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## The Off-Stoichiometric $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{3.3}\text{O}_x$ Target for Thin Films

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**Abstract.** X-ray diffraction (XRD), EDAX, AC susceptibility and resistivity measurements has been used as characterization methods for the Bi-2223 monophasic target with the starting stoichiometry  $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{3.3}\text{O}_x$ . Pressure parameter is playing an important role in obtaining good superconducting properties for this compound. Critical currents and activation energy has been calculated from susceptibility and magnetoresistivity curves, respectively. The results could be interpreted in terms of TAPS and TAFF models.

### 1. INTRODUCTION

Many efforts have been made to stabilise and to isolate the high  $T_c$  Bi-2223 single phase. Because the formation temperature range for 2223 phase in Bi-Sr-Ca-Cu-O system is very narrow, this phase is often coexisting with the 2212 phase. Several processes have been developed in order to synthesise a specimen having a Bi-2223 single phase such as: the addition of PbO or  $\text{Ca}_2\text{PbO}_4$ , composition control by addition of excess Ca and Cu, long-time sintering, the use of fine and homogeneous powders by liquid chemical methods, sintering under low oxygen pressure and the two powder process[1]. We found in addition that the pressure used to make pellets is playing also a very important role in obtaining good superconducting properties for this compound. Several mechanisms have been suggested for understanding the reaction kinetics and growth process of the Bi-2223 phase: disproportionation reaction precipitation from the partially melted phase, intergrowth, dissolution precipitation process and mobile liquid droplets. Although many studies have focused on the formation of the Bi-2223 phase they still leave room for further study to explain all the cases. In particular the effect of the Bi-2212 phase on the formation of the Bi-2223 phase has yet to be clarified. X-ray diffraction analysis (XRD), EDAX, magnetoresistivity, AC susceptibility has been used as characterization methods for our samples. The temperature dependence of critical currents close to  $T_c$ , calculated from the imaginary part of the AC susceptibility, gave us information about the nature and the quality of the grain boundaries. Due to the small magnitude of activation energies for flux motion caused by high  $T_c$ , short coherence length, layered structures and large anisotropy, thermal fluctuations and flux creep play an important role in these materials.

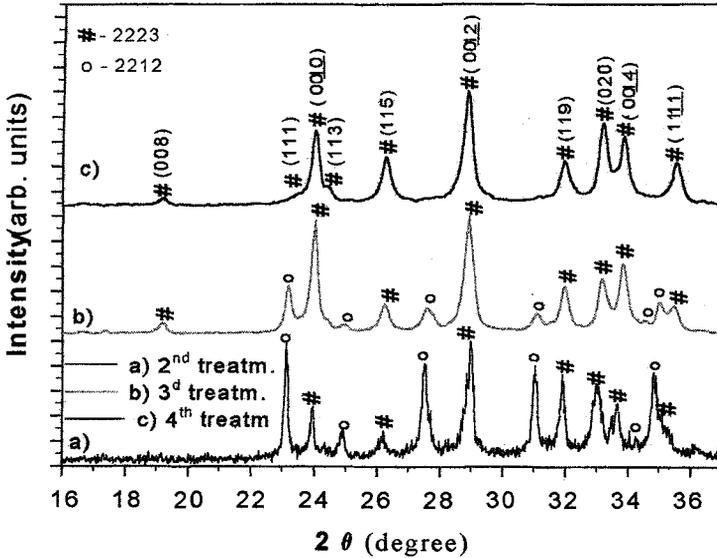
### 2. EXPERIMENTAL RESULTS AND DISCUSSION

The Bi-2223 monophasic target was prepared by the solid state reaction method. We have chosen an off-stoichiometric composition  $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_{3.3}\text{O}_x$  with Bi and Cu excess. The starting materials were high purity powders of  $\text{Bi}_2\text{O}_3$ , PbO,  $\text{SrCO}_3$  and CuO. The mixed powder was calcinated at  $800^\circ\text{C}$  for 38h. The resulting materials were ground, pressed into pellets and sintered at  $830^\circ\text{C}$  in flowing  $\text{N}_2$  gas for 6 days

and then quenched. The sintering was repeated three times at 846 °C, followed by quench in N<sub>2</sub> and air, respectively. In the fourth treatment the sintering temperature was 844°C, but instead of quench we used a furnace cooling to room temperature in N<sub>2</sub> atmosphere.

