

# A new model for the formation of high- $T_c$ phase in superconductive $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glass-ceramics

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The formation mechanism of the high- $T_c$  phase through the glass-ceramic route and the role of Pb on the formation of this phase have been investigated. It was found that a new compound with the chemical composition  $\text{Pb}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_y\text{O}_z$  ( $x = 1.8$ ) precipitates at around 550 °C. This phase is stable up to 800 °C, where it begins to decompose, and at 850 °C it completely disappears. It was found that some part of the released Pb diffuses into the 2212 phase leading to the formation of Pb-containing 2212 phase,  $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ . On the other hand, an endothermic peak, probably arising from the melting of  $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  phase or melting at grain boundaries containing  $\text{Pb}^{2+}$ , was observed at 856 °C only in Pb-containing samples that were heat treated. The liquid phase attributed to the endothermic peak may enhance the formation of high- $T_c$  phase (2223 phase). The growth kinetics for the high- $T_c$  phase were analysed using the Johnson–Mehl–Avrami equation; the results indicate that the growth of the high- $T_c$  phase is controlled by a diffusion process and the activation energy for its formation in the initial stage (shorter than 96 h) is  $576 \pm 45 \text{ kJ mol}^{-1}$ .

## 1. Introduction

Since the discovery of superconductivity in the system Bi–Sr–Ca–Cu–O (Bi-based system) by Maeda *et al.* [1], three superconducting phases with the general formula of  $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_x$  ( $n = 0, 1, 2$ ) have been observed. Their critical temperatures,  $T_c$ , are 20 K (2201 phase) for  $n = 0$ , 85 K (low- $T_c$  phase or 2212 phase) for  $n = 1$  and 110 K (high- $T_c$  phase or 2223 phase) for  $n = 2$ . The high- $T_c$  phase is the most difficult to produce by heat treatment even though its stoichiometric composition is adopted. Prolonged heat treatments in a partially melted state or in a low oxygen pressure, in which the melting temperature is lowered, were found very effective for the promotion of the high- $T_c$  phase. Takano *et al.* [2] reported that the substitution of Pb for a small part of Bi enormously enhances the formation of high- $T_c$  phase. Other substitutions such as Mo, Te and Sb [3–5] were tried but Pb remains the most effective. The difficulty in preparing the high- $T_c$  phase revealed that an understanding of the formation of high- $T_c$  phase is prerequisite for the fabrication of superconductors containing pure high- $T_c$  phase with high quality. The formation mechanism of the high- $T_c$  phase was extensively discussed by many authors [6–11]. Even

though different approaches were made so far, many points concerning the formation mechanism of the high- $T_c$  phase are still obscure.

Among various fabrication techniques of superconductors, the glass-ceramic processing is very attractive for the fabrication of dense superconductors with desired shapes such as fibres [12]. Recently, Sato *et al.* [13] clarified the formation mechanism of the 2212 phase in the glass-ceramic process of the Bi-based system. But the formation mechanism of the high- $T_c$  phase in the glass-ceramic process is still unclear. Detailed understanding of the formation of the high- $T_c$  phase will shed valuable light on the fabrication of excellent superconducting glass-ceramics and fibres. We examine the formation mechanism of the high- $T_c$  phase in the glass-ceramics with the composition  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . And we propose a new vision of the role of Pb, i.e. a new model of the formation mechanism.

## 2. Experimental procedure

Grade reagents of  $\text{Bi}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$  with high purity were weighed to the composition of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . They were mixed

with methanol in a ceramic mortar and released in air until no methanol was supposed to exist. The powders were then put in an alumina plate and calcined at 820 °C for 10 h in an electric furnace. The black powders were ground again and melted in a platinum crucible at 1250 °C for 10 min in an electric furnace. The melt was rapidly poured on an iron plate and pressed with another one to a thickness of about 1.5 mm. The obtained glassy samples were annealed at different temperatures for different periods. The crystalline phases present in the annealed samples were studied by X-ray diffraction (XRD) analyses using a Geigerflex model 2038 with  $\text{CuK}_\alpha$  radiation. Thermal behaviour was studied using a Seiko Instruments TG/DTA 220. Microstructure observations were performed using a JSM-5400 model scanning electron microscope. The a.c. magnetic susceptibility,  $\chi = \chi' - i\chi''$ , were measured by a four-probe Hart shorn-type-bridge with a frequency of 713 Hz at an a.c. field amplitude of 0.26 Oe ( $21 \text{ A m}^{-1}$ ).

