Dopants in high-T_c superconductors from rapidly quenched $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_w$ glasses

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High-T_c superconductors with a variety of metal dopants (M = V, Nb, Mo, Te, Ta and W, ordered by atomic number) were prepared by the heat treatment of rapidly quenched glass precursors. The optimum heat-treatment temperature, T_{opt}, was observed in all the glass-derived superconductors with different dopants; in all cases T_c (zero) higher than 105 K was observed on heat treatment at T_{opt} for each dopant. T_{opt} was related to the temperature at which a partial melting of the specimen occurred, as determined by differential thermal analyses. The dopants lower the partial melting temperature and thus lower T_{opt} for the formation of the 110 K phase.

1. Introduction

The discovery of glass formation in the system Bi–(Pb)–Ca–Sr–Cu–O [1–3] has encouraged us to fabricate high-T_c superconductor fibres via glass precursors. On the basis of our viscosity measurements for the precursor glasses, we demonstrated that the drawing technique for fluoride glass fibres was applicable to the bismith-based superconductor systems [4]. In fact, several researchers have succeeded in drawing glass fibres in the Bi–(Pb)–Ca–Sr–Cu–O systems and in obtaining glass-ceramic fibres by the heat treatment of the glass precursors [5–7]. However, the heat-treatment conditions for obtaining excellent superconductor fibres have not been optimized for the glass fibre precursors, probably because of their characterization difficulties caused by their extremely small dimensions.

Glass flakes obtained by a twin-roller quenching technique, which have a thickness of about 20 μm, similar to the diameter (or thickness) of glass fibres, are expected to have a similar crystallization behaviour. Because the handling of flakes is much easier compared to fibres, the twin-roller quenched glass flakes can be a good alternative to fibre glasses for characterization. We have previously found that the substitution of lead for bismith was effective to stabilize the high-T_c (110 K) phase and demonstrated the formation process of such a high-T_c phase from the twin-roller quenched glass flakes in the systems Bi–Pb–Ca–Sr–Cu–O [8, 9]. Our systematic study has also clarified that the optimum composition is $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_w$ and the optimum heat-treatment conditions are 855 °C for over 20 h from the viewpoint of T_c (zero). We have also found that the Ca_2PbO_4 phase, which is formed during heat treatment, plays an important role in the formation of the high-T_c (110 K) phase.

On the other hand, further doping of another metal into the system Bi–Pb–Ca–Sr–Cu–O has widely been investigated for glass-derived superconductors and also found to be effective in enhancing T_c (zero) in several cases [10–15]. However, the doping effect of such metals has been discussed only for each dopant individually and no systematic studies have been done so far.

In the present work, we prepared various metal-doped $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ (M = V, Nb, Mo, Te, Ta and W, ordered by atomic number) glasses using a twin-roller quenching technique. This paper reports the effect of the metal dopants above on the superconducting properties of final products in connection with the partial melting behaviour of the crystallized glass samples on the basis of resistivities, X-ray diffractions and differential thermal analyses.

2. Experimental procedure

Special grade chemicals of $Bi(NO_3)_3 \cdot 5H_2O$, $Pb(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, V_2O_5, Nb_2O_5, MoO_3, TeO_2, Ta_2O_5, and WO_3 were used as starting materials. The mixtures of raw materials were calcined at 800 °C for 20 h. The product was ground and pressed to form a rod and then sintered at about 800 °C. The twin-roller quenching apparatus, combined with a thermal-image furnace, was used for glass preparation from the sintered rod. Differential thermal analysis (DTA) was performed with a Rigaku Denki thermal analyser in air at a heating rate of 10 °C min^{-1}. The resistivity of the crystallized samples was measured by the standard four-probe method.