## 2.1 X-ray diffraction analysis

EDAX and XRD analysis were performed with a JEOL T100 type microscope and a SIEMENS 111 Diffractometer using Cu K<sub>α</sub> radiation, respectively. In Figure 1 are presented XRD patterns obtained for



**Figure 1:** The X-ray diffraction patterns of Bi<sub>1.8</sub>Pb<sub>0.3</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3.3</sub>O<sub>x</sub> recorded at room temperature. Peaks belonging to the 2223 phases are indicated by (#) and those belonging to the 2212 phase by (o).

different sintering time (a-13 days; b-18 days; c-25 days). The amount of Bi-2223 phase increases as the sintering time increases. The final treatment ( 25 sintering days) has eliminated completely the Bi-2212 phase. The volume fraction of Bi-2223 phase ( $f_{2223}$ ) present in our samples after each thermal treatment was determined using the relation [5]:

$$f_{2223} = \frac{I_{2223}(0010)}{I_{2223}(0010) + I_{2212}(008)} \times 100\%$$

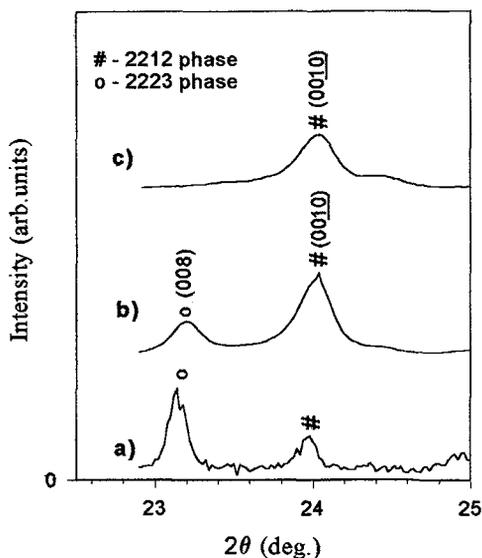
where  $I_{2223}(0010)$  is the XRD peak intensity of (0010) in Bi-2223 phase and  $I_{2212}(008)$  is the peak intensity of the neighbouring peak (008) in Bi-2212 phase ( see Figure 2). Volume fraction dependence of Bi- 2223 phase on the sintering time is shown in Figure 3. For the phase analysis the reflection peaks (008)<sub>2212</sub> of Bi-2212 and (0010)<sub>2223</sub> of Bi-2223 are chosen as most other researchers do [5], because they do not overlap and their  $2\theta$  ( 23.2 deg. for (008)<sub>2212</sub> and 24 deg. for (0010)<sub>2223</sub>) are very close each other.

EDAX results confirm the homogeneity of the samples. Even if X-ray diffraction patterns exhibited a monophasic compound, some impurities are still present. According to the results of X-ray spectrum we can suppose that 2223 phase can be formed by solubilization of 2212 phase into the (Ca, Cu)-rich liquid phase containing Pb. The reaction forming the Bi-2223 phase is the following:

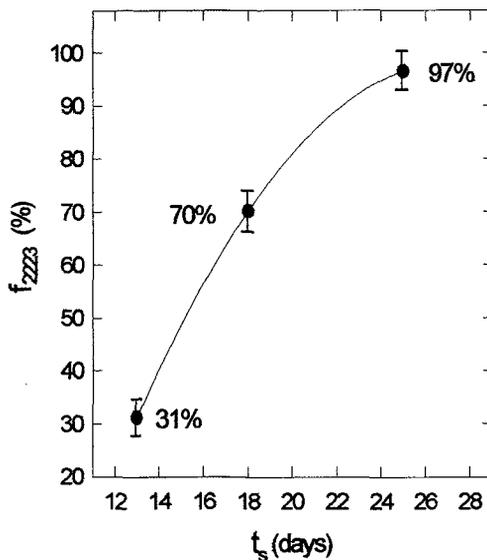


where SP denotes the second phases.

The  $\text{Ca}_2\text{PbO}_4$  phase, resulting from the addition of  $\text{PbO}$ , promotes the partial melting of the second phases. In this case the cations  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  in the melt can be transported to the surface of Bi-2212 where the Bi-2223 phase nucleates and grows up [5, 7].



