

Non-*in situ* pressure effects on the superconducting characteristics and microstructure in Bi-Ca-Sr-Cu-O systems

B. P. SINGH, S. K. AGARWAL, V. N. MOORTHY, B. V. KUMARASWAMY, R. K. NAYAR, A. V. NARLIKAR
National Physical Laboratory, Hillside Road, New Delhi 110012, India

Results on the pressure dependence of the transition temperature T_c and the resistance-temperature behaviour of $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ compound are presented. Both the onset T_c and the T_c ($R = 0$) are found to decrease with increasing pressure in the 0 to 50 kbar (1 bar = 10^5 Pa) range. Up to 20 kbar, the normal state resistivity is seen to be metallic beyond which it becomes semiconducting. The pressure is found to reduce the T_c at a rate of 0.2 K kbar^{-1} . The scanning electron micrographs of the starting bismuth cuprates showed characteristic needle-like structure, whereas the pressurized samples were found to be particularly different, consisting of small grains.

1. Introduction

Since the pioneering discovery of superconductivity in La-Ba-Cu-O system, extensive investigations have been carried out to discover new superconducting compounds with higher transition temperatures, T_c , and to look into the mechanism of high T_c superconductivity. In a bid to enhance the transition temperature, pressure effects have been studied in various systems. Chu *et al.* [1] reported an enhanced T_c of 40 K on application of hydrostatic pressure of 14 kbar (1 bar = 10^5 Pa) in the 30 K lanthanum-based cuprate. The pressure dependence in the Y-Ba-Cu-O superconductor has, however, been reported to be much smaller [2-4]. Even negative values for the derivative dT_c/dP have been found [5] in $\text{Y}_{1-x}\text{Ba}_x\text{CuO}_{3-y}$ system. Apart from the above two systems, Maeda *et al.* [6] discovered another high-temperature superconductor, Bi-Ca-Sr-Cu-O, which displayed two transitions at 85 and 110 K, indicating the presence of two superconducting phases. These have been identified as $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$ with two and three Cu-O networks sandwiching single and double calcium planes, respectively. Superstructures possessing a still higher number of Cu-O networks have also been reported which are suggestive of extra high T_c phases in these materials. Therefore, pressure studies in bismuth compounds are also considered worthwhile to throw some light on this aspect.

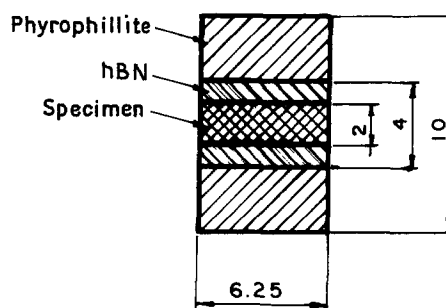
In this paper we present experimental results on the pressure dependence of the transition temperature, T_c , and the resistance-temperature behaviour of $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ compound. Results are also compared with the recently reported data on bismuth-cuprates [7-11].

2. Experimental procedure

Samples of the nominal $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ composition

for the present studies were prepared by mixing Bi_2O_3 , CaCO_3 , SrCO_3 and CuO , each with 99.99% purity in appropriate amounts. Well homogeneously mixed powders were cold pressed into disc-shaped pellets. Solid state reaction was achieved by heating the pellets at 820°C for 12 h in air. The calcined pellets were powdered, pelletized (~ 6 mm diameter, 3 mm thick) and sintered at 870°C for 12 h in air and finally cooled to ambient temperature in the furnace. Resistance measurements, confined in the temperature range 63 to 273 K, were carried out using the standard four-probe technique. Air-drying silver paste was used to make electrical contacts on the samples. The temperature was monitored using a standard 100Ω platinum resistance thermometer.

For high-pressure study, the superconducting pellet was subjected to different pressures up to 50 kbar in a 200 tonne cubic press. The cubic press [12] has six tungsten carbide 0.5 in (1.27 cm) tip anvils which are advanced by six hydraulic rams and move synchronously with one another. A uniform pressure is applied on the six faces of the reaction cell in the form of a cube. The reaction cell containing the superconducting



Dimensions in mm

Figure 1 Pressure cell configuration.