3. Results and discussion

Fig. 1 shows some examples of the temperature dependence of resistivity for the glass-ceramic flakes with and without dopants heat treated at 855 °C for 20 h. The heat-treatment temperature of 855 °C was chosen because it was found to be the optimum heat-treatment temperature, T_{opt}, in the undoped
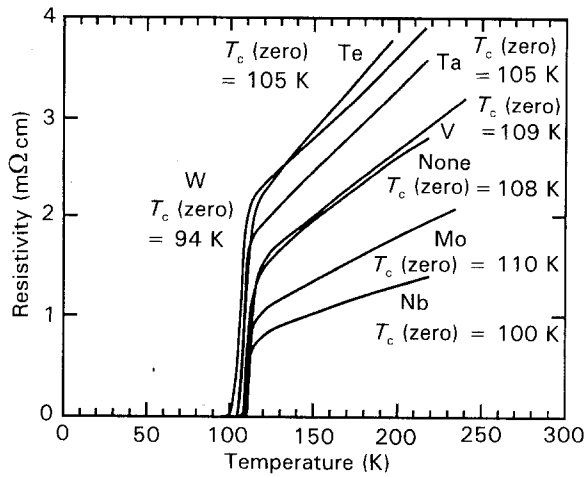
Figure 1 Temperature dependence of resistivity for the $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ (M = none, V, Nb, Mo, Te, Ta and W) twin-roller quenched samples heat-treated at 855 °C for 20 h.

$Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_w$ glass-ceramics. All the samples exhibit metallic behaviour and show superconducting transition at around 100 K. The T_c (zero) values ranging from 94–110 K seem to be considerably influenced by a small amount of dopant; the doping of tellurium, niobium, tantalum or tungsten tends to lower T_c (zero), whereas the samples doped with vanadium or molybdenum exhibit higher T_c (zero) than the undoped sample. From Fig. 1, a small amount of dopant appears to considerably affect the superconducting properties of the glass-ceramics via twin-roller quenched glasses.

Fig. 2a shows the T_c (zero) values and the relative XRD peak intensities of the 110 K phase plotted against the heat-treatment temperature, together with the DTA curve for the twin-roller quenched $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_w$ (undoped) glasses. The relative XRD peak intensities of the 110 K phase are calculated from $I_{110\ K(0\ 0\ 2)}/(I_{110\ K(0\ 0\ 2)} + I_{80\ K(0\ 0\ 2)})$, where $I_{110\ K(0\ 0\ 2)}$ and $I_{80\ K(0\ 0\ 2)}$ are the intensities of the XRD peaks due to the diffraction from the (0 0 2) plane of the 110 K phase and of the 80 K phase, respectively.

The T_c (zero) values, which range from 85–108 K, are maximized when the heat treatment was performed at 855 °C. The relative peak intensities of the 110 K phase are also maximized at around 850–857 °C. In the DTA curve, two endothermic peaks, T_1 and T_2, are observed at about 858 and 875 °C, respectively. The higher temperature peak, T_2, is due to the melting of the 80 K phase $Bi_2CaSr_2Cu_2O_w$ on the basis of the comparison with the DTA curve for the pure 80 K phase, and the lower temperature peak, T_1, is attributable to the partial melting caused by the presence of Ca_2PbO_4 and CuO, pointed out in our previous papers [8, 9]. It is noteworthy that T_{opt}, at which the T_c (zero) values were maximized, is close to T_1, suggesting that the partial melting of some crystallized phases is very important to form the 110 K phase and thus enhance the T_c (zero).

Fig. 2b–g show the T_c (zero) values and the relative XRD peak intensities of the 110 K phase plotted