### 3. Results and discussion

Fig. 1 shows the differential thermal analysis (DTA) curve for the as-quenched sample carried out on bulk in air at a heating rate of  $10 \text{ K min}^{-1}$ . The glass transition  $T_g$  and crystallization peak  $T_x$  temperatures are 378 °C and 451 °C, respectively. Similar to all Bi-based cuprates prepared by a melting method, an endothermic peak and an exothermic peak are observed at 760 °C and 780 °C, respectively. According to Komatsu *et al.* [14], it is considered that the endothermic peak is attributable to the formation of a liquid phase and the exothermic peak is related to the formation of the 2212 phase. The sample melts at around 880 °C.

Before discussing the formation mechanism of the high- $T_c$  phase, we briefly describe the crystalline phases present in various annealed samples. Fig. 2 shows the XRD patterns for the samples annealed at different temperatures for 24 h in air. At 550 °C the 2201 phase is well formed, and  $\text{Cu}_2\text{O}$  and

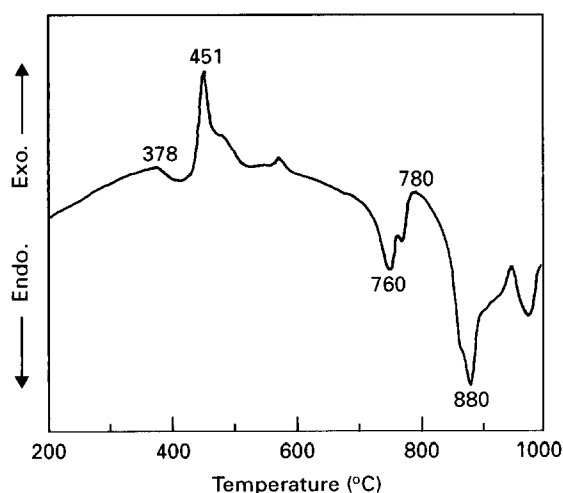


Figure 1 DTA curve for the as-quenched sample of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ; heating rate was  $10 \text{ K min}^{-1}$ .

$(\text{Sr}, \text{Ca})_3\text{Cu}_5\text{O}_x$  are detected. Other peaks appeared at  $2\theta = 17.8^\circ$  and  $31.0^\circ$ . The phase causing those peaks is designated "Pb-compound" because the peaks are observed for the sample of  $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  containing Pb, but not for the sample of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . At 750 °C the 2212 phase is formed, and the 2201 phase is still traced. The peaks assigned to  $\text{CuO}$  are observed, indicating the oxidation of some part of  $\text{Cu}^+$  into  $\text{Cu}^{2+}$ . The intensity of the  $\text{CaO}$  peak is weak, indicating that  $\text{CaO}$  participates in the formation of the 2212 phase. The intensity of peaks attributing to the Pb-compound is very strong. At 800 °C the main crystalline phases are the 2212 phase and Pb-compound. The 2201 phase and  $\text{Cu}_2\text{O}$  are no longer detectable in the XRD pattern. This suggests that the 2201 phase is stable thermally at least below 800 °C and that all  $\text{Cu}_2\text{O}$  is oxidized into  $\text{CuO}$ . At 850 °C only 2212 phase and  $(\text{Sr}, \text{Ca})_3\text{Cu}_5\text{O}_x$  are present, and the Pb-compound disappears completely.

