corresponding peaks in XRD spectra occur only in the presence of the high T_c phase. This has been attributed to the 2223 composition. The reported literature values (Zandbergen *et al* 1988) again suggest several divergent compositions. We believe that compositions for the low and high T_c phases are 2212 and 2223 incorporating double and triple copper oxide layers respectively. Both phases are Aurivillius phases with double bismuth oxide layers.

4. Conclusions

Starting compositions 1112 for Bi-Sr-Ca-Cu oxide superconductor yield multiphase superconductors. Strong sensitivity to annealing temperatures is noticed in the attainment of final compositions ranging from amorphous semiconductor, the low T_c to the high T_c superconducting phases in the increasing order of annealing temperatures. The R-T curves show the low T_c phase (80 K) prominently with smearing of high T_c phase (108 K) transitions. Obscurity of the high T_c phase is due to lack of connectivity amongst the corresponding range as evidenced in the micrographic studies. The XRD spectra were indexed for prominent peaks by matching the observed and calculated lattice spacings (d) for several sets of lattice parameters for orthorhombic and (pseudo) tetragonal structures. We get two distinct superconducting phases corresponding to 80 K and 108 K transitions. The low T_c phase corresponds to the orthorhombic

structure with a unit cell of dimensions $a = 5.4 \text{ \AA}$, $b = 27 \text{ \AA}$ and $c = 30.56 \text{ \AA}$. This is understood to be composed of a pseudotetragonal cell of $a = b = 5.41 \text{ \AA}$. The high T_c phase has a similar orthorhombic structure with the unit cell of dimensions same as that of low T_c phase except $c = 36 \text{ \AA}$. Both phases have double bismuth oxide layers. The compositions for low and high T_c phases are 2212 and 2223 incorporating double and triple copper oxide layers respectively. The structures are the pseudo-morphs. The high T_c phase grows as intergrowth and at the expense of the low T_c phase prominently in the premelting region. The study of annealing temperature effects indicates that crystallinity is a prerequisite for the occurrence of superconductivity in these perovskite materials.

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References

- Akimitsu J, Yamazaki K, Sawa H and Fujiki H 1987 *Jpn. J. Appl. Phys.* **26** L2080
Aurivillius B 1949 *Arkiv. f. Kemi.* **1**, 463, 499 and 519
Bok J 1988 *Solid State Commun.* **67** 251
Cava R J et al 1988 *Physica* **C153-155** 560
Green S M, Jiang C, Mei Yu and Politis C 1988 *Phys. Rev.* **B38** 5016
Hazen R M et al 1988 *Phys. Rev. Lett.* **60** 1174
Iguchi I and Sugishita A 1988 *Physica* **C152** 228
Itoh T, Uchikawa H and Uzawa M 1988 *J. Cryst. Growth* **91** 430
Kajitani T, Hirabayashi M, Kikuchi M, Kusaba K, Syono Y, Kobayashi N, Iwasaki H and Muto Y 1988 *Jpn. J. Appl. Phys.* **27** L1453
Kugimiya K, Kawashima S, Inoue O and Adachi S 1988 *Appl. Phys. Lett.* **52** 1895
Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Jpn. J. Appl. Phys.* **27** L209
Matsui Y 1988 *Jpn. J. Appl. Phys.* **27** L361
Matsui Y, Maeda H, Tanaka Y, Takayama-Muromachi A, Takehawa S and Horiuchi S 1988 *Jpn. J. Appl. Phys.* **27** L827 and references therein
Michel C, Hervieu M, Borel M M, Grandin A, Deslandes F, Provost J and Raveau B 1987 *Z. Phys.* **B68** 421
Nobumasa H, Shimizu K, Kitano and Kawai T 1988 *Jpn. J. Appl. Phys.* **27** L8416
Ono A, Kosuda K, Sueno S and Ishizawa Y 1988 *Jpn. J. Appl. Phys.* **27** L1007
Sawa H, Fujiki H, Tomimoto K and Akimitsu J 1988 *Jpn. J. Appl. Phys.* **27** L830
Statt B W, Wang Z, Lee M J G, Yakhmi J V, De Camargo P C, Major J F and Rutter J W 1988 *Physica* **C156** 251
Subramanian M A, Torardi C C, Calabrese J C, Gopal Krishnan J, Morrissey K J, Askew T F, Flippen R S, Chowdhry U and Sleight A W 1988 *Science* **239** 1015
Sunshine S A et al 1988 *Phys. Rev.* **B38** 893
Syono Y, Hiraga K, Kobayashi N, Kikuchi M, Kusaba K, Kajitani T, Shindo D, Hosoya S, Tokiwa A, Terada S and Muto Y 1988 *Jpn. J. Appl. Phys.* **27** L569
Takayama-Muromachi E, Uchida Y, Ono A, Izumi F, Onoda M, Mutsui Y, Kosuda K, Takekawa S and Kato K 1988 *Jpn. J. Appl. Phys.* **27** L365
Tarascon J M, Le Page Y, Barboux P, Bagley B G, Greene L H, Mc Kinnon W R, Hull G W, Giroud M and Hwang D M 1988 *Phys. Rev.* **B37** 9382 and references therein
Yavari A R and Lejay P 1988 *J. Cryst. Growth.* **91** 290
Zandbergen H W, Huang Y K, Menken M J V, Li J N, Kadowaki K, Menovsky A A, Van Tendeloo G and Amelinckx S 1988 *Nature (London)* **332** 620