**Figure 2:** X-ray diffraction spectrum with the peaks (008) of Bi-2212 and (0010) of Bi-2223 for the powders characterized by different sintering time: a) 13 days; b) 18 days; c) 25 days.



**Figure 3:** Volume fraction ( $f_{2223}$ ) dependence on sintering time ( $t_s$ ).

## 2.2 Susceptibility and intergranular critical currents

The AC susceptibility measurements performed with a LAKE SHORE Susceptometer Model 7000 show the evolution of superconducting properties after each sintering process (Figure 4). There is evidence that increasing the sintering time has a large influence on the diamagnetic response due to the continuous increase of the Bi-2223 phase amount in the samples. As shown in Figure 4 (b-susceptibility curves), the samples with 70% of Bi-2223 phase display only one strong diamagnetic signal and a sharp drop of resistivity. The results of phase analysis (see b-spectrum of X-ray diffraction shown in Figure 1) contradict the electrical and magnetic data. This is because there is a residual 2212 phase enclosed by 2223 phase and the covering layer of 2223 phase is so thick that it could not only form a superconducting path but also shield the diamagnetic signal of the enclosed residual 2212 phase. This confirms our hypothesis concerning the possible mechanism of Bi-2223 phase formation proposed in the previous subsection. Another observation, which has to be noted, is that for a precise characterization of this compound susceptibility and resistivity data should be correlated with XRD analysis.

What is also to be noted, is that different pressures for making pellets lead to different intergranular behaviours of the samples (see Figures 5 and 6, respectively).

For example, even if 2212 phase is still present (after the third sintering) there is a very distinct separation between the superconducting behavior of two samples which were pressed at 30 MPa and 40 MPa, respectively (see Figure 5).

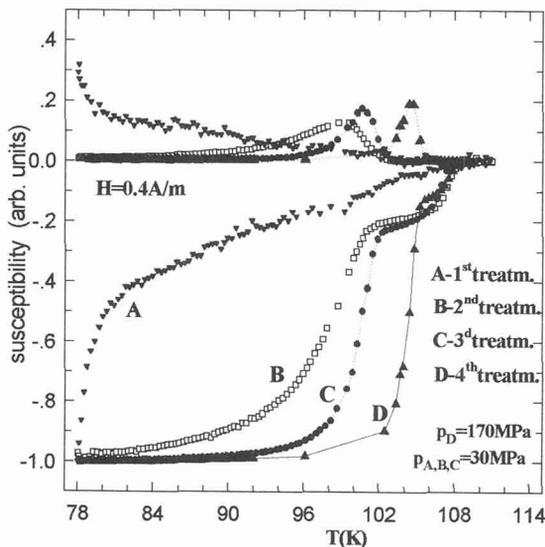


Figure 4: Results of susceptibility measurements performed after each thermal treatment.

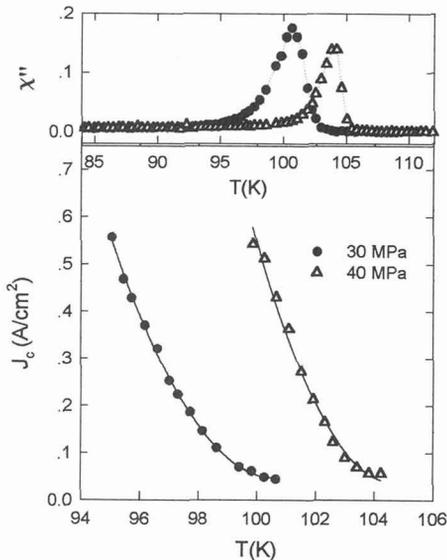


Figure 5: Critical currents calculated from susceptibility curves ( $H=0.4A/m$ ) in the case of two pressures. The solid lines are the fitting curves[2].

From Figure 5 one can see that the intergranular peaks of the imaginary part of the susceptibility measured at  $0.4A/m$  (the magnetic field was applied parallel to the uniaxial pressure) shift to higher temperatures when we are increasing the pressure. This behaviour is consistent with Evetts model [4]. Using critical state model (CSM), we calculated intergranular critical currents from imaginary part of susceptibility. In the vicinity of critical temperature, the effect of thermal activation is significant, resulting in a rapid decrease in the values of critical current density.

