Amorphous Bi2Pb0.6Sr2Ca2Cu3Ox obtained by melt-spinning and its superconductivity after crystallisation

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Amorphous $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ obtained by melt-spinning and its superconductivity after crystallisation

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Résumé. — La technique d'amorphisation par trempe d'oxyde fondu a été appliquée aux supraconducteurs à haute T_c de type 2223 à base de bismuth avec addition de plomb. Des échantillons de $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ amorphe ont été obtenus sous forme de petits fils ou rubans. L'évolution lors de traitement thermique, de cet oxyde amorphe a été suivie par calorimétrie différentielle à balayage (DSC). Une transition vitreuse intervient à $T_g = 680$ K et la cristallisation commence à $T = 730$ K. Après recuit sous oxygène, la susceptibilité magnétique met en évidence deux phases supraconductrices avec $T_c = 110$ K et $T_c = 75$ K respectivement.

Abstract. — Previous quenching experiments on 2212 bismuth containing high T_c oxides have been extended to the 2223 compound with lead addition. Amorphous $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ was prepared by a modified melt-spinning technique and samples in the form of small tapes and wires were obtained. The subsequent evolution of the amorphous oxide during annealing was monitored by differential scanning calorimetry (DSC). The glass transition was found to occur at $T_g = 680$ K and the onset of crystallisation at $T = 730$ K. After oxygen annealing, magnetic susceptibility measurements showed evidence of two superconducting phases with transition temperatures at $T_c = 110$ K and $T_c = 75$ K respectively.

Introduction.

There are now several well known techniques for the preparation of high T_c oxide superconductors. We have used rapid solidification to prepare precursors of high T_c superconductors directly from the liquid state thus fixing their shape in a low porosity state. Three different improvements may become accessible *via* rapid solidification : a) the shaping of the brittle product ; b) the achievement of high dense homogeneous liquid state is a prerequisite for homogeneity after solidification and careful attention is needed when the liquid state contains immiscible elements. Yurek *et al.* [1] have reported the preparation of high T_c ceramics *via* oxidation of crushed alloy ingots but this technique does not present the possible potential improvements cited for rapid solidification and appears to produce heterogeneous (multiphase) oxides.

When the liquid alloy of composition corresponding to the metallic components of the superconducting oxides is homogeneous, it can be liquid-quenched to an amorphous or microcrystalline state usually in the shape of a ribbon. The ribbon can subsequently be oxidized at appropriate temperatures to obtain the oxide superconductor in ribbon shape [2]. Liquid $Y_1Ba_2Cu_3$ phase-separates due to unmixing tendency between Y and Ba. But we and others [3-6] have shown that the technique consisting of rapid solidification of the alloy followed by oxidation of $Eu_1Ba_2Cu_3O_x$ and $Yb_1Ba_2Cu_3O_x$.

Like the YBaCu alloys, BiCu and PbCu containing alloys also tend to phase separate. In such cases a second technique consisting of the rapid quenching of the oxide melt is applicable as demonstrated by Kim *et al.* [7] for the $Y_1Ba_2Cu_3O_x$ system and by us and others [8-14] for the $Bi_2Sr_2Ca_1Cu_2O_x$ system. In the latter case, we found that the oxide melt is an easy glass former. In this work, we extend the application of this technique to $Bi_2Sr_2Ca_2Cu_3O_x$ to which 0.6 moles of PbO were added.

Experimental results and discussion.

Oxide powders of Bi, Ca, Cu and Pb and $SrCo_3$ were mixed to obtain a nominal composition of metal components corresponding to $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ and calcinated for diffusive mixing. The resulting black powder was molten and melt spun from $T \sim 1425$ K on a copper wheel in air at a substrats speed of about 10 m/s. Depending on the oxide melt temperature and substrate preparation, solidified samples took wire like forms with cylindrical cross section or ribbon shapes. The present castings were obtained in a closed chamber and broke into 1 to 2 cm long pieces upon collision with the chamber walls. Nevertheless they allow the conclusion that long oxide ribbons of constant shape can be obtained under optimum conditions. Abe *et*