against the heat-treatment temperature, together with the DTA curves for metal-doped glasses $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ (M = V, Nb, Mo, Te, Ta and W) prepared by twin-roller quenching. The
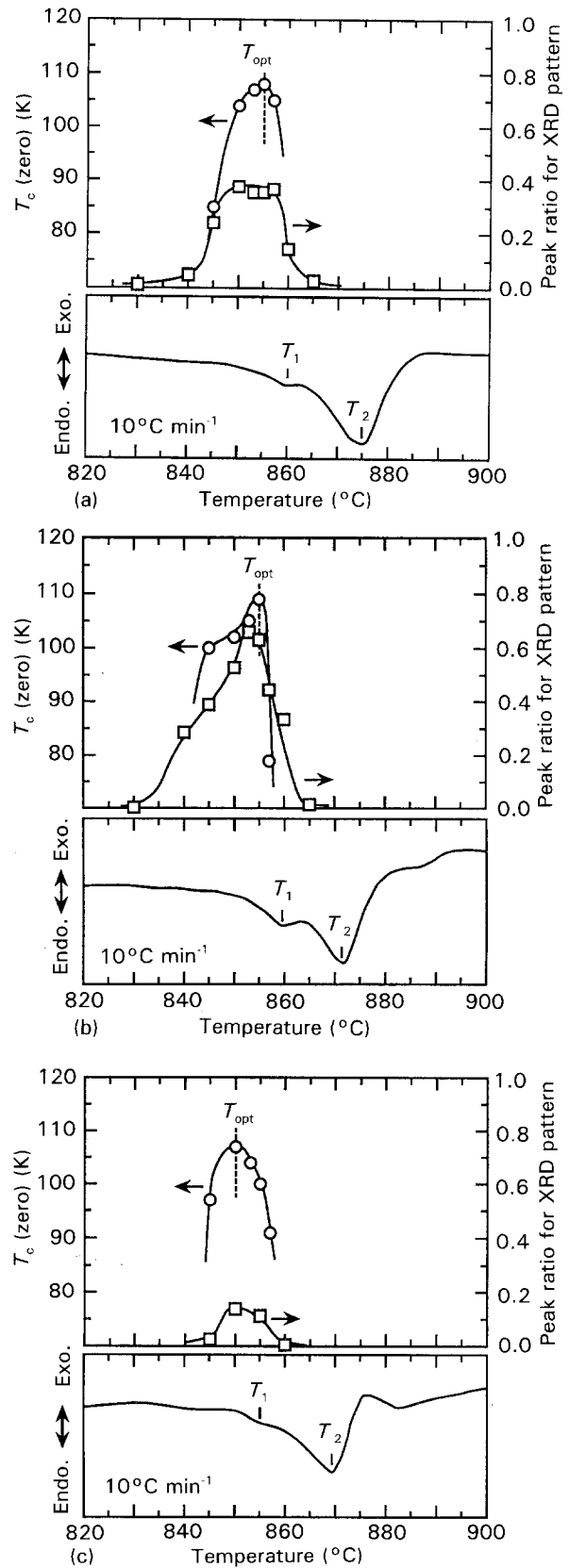

