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Appropriate thermal procedure for the preparation of high-T_c phase of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ superconductor

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The high-T_c phase of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ has been synthesized using an appropriate thermal procedure. D.c. electrical resistivity and X-ray diffraction studies have been done. The measurements show that a slow cooling process is necessary for a better control of the thermal process. The variation in T_c as a function of annealing time is also reported. Indexed X-ray diffraction patterns indicate the formation of high- as well as low-T_c phases.

1. Introduction

Since the discovery [1] of high-temperature superconductivity in the Bi–Sr–Ca–Cu–O system, a variety of synthesis methods and compositions have been explored. Two basic superconducting phases exist in the system Bi–Sr–Ca–Cu–O, namely $Bi_2Sr_2Ca_1Cu_2O_y$ (2212) with a critical temperature of 85 K and $Bi_2Sr_2Ca_2Cu_3O_y$ (2223) with a critical temperature of 110 K. The synthesis of the high-temperature phase is more difficult than that of the low-temperature phase. It has been established [2, 3] that the addition of lead helps the formation of the 110 K superconducting phase. The exact role of Pb is still not well understood: Pb^{2+} and Bi^{3+} have similar outer electronic configurations which would allow the easy incorporation of Pb into the structure. Nobumasa *et al.* [4], using high-resolution analytical electron microscopy on thin films prepared on a (1 0 0) MgO single crystal, found that Pb atoms were located in the Bi–O layers. Other authors suggested that lead acts only as a catalyst in the stabilization of the high-T_c phase [5]. On the other hand a number of authors point out that the content of Pb is greatly reduced with an increase in the time of synthesis [3]. In order to identify the optimum starting composition and processing parameters for achieving the best bulk superconductive properties, the composition $(Bi_{1-x}Pb_x)_2$ $Sr_2Ca_2Cu_3O_y$ with $x = 0$, 0.1, 0.2, 0.25 and 0.3 has been studied by Maqsood *et al.* [6] at length. The study also indicated that a single high-T_c superconducting phase was most stable in the sample corresponding to $x = 0.2$. The present paper discusses experimental results for the high-temperature phase as a function of the annealing time for superconducting bulk samples with a nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$.

2. Experimental procedure

A number of samples with starting composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ were prepared by the solid-state reaction technique under a normal atmosphere. Starting materials Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO of at least 99.9% purity were mixed thoroughly in appropriate amounts using an agate mortar and pestle. The mixture was calcined at 800 °C in a porcelain boat for 24 h. A tube furnace was used for heat treatment. Both ends of the tube furnace were closed with high-temperature wool during the heat treatment. The temperature was measured with the help of a Pt/Pt–13% Rh thermocouple. Pellets of diameter 14 mm and thickness 1–2 mm were pressed at a pressure of 4–6 cm^{-2} (samples 2 and 3). In a few pellets no pressure was applied (sample 1). The pellets were sintered in a normal atmosphere of 840 ± 10 °C for different times. This particular temperature was found to be most suitable for these experiments, as determined by some preliminary experiments [3]. Samples were either air-quenched or slowly cooled in the furnace. The samples were characterized by measuring the electrical resistance with the d.c. four-probe method, within the range 77–300 K. Crystalline phases formed in the annealed specimens were identified from X-ray powder diffraction (XRD) patterns which were recorded at room temperature employing CuK_α radiation.

3. Results and discussion

A true superconductor not only shows zero resistance but also excludes a magnetic field completely, the Meissner effect. Two tests were performed on the pellets to check whether the material was a superconductor or not.

First, the resistance of the pellets was checked with the help of an Avo meter. It was observed that if the resistance of the pellets at room temperature was less than 20 Ω, the material was often a superconductor. The second and positive test for superconductivity behaviour of our sample was the observation of the Meissner effect. The visual demonstration [6] of the