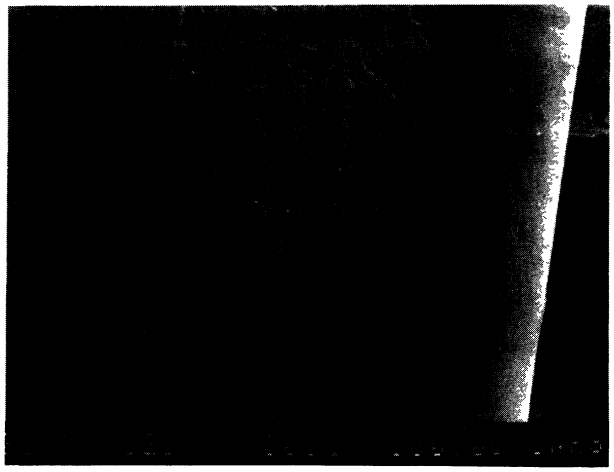

Fig. 1. — Amorphous $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ ribbon.

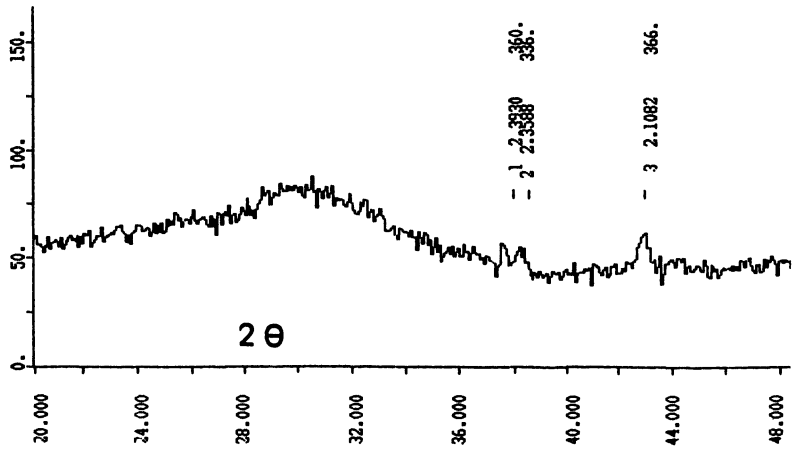

Fig. 2. — X-ray diffraction pattern of melt-spun $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$.

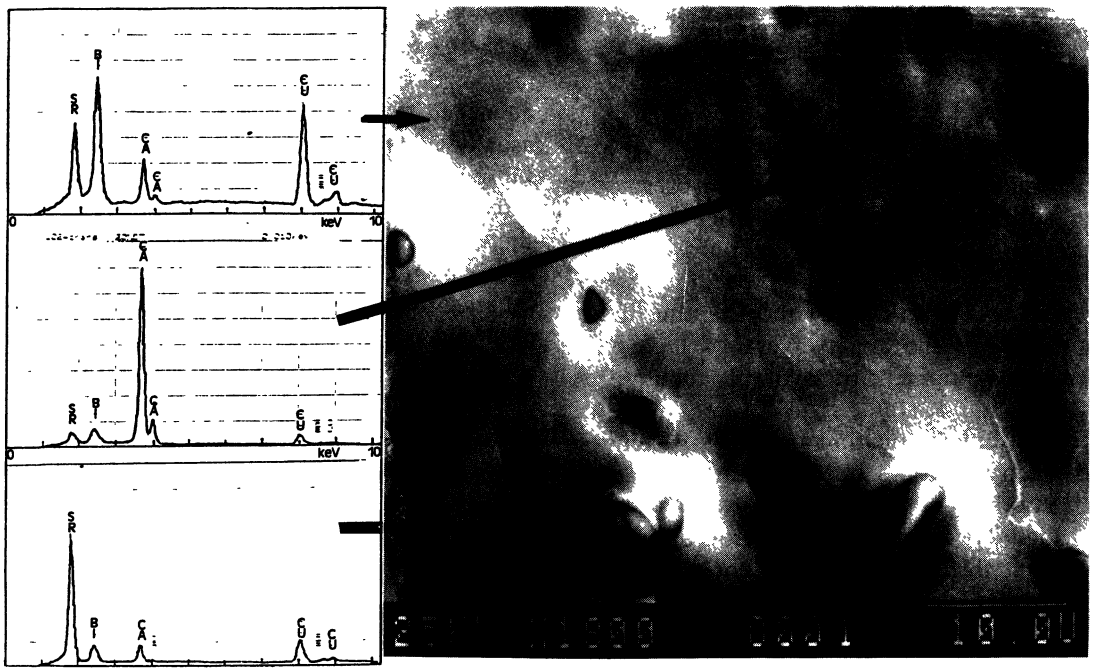

Fig. 3. — SEM secondary electron image of sample of figure 2 showing amorphous matrix and Ca and Sr rich precipitates.