Figure 2 T_c (zero) values and relative intensities of the 110 K phase peak (0 0 2) for the metal-doped $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ samples plotted against the heat-treatment temperature. Differential thermal analyses for the twin-roller quenched glasses are also shown. M: (a) none (b) vanadium, (c) niobium, (d) molybdenum, (e) tellurium, (f) tantalum, (g) tungsten.
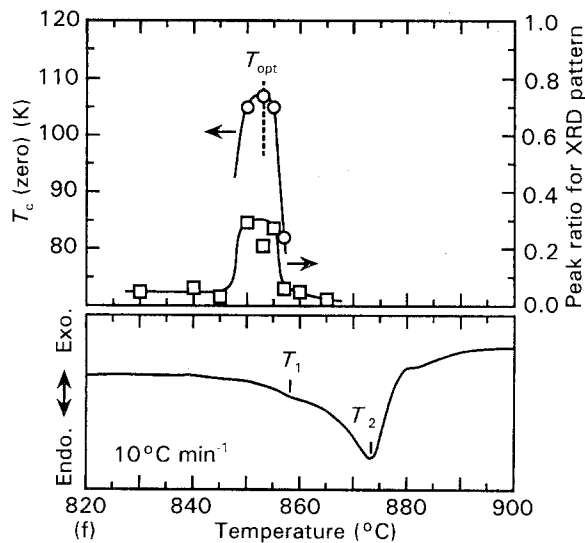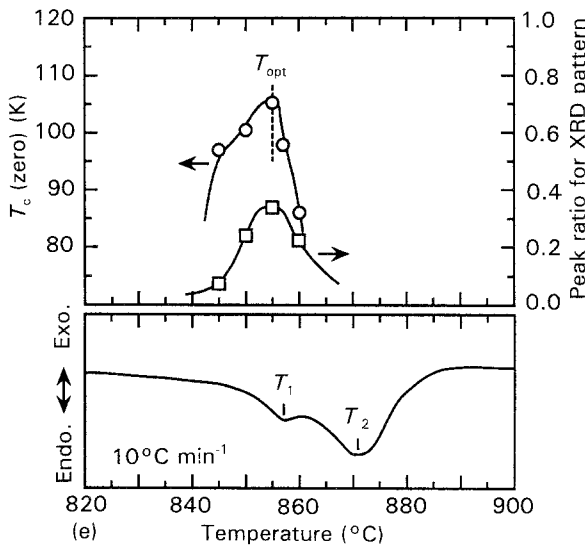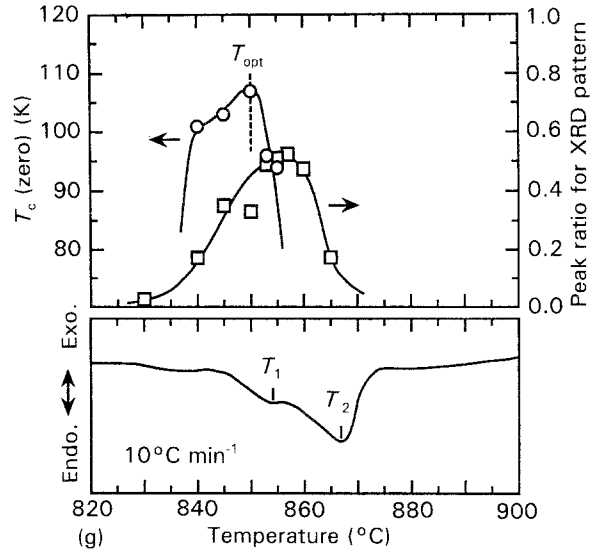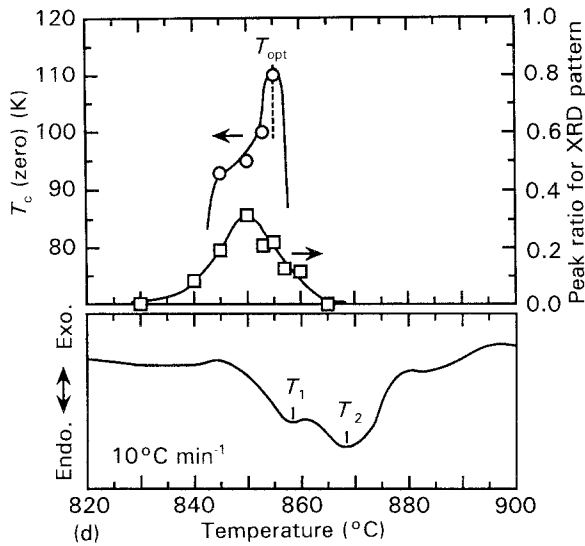
(d)

(e)

(f)

Figure 2 continued.

optimum heat-treatment temperatures for T_c (zero), T_{opt}, and for relative XRD peak intensities of the 110 K phase are observed in all the cases with dopants. T_{opt} are basically in good agreement with the optimum heat-treatment temperatures based on XRD for each case, although the deviation is marked in the

(g)

case of tungsten-doped sample (Fig. 2g). For all the DTA curves, two endothermic peaks T_1 and T_2 are also observed in the temperature regions 850–880 °C as in the case for the undoped glass. It is noteworthy that T_{opt} for the metal-doped samples tends to be lower than that for the undoped sample. The endothermic peak temperatures of T_1 and T_2 are also lower in the doped samples.

Fig. 3 shows the temperature dependence of resistivity for the twin-roller quenched glass-ceramic flakes heat treated at T_{opt} for each dopant; the heat-treatment period was 20 h for each case. All the glass-ceramic flakes exhibit relatively high T_c (zero) values, higher than 105 K by the heat treatment at T_{opt} for each dopant. From the comparison of Figs 1 and 3, it becomes obvious that the superconducting properties such as T_c (zero), are not much influenced by the species of dopants when the heat treatment was done at the optimum temperature for each dopant.