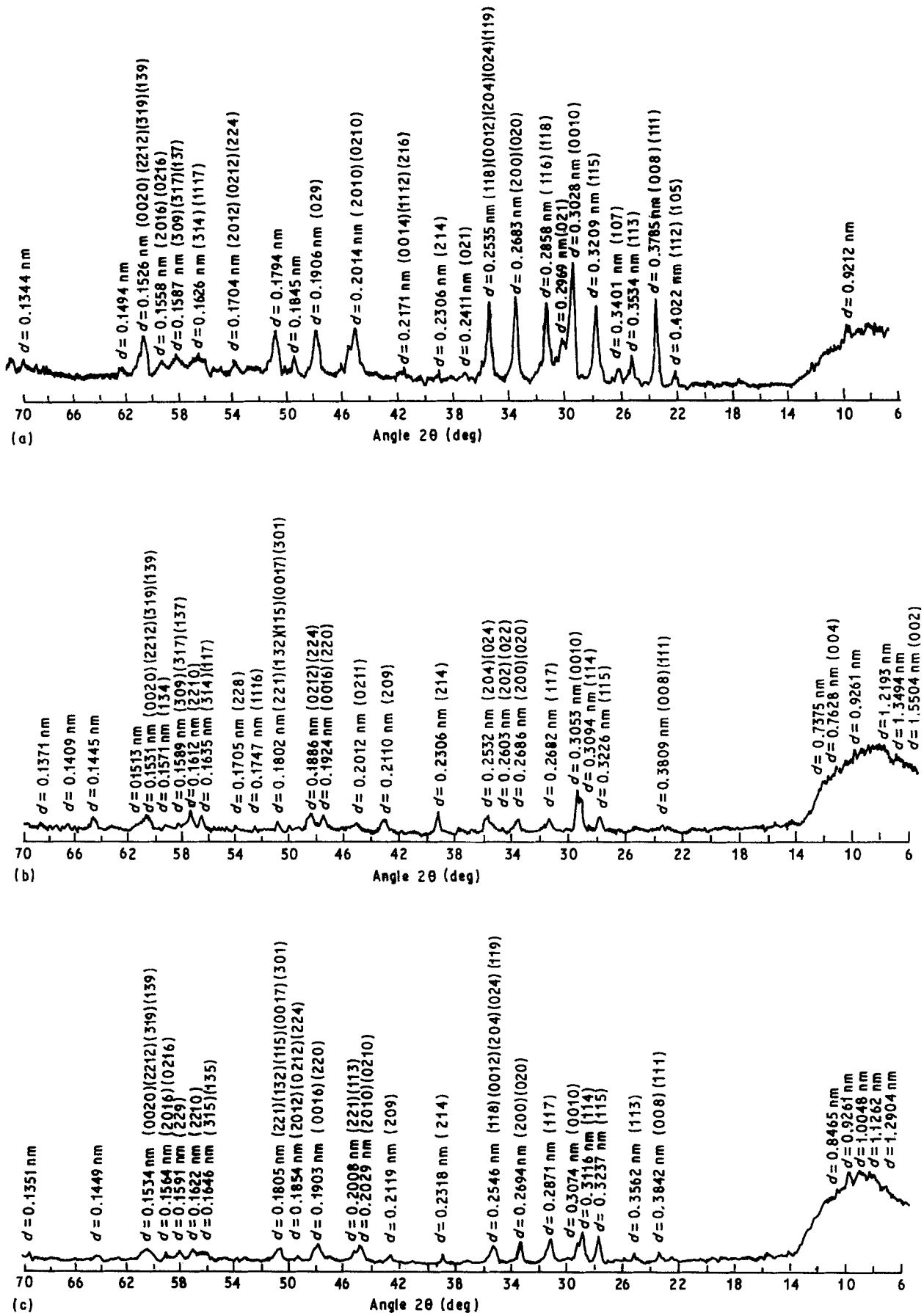


Figure 2 X-ray diffractogram of the $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ specimen: (a) without pressure; and pressurized at (b) 40 kbar, and (c) 50 kbar.

disc was made of pyrophyllite of edge length 16 mm with a cylindrical cavity of about 6 mm diameter drilled through it. The cell configuration is shown in Fig. 1. Pressure calibration was carried out using the pressure-fixed reference points of the phase transition of bismuth (I-II) at 25.4 kbar and ytterbium (fcc-

bcc) at 39 kbar. The sample was subjected to different pressures at ambient temperature in the following schedule. The sample of $\text{Bi}_2\text{Ca}_1\text{Sr}_2\text{Cu}_2\text{O}_x$ whose superconducting transition temperature, T_c , was measured at ambient pressure earlier, was pressurized to 20 kbar. The sample was then removed from the press and