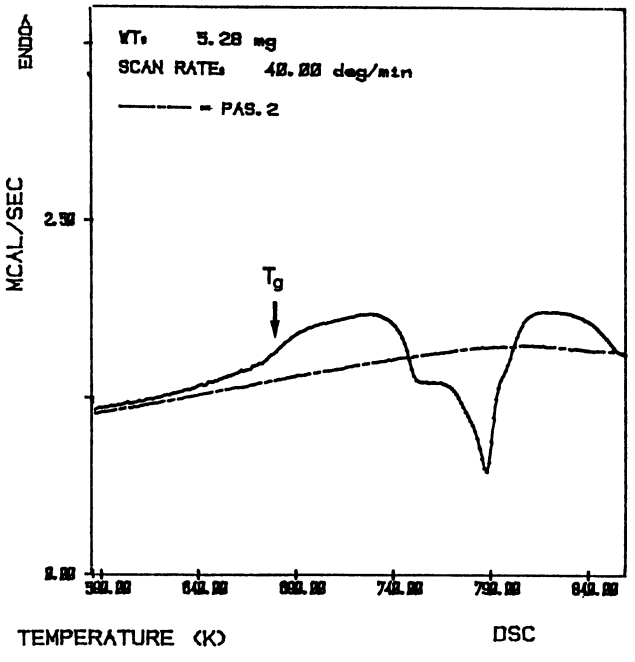

Fig. 4. — DSC thermogram of sample of figures 2 and 3 showing glass transition at $T_g \sim 680$ K and crystallisation at $T > 730$ K.

al. [15] have previously obtained BiCaSrCuO rods *via* the liquid state using a lower quench rate.

Figure 1 shows the substrate-side SEM micrograph of a ribbon segment. X-ray diffraction pattern taken on this sample with a copper tube (wavelength 1.54 Å) showed the typical principal amorphous halo with traces of crystallinity of an unknown phase (Fig. 2). The SEM micrograph of figure 3 shows a secondary electron image of the amorphous bulk of a sample (this view is from a freely solidified side of a fairly thick sample). Amidst the glassy bulk that appears clear, one notes large grey and darker and smaller diffuse particles. These particles which are likely to be at the origin of the weak Bragg peaks of figure 1 were found to be respectively predominantly calcium and strontrium oxide derivatives as can be seen on the X-ray microanalysis peaks of figure 3. (The Pb peak is covered by that of Bi). The oxide nature is deduced from their darker colors indicating their low electron density. Such precipitation of Ca-rich and Sr-rich oxides, during quenching would be important thermodynamic indications for the study of the phase diagram in the liquidus region of composition $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ but require crystallographic (TEM) confirmation.

Differential scanning calorimetry (DSC) also showed the rapidly quenched oxide to be glassy with marked glass transition temperature $T_g \sim 680$ K and crystallisation beginning at ~ 730 K for a heating rate of 40 K/min (see Fig. 4). The glassy oxide was then annealed at $\sim 1\,100$ K under oxygen partial pressure.

Figure 5a shows a low magnification SEM micrograph of a wire like segment after such annealing. Figure 5b shows the microstructure of this sample at higher magnification : it can be seen that the amorphous featureless phase of figure 3 has been replaced by a crystalline phase with a predominant morphology of very anisotropic plate-like shapes of submicron thickness and diameters greater than 10 μm similar but more anisotropic than those previously observed to appear in the Pb-free 2212 tetragonal bismuth oxide [9, 16].

The appearance of these plates corresponds to the appearance of superconductivity as previously reported by resistivity measurements [9].