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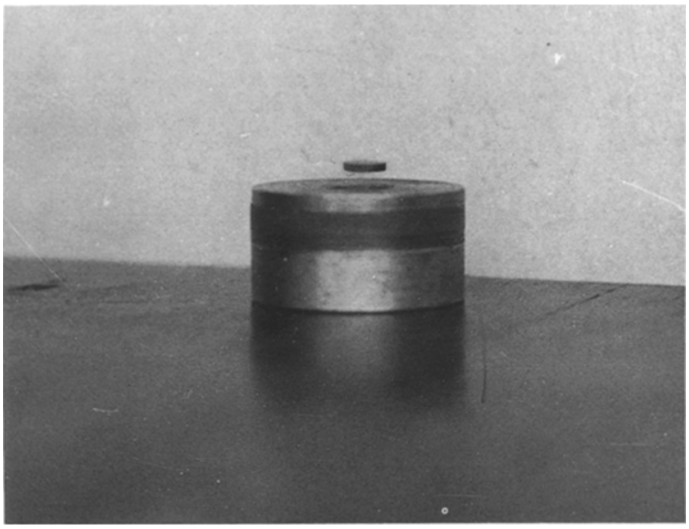

Figure 1 Visual demonstration of the Meissner effect.

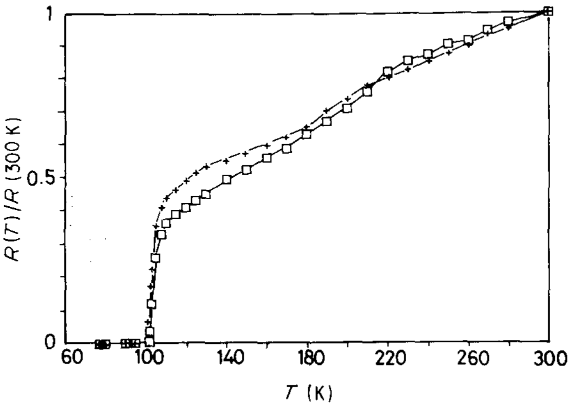

Figure 2 Effect of cooling rate on the temperature dependence of resistance, normalized to 300 K, of two specimens of starting composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ annealed for 160 h in air at 840 °C: (□) slow cooling in air, (+) air-quenched.

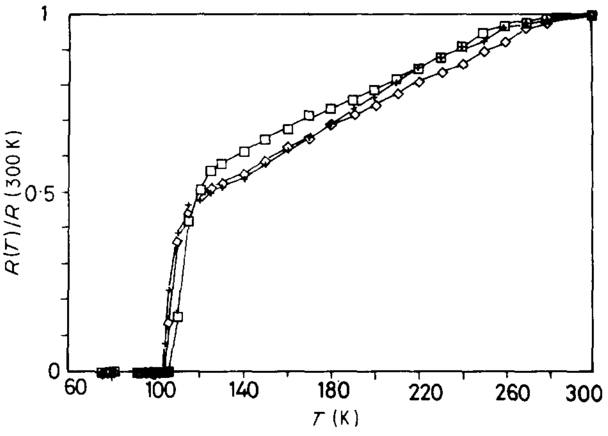

Figure 3 Temperature dependence of resistance, normalized to 300 K, of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ samples annealed in air: (□) sample 1 (96 h), (+) sample 2 (192 h), (◇) sample 3 (120 h).

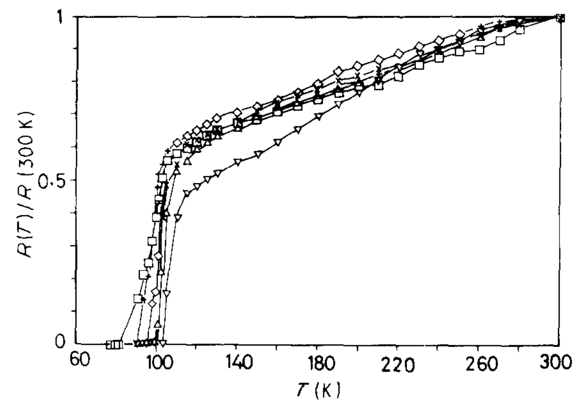

Figure 4 Influence of annealing time on the temperature dependence of resistance, normalized to 300 K, of starting composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ annealed in air at 840 °C, and furnace-cooled. Annealing time (□) 72 h, (+) 96 h, (◇) 120 h, (△) 144 h, (▽) 192 h.

Meissner effect was carried out by placing a pellet, already cooled to liquid nitrogen temperature, on a magnet. The results of this test are shown in Fig. 1.

The d.c. electrical resistance was measured at a current of 10 mA. High-quality Ag paste was used for electrical contacts. Fig. 2 shows the effect of cooling rate on the temperature dependence of resistance, normalized to 300 K, of two specimens of starting composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ annealed for 160 h in air at 840 °C.

