Bull. Mater. Sci., Vol. 14, No. 2, April 1991, pp. 223–226. © Printed in India.

On the synthesis and structure of single-phase (Bi, Pb)$_2$Ca$_2$Sr$_2$Cu$_3$O$_{10}$

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Abstract. We report an elegant method for the synthesis of single-phase Bi-2223 superconductor from a stoichiometric composition $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$ by a matrix reaction route. The superconducting transition temperature T_c ($R = 0$) of this single-phase compound is 120 K. The effect of Pb-content and sintering temperature on the formation and stability of Bi-2223 phase is described.

Keywords. Single phase Bi-2223 superconductor; stoichiometric composition; superconducting transition temperature.

1. Introduction

Three superconducting phases in the Bi-Ca-Sr-Cu-O system have been established which can be represented as $Bi_2Ca_{n-1}Sr_2Cu_nC_{2n+4}$ with $T_c = 10$ K, 85 K and 110 K for $n = 1,2$ and 3 respectively (Tarascon *et al* 1988). Extensive studies by a large number of groups have shown that the synthesis of the 110 K phase ($Bi_2Ca_2Sr_2Cu_3O_x$) is extremely difficult because of the intergrowth of the lower-T_c phases which invariably form in substantial amounts during synthesis of this phase. The volume fraction of the Bi-2223 phase can, however, be enhanced by prolonged heat-treatment of the starting oxide mixtures with slight excess of Ca and Cu (Shi *et al* 1989). Difficulty of synthesizing pure 2223 phase is attributed to the slow kinetics of the growth of this phase with a large c-parameter (37 Å) and also to the problem inherent in the high temperature sintering of $Bi_2O_3 + CaCO_3 + SrCO_3 + CuO$ mixture which would invariably lead to Bi-losses since Bi_2O_3 has a melting point (1090 K) significantly lower than the temperature required for the reaction of the constituent oxides. Recently numerous investigators have reported that partial substitution of Pb for Bi when coupled with long-term sintering at temperatures close to the melting point (1145 K) enhances the formation of Bi-2223 phase giving T_c-values between 100 and 120 K (Statt *et al* 1988; Oota *et al* 1988). But all these samples usually contain, in addition to the 2223-phase, impurity phases like 2122, 2021, Ca_2PbO_4, Ca_2CuO_3 or unreacted oxides. Recently Jin *et al* (1989), Endo *et al* (1989), Calestani *et al* (1989) and Maeda *et al* (1989) have reported the synthesis of single-phase Bi(Pb)-2223 product from starting compositions which are rich in Cu and Ca and deficient in Sr. There is wide disparity between the composition chosen by different groups and the actual stoichiometric composition of the 2223 phase. But detailed structural investigations by, say, neutron diffraction demand pure single phase samples preferably made from stoichiometric compositions. So far there are no detailed neutron diffraction studies on Bi-2223 related compounds because of the non-availability of the single-phase samples in sufficient quantities (few grams). In this paper, we report a simple and elegant method for synthesizing single-phase Bi(Pb)-2223 product in bulk from a stoichiometric composition $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$.

2. Experimental

Samples were synthesized in a two-step process. This is similar to the method originally developed by us for the synthesis of Bi-2122 compound (Sastry *et al* 1988). First, a matrix of $Ca_2Sr_2Cu_3O_7$ was made by reacting the individual oxide mixture in appropriate ratio at 1235 K for two days with intermediate grindings. In the second step, appropriate amounts of this matrix, Bi_2O_3 and lead acetate were thoroughly mixed, made into a pellet and heated at 1200 K in air for short duration (5–10 min) till the mass turned completely black. The product was cooled, ground well, repelletized and sintered at 1140 K for 200 h with several intermediate grindings. This product was again made into thin pellets (2 mm thick) and were heated separately at 1190 K for 3–5 min during which period the pellet partially melted and warped. At this stage the pellet was withdrawn from the furnace and reannealed at 1140 K for 50 hr and furnace-cooled.

Electrical resistivity was measured using a standard DC four-probe method. X-ray powder diffraction patterns were recorded at room temperature with Ni-filtered CuK_α radiation on a Philips PW 1050 wide angle goniometer.

3. Results and discussion

In order to evaluate the influence of Pb-content on the formation of 2223-phase, a number of samples with nominal composition $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ ($x = 0$–0.5) were synthesized under identical synthesis protocol explained above but for the sintering temperature which was fixed at a value 2–3° below the melting point of each composition (the melting point comes down monotonically with increase in the Pb-content). The composition with $x = 0.3$, i.e. $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$ gave a single-phase sample whereas all other compositions resulted in samples which contain Bi-2122 phase as the only impurity phase. This demonstrates the superiority of our matrix reaction method compared to the usual solid state reaction method followed by most of the investigators, where in addition to the 2122 phase, Ca_2PbO_4 and Ca_2CuO_3 are commonly found as impurity phases. This, we believe, is due to the fact that in our method $Pb(Ac)_2$ is added only after prereaction of the other oxides.

Figure 1 shows the resistivity behaviour of the single-phase $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$ compound as a function of temperature. The superconducting transition occurs in a single-step beginning at 130 K with zero resistance obtained at 120 K. Figure 2 shows the X-ray diffraction pattern for the same sample. All the peaks could be indexed due to the Bi(Pb)-2223 phase. Detailed neutron diffraction studies carried out on this sample also confirmed the single-phase nature of this sample as there were no extraneous peaks and the observed pattern matched well with the calculated pattern. The neutron diffraction profile refinement based on the space group Amaa yields the cell parameters, $a = 5.399(6)$ Å, $b = 5.413(6)$ Å and $c = 37.13(2)$ Å. The structural details obtained from neutron diffraction profile refinement analysis have been reported elsewhere (Sequeira *et al* 1989).