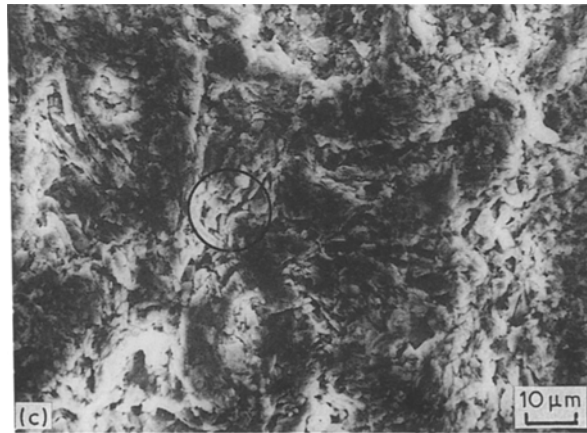
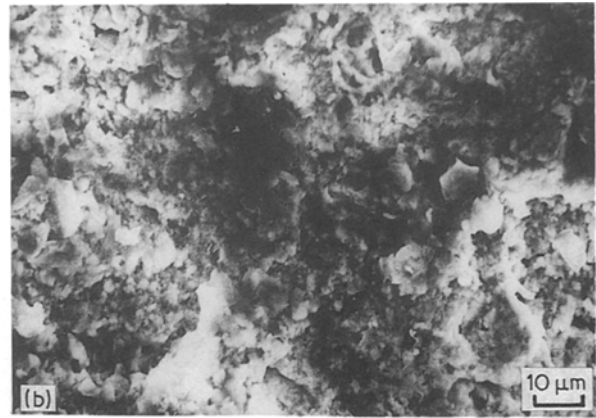


Figure 3 Scanning electron micrograph of (a) starting sample and the sample pressurized at (b) 40 kbar and (c) 50 kbar. Regions in and around the circle in (c) represent microcracks.

superconducting transition was measured. This procedure was repeated on the same specimen for pressures of 30, 40 and 50 kbar. The lattice parameters a_0 , b_0 and c_0 of the sample before and after pressurization were determined from the powder X-ray diffractograms recorded on Siemens D-500 X-ray diffractometer using $\text{CuK}\alpha$ radiation. Scanning electron micrographs were obtained using a Jeol JSM 35 CF scanning electron microscope.

3. Results and discussion

Figs 2a to c represent the X-ray diffractograms of the starting sample (prior to pressurization) and the samples subjected to pressures of 40 and 50 kbar, respectively. Little change in the lattice parameters was observed from those of the starting sample ($a_0 = 0.5405$ nm, $b_0 = 0.5489$ nm and $c_0 = 3.0625$ nm). Various reflections corresponding to the 2 1 2 2 phase have been indexed on the basis of the diffraction pattern of $\text{Bi}_2(\text{Ca}, \text{Sr})_{3-x}\text{Cu}_2\text{O}_x$ by Onada *et al.* [13]. However, the low angle ($2\theta \sim 10^\circ$) reflections developing with pressure were not indexable and perhaps indicate the presence of another phase apart from the major 2 1 2 2 phase. Figs 3a to c, respectively, are the scanning electron micrographs of the starting sample, 40 kbar and 50 kbar samples. While the starting sample can be seen to possess the characteristic needle-like structure (Fig. 3a), the pressurized samples were found to be particularly different, consisting of very small grains (Figs 3b and c).

The resistance–temperature behaviour of the sample subjected to various pressures from 0 to

50 kbar is depicted in Fig. 4. The starting sample showed a T_c ($R = 0$) at 82 K with the onset at 93 K. Both the onset T_c and the T_c ($R = 0$) are seen to decrease with the increasing pressure from 0 to 50 kbar. Up to a pressure of 20 kbar, the normal state resistivity is seen to be metallic, beyond which it turns to semiconducting state. Fig. 5 shows a plot of $T_{c(\text{onset})}$ and the $T_{c(\text{mid-point})}$ (at which the resistance drops to half its normal-state value) with pressure. The transition width, $\Delta T_c (T_{c(\text{onset})} - T_{c(\text{mid-point})})$ can be seen to increase with pressure. Such a behaviour has also been observed earlier in $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples [2, 4]. The pressure has been found to reduce the T_c at a rate of $dT_c/dP = -0.2 \text{ K kbar}^{-1}$ which is consistent with the