The graph shows a large resistance drop at T_c (onset) = 110 K for the samples prepared by the two different thermal treatments. However, $T_c(R = 0)$ for the slow-cooled sample is 103 ± 1 K and the corresponding temperature for the air-quenched sample is 100 ± 1 K. A similar effect has been noted in the previous report [7] on quenched material. Therefore, it was decided to use the slow-cooling technique for studying the effect of the annealing time of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_2O_y$ samples. Fig. 3 shows the temperature dependence of the normalized resistance for samples annealed for times of 96, 192 and 120 h; the critical temperature T_c ($R = 0$) is 106, 103 and 104 K, respectively. The onset is at 112, 109 and 110 K, respectively. These results indicate the formation of 2223 phase, but it will be evident from the X-ray diffraction patterns that the formation of the

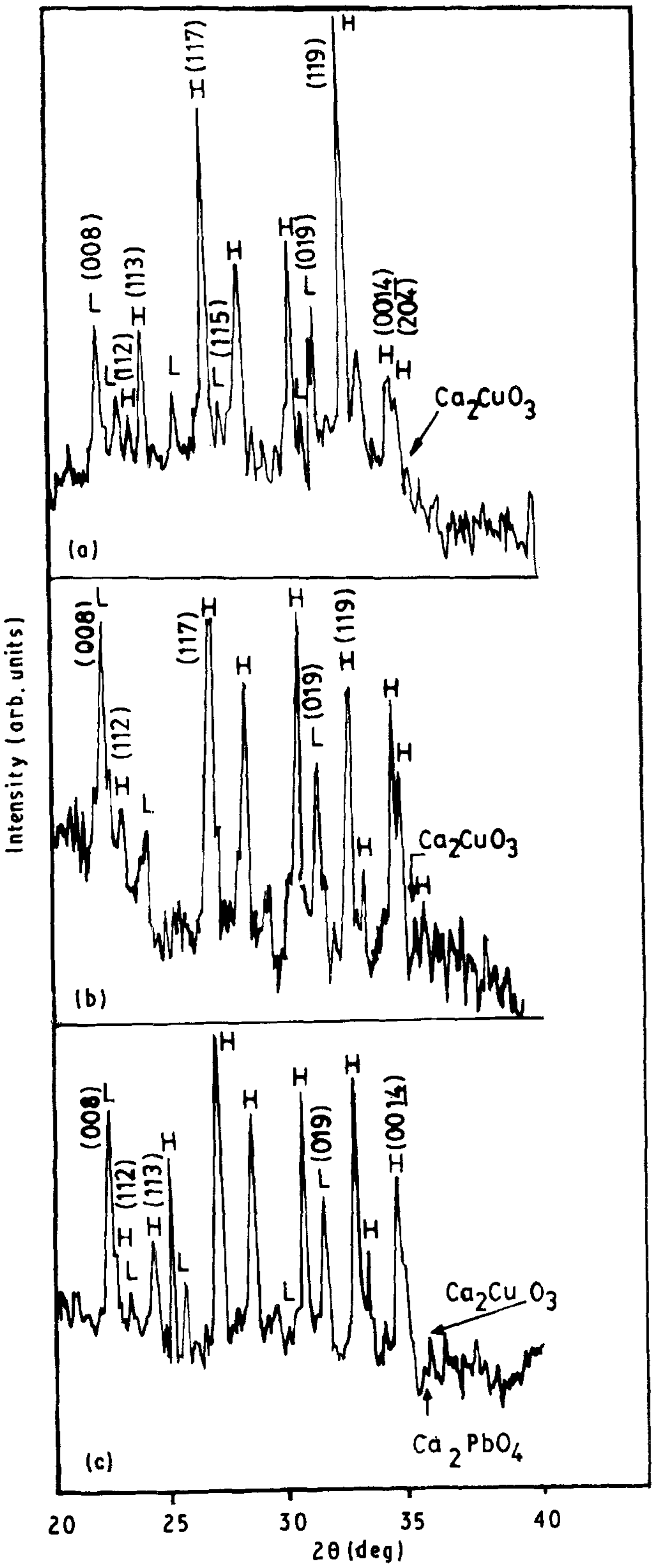

Figure 5 Typical powder X-ray diffraction patterns of samples annealed for (a) 96 h, (b) 120 h, (c) 196 h; the peaks marked by H, L correspond to the 2223 and 2212 phases, respectively.

high-T_c phase is very sluggish due to the relatively long-range diffusive ordering involved. Even after prolonged annealing at 840 °C for over ten days, the product contained an appreciable amount of the 2212 phase in addition to 2223 as seen from the XRD results.