Fig. 4 shows the relation between the optimum heat-treatment temperature, T_{opt}, and the DTA peak temperature of T_1 for the metal-doped samples. The temperature T_{opt} has a correlation to the partial mel-
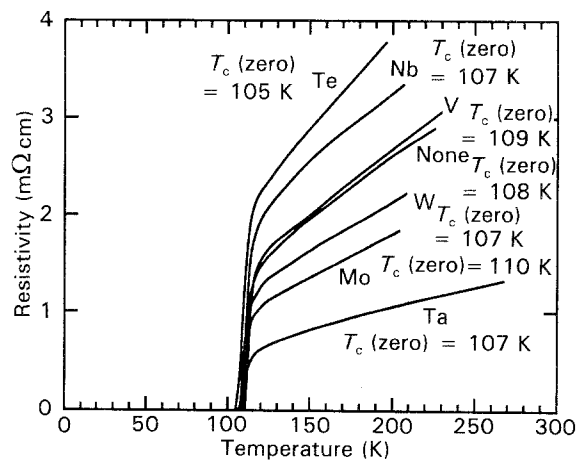

Figure 3 Temperature dependence of resistivity for the $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ (M = none, V, Nb, Mo, Te, Ta and W) Twin-roller quenched samples heat treated for 20 h at the optimum temperature, T_{opt}, for each glass.
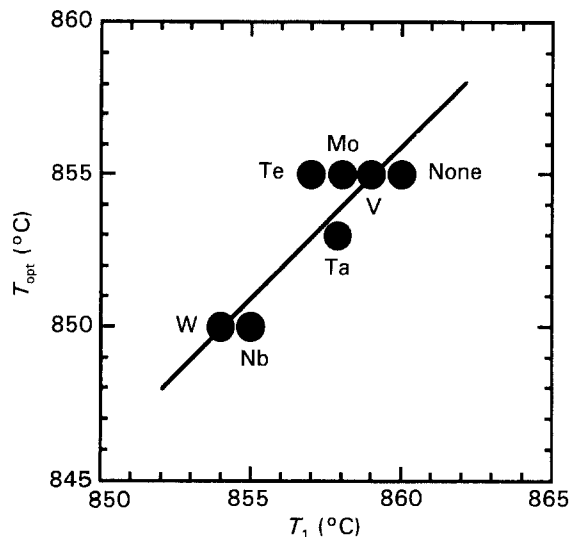
Figure 4 Relation between the optimum heat-treatment temperatures, T_{opt}, and the partial melting temperatures, T_1, observed in DTA for the $Bi_{1.6}Pb_{0.4}M_{0.1}Ca_2Sr_2Cu_3O_w$ (M = none, V, Nb, Mo, Te, Ta and W) twin-roller quenched glasses.

ting temperature T_1, indicating that in all the metal-doped samples the partial melting plays an important role in the formation of the 110 K phase. In addition, compared with the undoped sample, metal-doped samples tend to have lower T_1 and also T_{opt}. This is probably due to the fact that the dopants participate to form a liquid phase containing Pb^{2+}, Ca^{2+} and Cu^{2+} and thus lower the partial melting temperatures [8]. Good correlation between T_{opt} and T_1 has also been observed in the melt-solidified $Bi_{1.6}Pb_{0.4}M_{0.1}$ $Ca_2Sr_2Cu_3O_w$ (M = V, Nb, Mo, In, Sn, Sb and W) thick films [16]; it thus becomes clear that the dopant effect in the glass-derived samples is basically the same in the melt-solidified samples.

It is concluded that a small amount of dopant in the twin-roller quenched Bi–Pb–Ca–Sr–Cu–O glass-ceramics lower the temperature at which the partial melting occurs and the optimum heat-treatment temperature for the formation of the 110 K phases compared to the undoped samples. The T_c (zero) values are, however, little influenced by the species of dopants when the heat treatment was carried out at the optimum temperature for each dopant.

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