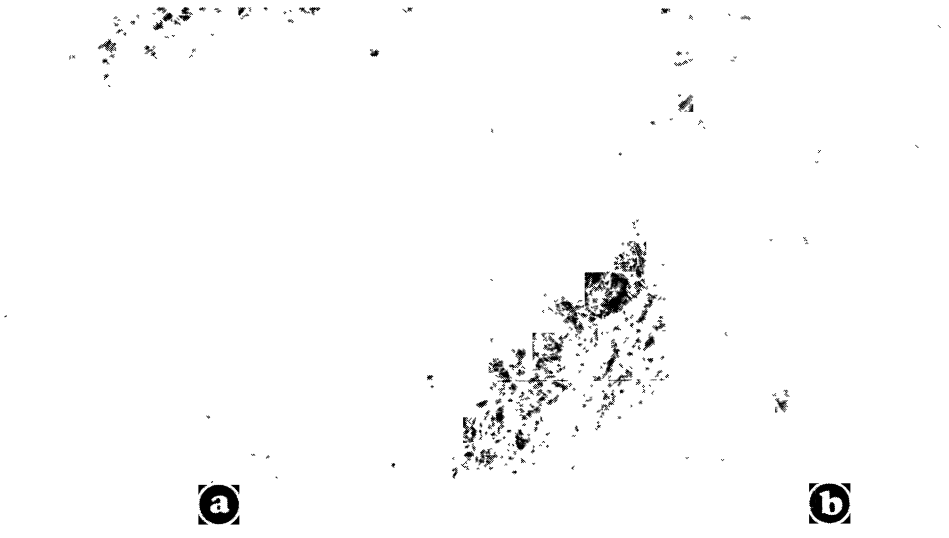

Fig. 5. — (a) SEM image of $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ melt-spun wire-like sample after oxygen annealing at $T \sim 1\,100$ K. (b) Higher magnification details showing thin plate-like crystals of superconducting phase.

Figure 6 shows d.c. magnetic susceptibility measured as a function of temperature on an annealed sample. Two transitions are clearly detected at $T \sim 107$ K and $T \sim 77$ K corresponding to the so-called 110 K and 80 K superconducting phases. X-ray diffraction patterns confirmed the two phase nature of the sample with the 110 K superconductor increasing its volume-fraction with increasing annealing time [17]. It is expected that oxygen diffusion into these samples which have little or no porosity is slower and requires much longer annealing times for optimisation of the superconducting properties of the 2223 phase.

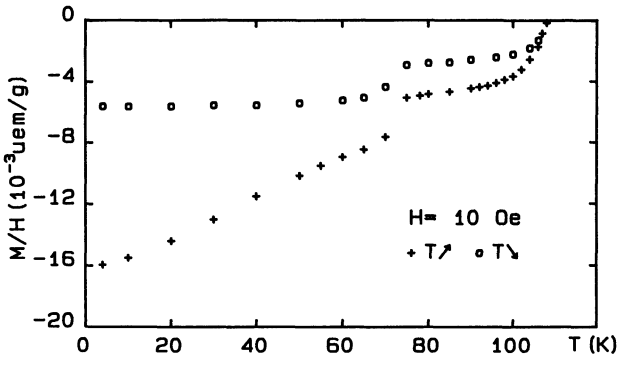

Fig. 6. — Susceptibility *versus* temperature for melt-spun $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ after oxygen annealing showing transitions T_c at 107 and 77 K.

Conclusion.

We have found that addition of Pb to $Bi_2Sr_2Ca_2Cu_3O_x$ oxides increases their glass formability *via* melt-spinning. T_g is about 680 K, crystallisation occurs some 50 above T_g and the heat of crystallisation is of the order of that measured for metallic glasses (1 to 2 kCal/gm.at). High T annealing results in the formation of the tetragonal superconducting phase with $T_c \sim 110$ K but long annealing times are required to reach optimum superconductivity inside the samples. A detailed study of evolution with annealing, of the superconducting volume-fraction and phase distribution is now in progress [17]. It was found that melt-spinning is a viable technique for preparation of these oxide compositions in ribbon form but the experimental set-up has to be optimised to avoid high stresses and shocks below T_g.

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