The influence of annealing time as a function of temperature for sample 2 is shown in Fig. 4. Similar results were obtained for specimens 1 and 3.

Fig. 5 shows the results of XRD analysis. All samples have two phases. The high- and low-T_c phases are characterized by lattice parameters. The lattice parameters ascertained by our optimization programme for the high-T_c phase are $a_H = 0.5483(4)$ nm, $b_H = 0.5339(2)$ nm and $c_H = 3.772(2)$ nm while the lattice constants for the low-T_c phase are $a_L = 0.5004(4)$ nm, $b_L = 0.5445(5)$ nm and $c_L = 3.084(2)$ nm. The experimental errors are indicated in parentheses.

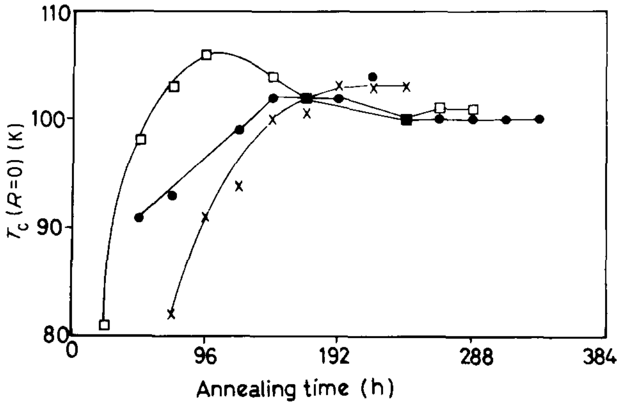

Figure 6 T_c values as a function of annealing time for different samples: (□) sample 1, (×) sample 2, (●) sample 3.

It is difficult to estimate the relative proportion of each phase from these X-ray patterns. A small impurity peak due to insulating Ca_2CuO_3 is also observed in Fig. 5a and c. Traces of admixture phase Ca_2PbO_4 are also observed.

Furthermore, a small contribution to the superconductive composition from double oxides such as $CaCu_2O_3$, Ca_2CuO_3 and Sr_2CuO_3 should not be excluded. Comparing the data in the literature for the superconducting phases, the high-T_c phase can be attributed to the 2223 phase with partial substitution of Bi^{3+} by Pb^{2+}, and the low phase to the 2212 phase which is free of lead [7, 8]. The data also confirm that high and low phases differ mainly in the length of the *c* axis, i.e. in the number of layers stacked in a unit cell.

Fig. 6 shows the dependence of the value of $T_c(R = 0)$ as a function of the annealing time. It is evident that longer annealing times under constant temperature contribute to the increase of T_c up to a certain critical time, after which T_c becomes constant within the experimental errors. After 20–300 days of exposure of the samples to the ambient atmosphere the $T_c(R = 0)$ of the samples was observed to be constant. No ageing effect was observed in our specimens as reported by Goia *et al.* [9].

4. Conclusions

Fig. 2 shows the evidence that a slow-cooling technique gives a high $T_c(R = 0)$. The phases identified in the Bi–Pb–Sr–Ca–Cu–O ceramic seem to be the superconducting 2223 and 2212 phases. The values of the lattice parameters obtained for these phases are similar to those reported recently [3, 7, 9, 10].

The addition of 0.4 Pb in the starting mixture results in a superconductor exhibiting $T_c(R = 0) = 106 \pm 1$ K and having a greater fraction of high-T_c phase. The annealing time increases T_c up to a certain time, after which the T_c of the superconducting material becomes constant. This observation also agrees with the experimental results, according to which Pb atoms substitute for some of the Bi, Sr and Ca atoms. This is possible in the case where the annealing time is not much prolonged and the concentration of lead in the material is sufficient. The high-T_c phase is less sensitive to ambient atmosphere and stays a superconductor even after one year of exposure to environmental conditions.

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