To study the influence of sintering temperature on the formation and stability of the 2223 phase, we have subjected the single-phase 2223 product, prepared by the above method, to heatings at different temperatures. For this purpose we have chosen two temperatures 1123 K and 1141 K, the former being the ideal sintering temperature for

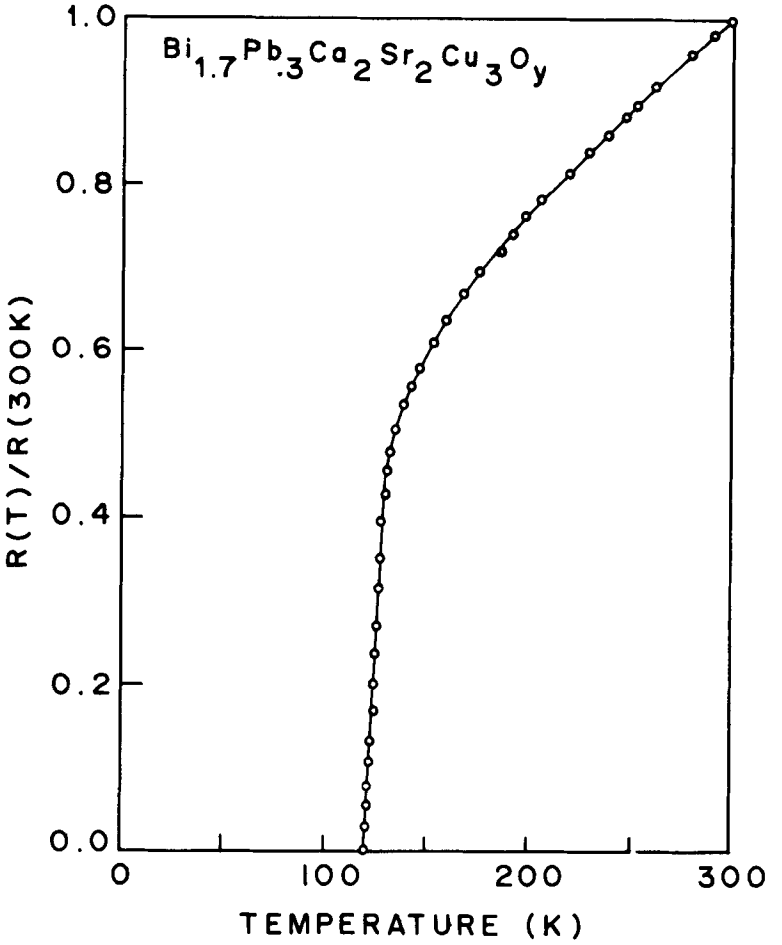

Figure 1. Normalized resistance $R(T)/R(300\,K)$ vs temperature K for the sample $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$.

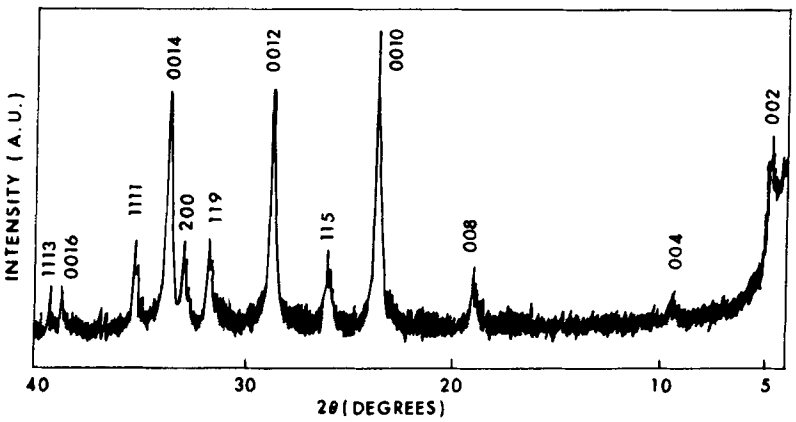

Figure 2. X-ray diffraction pattern for the sample $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_y$.

the formation of 2122 phase, and the latter for the 2223 phase. X-ray diffraction patterns and resistivity behaviour were recorded after each heating stage. No significant change was observed in either the X-ray pattern or the $R(T)$ behaviour even after heating the sample for 100 hr at 1141 K thus indicating that the 2223 phase is stable at this temperature. But in the case of heating at 1123 K, the sample undergoes degradation and gradually transforms to Bi-2122 phase as indicated by the appearance of XRD peaks corresponding to the 2122 phase. The $R(T)$ curve showed a two-step behaviour giving a drop at 110 K and going to zero only at 85 K which also confirms the formation of 2122 phase in significant amounts. It is interesting to note that this degraded sample could, however, be transformed back to majority 2223 phase by subjecting it to reheating at 1141 K for 5 days. This demonstrates that 2122 and 2223 phases are interconvertible depending on the sintering temperature. Detailed studies on this are in progress.

4. Conclusions

We have reported an elegant method for the synthesis of single-phase Bi(Pb)-2223 superconductor with $T_c = 120$ K from stoichiometric compositions. The influence of Pb content and sintering temperature on the formation and stability of the 2223 phase have been described.

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