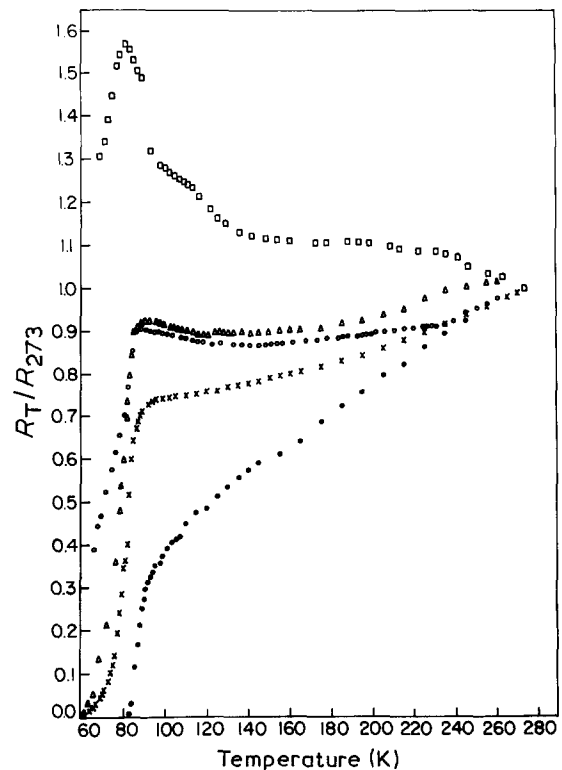


Figure 4 Resistance–temperature behaviour for (●) the reference sample and the samples pressurized at (×) 20, (○) 30, (Δ) 40, (□) 50 kbar.

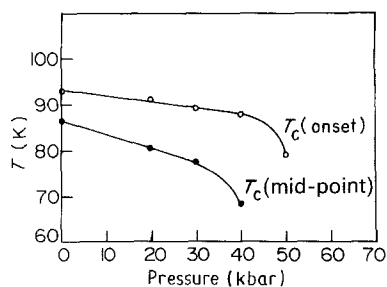


Figure 5 Plots of $T_{c(\text{onset})}$ and $T_{c(\text{mid-point})}$ as a function of pressure.

pressure derivative of $-0.16 \text{ K kbar}^{-1}$ reported by Wijngaarden *et al.* [8] on Bi-Ca-Sr-Cu-O compound. The negative value is also corroborated by Okai *et al.* [10]. It is, however, worth pointing out that the reported pressure dependence of T_c by the present authors has not been carried out *in situ*, as reported by others. Rather the pressure has been applied on the sample which was subsequently subjected to resistance measurements at ambient pressure. Similar behaviour of the negative-pressure effect has also been reported earlier on the Y-Ba-Cu-O system [14]. The semiconducting-like behaviour of the resistivity just above the transition beyond 20 kbar pressure might be a result of several factors, namely cracks or deficiency of calcium [15, 16], or the presence of multiphases and/or the presence of oxygen defects [9]. Scanning electron microscopic studies of the samples failed to reveal any large-scale cracks, and only occasionally some microcracks (Fig. 3c) were seen. EDAX analysis for the composition also did not provide any concrete evidence for the constituent calcium deficiency. Such a behaviour might, therefore, be a result of the presence of multiphases and oxygen defects in the form of vacancies or disorders as suggested by Matsumoto *et al.* [9]. The possible presence of the multiphases in the compound can be ruled out, as no further temperature treatment was given to the samples after their removal from the press and also the X-ray diffraction data did not reveal any other major phase apart from the usual 2122. The disorder aspect seems to receive credence from the observation that apart from T_c decrease, the transition width, ΔT_c , also increases with pressure. Macroscopic manifestation of this is presumably the observed breaking of the needle-like crystallites into finer grains as revealed by Figs 3b and c. Such a behaviour of breaking of equiaxed grains has

also been observed by the present authors in the Y-Ba-Cu-O system [12]. Further work on the higher T_c phase 2223 of the bismuth compounds is in progress and will form the subject of a separate publication.

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