A fit square method was used to prove that thermally activated phase slippage (TAPS) could explain the temperature dependence of intergranular critical currents, near  $T_c$ , which is in conformity with Ambegaokar-Halperin (AH) model [2] for Josephson junctions. On the basis of Ginsburg-Landau theory, de Gennes has predicted the following behaviour of the critical currents in the case of SNS-type Josephson junctions, near  $T_c$  :

$$J_c \sim (1-T/T_c)^2$$

There is a very good fitting between theoretical curves (solid line) and experimental data (see Figure 5)

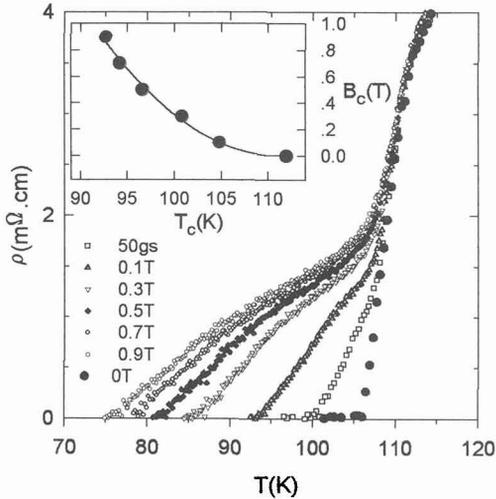
As the temperature decreases the coupling of the grains boundaries increases. As a result,  $J_c$  is dominated by flux motion in the low temperature regime and a linear temperature dependence of  $J_c$  is expected from the flux creep theory of Anderson and Kim [8]:

$$J_c = J_{c0} [1 + kT/U \ln(E_c/a_0 B \omega)]$$

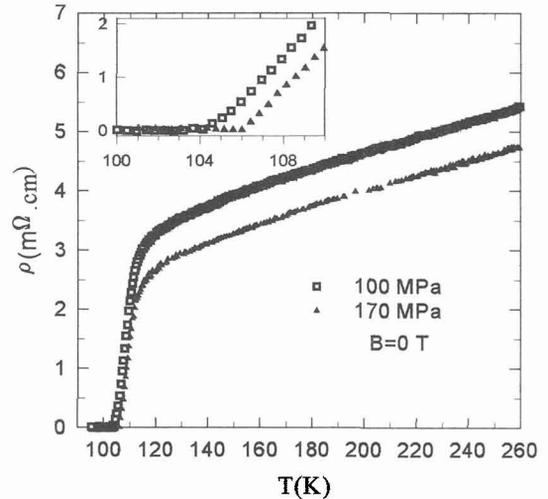
where  $J_{c0}$  is the critical density in the absence of the flux creep,  $B$  is the magnetic induction,  $U$  is the activation energy,  $a_0$  is the spacing between pinning centres,  $\omega$  is the attempt frequency, and  $E_c$  is the electric field criterion for  $J_c$  determination. These samples are characterized by low values for critical currents (calculated from AC susceptibility measurements). This is a prove of the general accepted idea that the low intergrains critical current densities of polycrystalline HTSC are determined by weak links at grain boundaries like as Josephson junctions.

### 2.3 Magnetoresistivity and activation energy

The magnetoresistivity measurements for a monophasic Bi-2223 sample, pressed at 170 MPa, has been performed with magnetic fields applied perpendicular to the surface up to 1T and at a current of 3 mA (see Figure 6). The influence of the pressures on  $\rho(T)$  is shown in Figure 7.



**Figure 6:** Magnetoresistivity for the sample pressed at 170 MPa. A current of 3mA parallel to the surface has been applied.



**Figure 7:** Resistivity for two Bi-2223 monophasic samples, prepared by the same thermal treatments but pressed at different pressures: 100 MPa uniaxial and 170 MPa isostatic.

The small coherence length and the large anisotropy of Bi-2223, the thermal fluctuations and the flux creep play an important role in this material also at temperature well below the thermodynamic critical temperature  $T_c$ . As a consequence, one may observe a distinct broadening of the resistive transition in the presence of a magnetic field and a considerable field dependence of AC susceptibility transition.

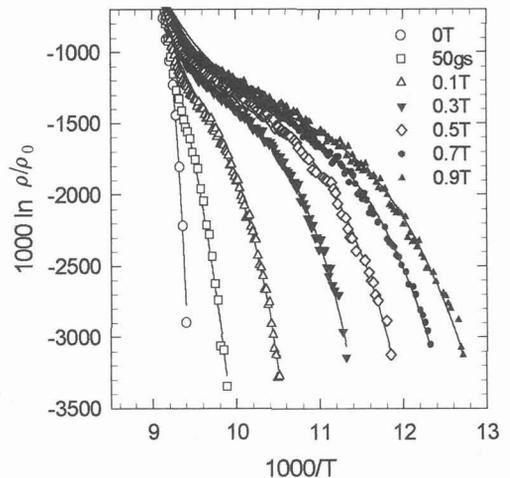
Our experimental results revealed that the thermally activated motion of flux has to be taken into account even for temperature well below  $T_c$ . In the thermally assisted flux flow (TAFF) regime, the resistivity can be written as:

$$\rho \sim \exp(-U_0/k_B T)$$

where  $k_B$  is the Boltzmann constant,  $T$  the temperature and  $U_0$  is the activation energy which characterises the flux-pinning strength.

The slopes of the Arrhenius plots  $\ln(\rho/\rho_0)$  versus  $1/T$ , given in Figure 8, yields an estimate of the activation barrier for thermally activated flux motion at different magnetic fields for a sample isostatically pressed at 170MPa. The behaviour of the activation energies versus temperature obtained from the slopes of Arrhenius is typical for the dissipation induced by TAFF (Figure 9). For the fitting procedure we have to take into account the magnetic field and the temperature dependence of the activation barrier energy[9]:

$$U(B,t) = f B^{-\beta} g(t)$$



**Figure 8:** Arrhenius plot of resistivity at magnetic fields applied normal to the sample surface. The solid lines are the fits within the TAFF theory.

where  $g(t)$  is some appropriate function of reduced temperature  $t=T/T_c$ , and  $f$  is a numerical factor [3]. Within the TAFF model we found a very good fit if we consider  $g(t)$  as given by the expression:

$$g(t)=g_0(1-t)^2$$

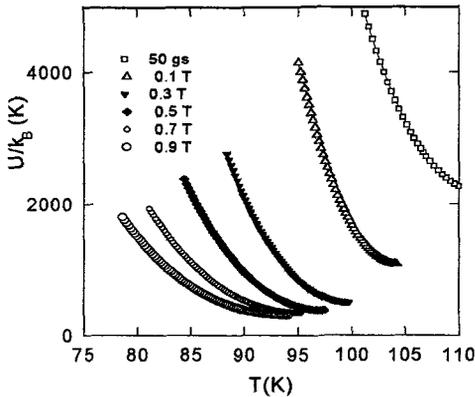


Figure 9: Temperature dependence of the activation energies from the slopes of Figure 8. The solid lines show the best fits.

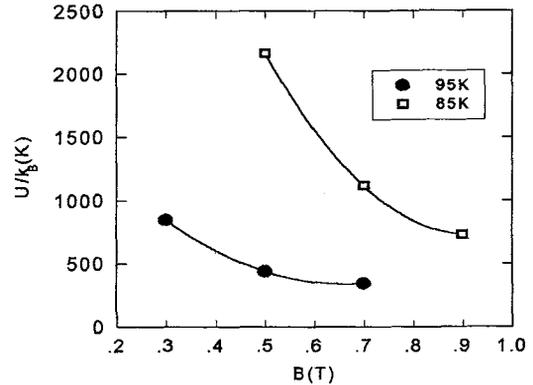


Figure 10: The plot of the activation energies versus applied magnetic field for two temperature. A power law has been used for the fits (solid lines).

### 3. CONCLUSIONS

EDAX and XRD analysis revealed that a Bi-2223 monophasic target was obtained by a solid state reaction method. The different pressures used for making pellets influence the intergranular behaviour as deduced from magnetoresistivity and AC susceptibility data.

The temperature dependence of  $\chi$  is consistent with the Evetts model. The  $J_c(T)$  dependence calculated from  $\chi(T)$  data is explained within the AH model for SNS type Josephson junctions.

The magnetoresistivity data are in agreement with the TAFF model. The  $U(t, B)$  dependence is very well fitted by the function  $g(t)=g_0(1-t)^2$  and by a power law (as shown in Figure 10), respectively [9].

### Acknowledgements

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