#### 3.1. Composition of Pb-compound

Up to now, the Pb-compound which has been considered to form in samples of  $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  is  $\text{Ca}_2\text{PbO}_4$  [15]. But the peak positions corresponding to the Pb-compound shown in Fig. 2

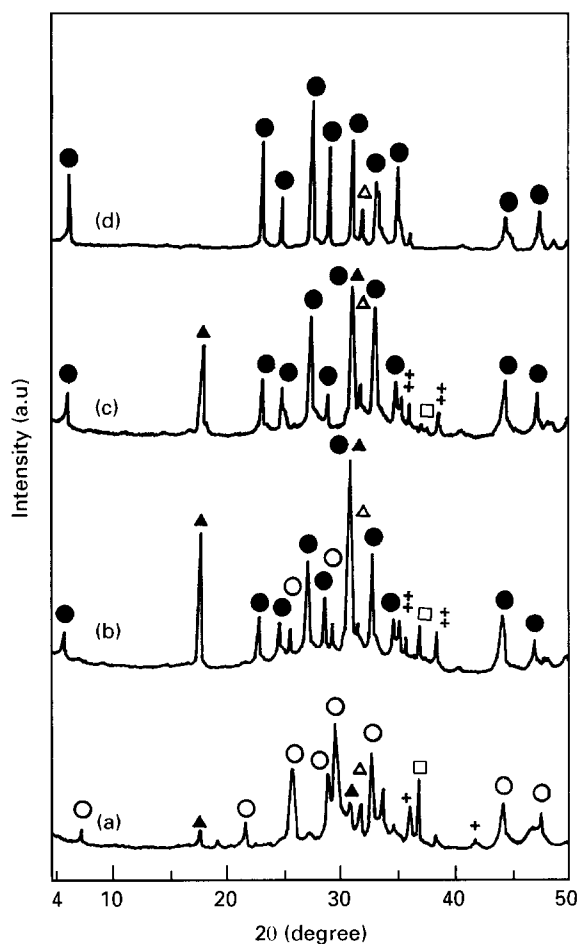


Figure 2 XRD powder patterns for  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  heat-treated at different temperatures for 24 h in air (a) 550 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C; (●) 2212 phase, (○) 2201 phase, (□)  $\text{CaO}$ , (▲)  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_x$ , (△)  $\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_5\text{O}_x$ , (+)  $\text{Cu}_2\text{O}$ , (++)  $\text{CuO}$ .

are slightly different from those of  $\text{Ca}_2\text{PbO}_4$ , implying the presence of other Pb-compounds. Several peaks of the Pb-compound overlap with those of the 2212 phase, so it is essential to study the XRD pattern of Pb-compound in a temperature region where the 2212 phase does not appear. For this reason, the sample obtained by annealing at  $650^\circ\text{C}$  for 48 h was used, in which the 2201 phase and the Pb-compound are mainly formed. The XRD pattern of this sample and  $\text{Ca}_2\text{PbO}_4$  (obtained by sintering at  $850^\circ\text{C}$  for 24 h) are shown in Fig. 3, indicating that it is questionable to assign the Pb-compound to  $\text{Ca}_2\text{PbO}_4$  from the XRD patterns.

Takada *et al.* [16] studied phase formation in the ternary system of  $\text{PbO-SrO-CuO}$  in air and reported the existence of  $\text{Pb}_2\text{Sr}_3\text{CuO}_x$  at  $800^\circ\text{C}$ . Note that  $\text{Pb}_2\text{Sr}_3\text{CuO}_x$  has an XRD pattern nearly identical to that observed for the Pb-compound mentioned above. Green *et al.* [17] reported that secondary phase (phases), probably composed of  $\text{Pb-Sr-Ca-Cu-O}$ , forms in  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , when  $x$  exceeds 0.35. We therefore prepared some  $\text{Pb}_2(\text{Sr, Ca})_3\text{CuO}_x$  compounds with the different Sr/Ca ratio by a conventional solid-state reaction and examined XRD patterns of those samples. It was found that the  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$  has the same XRD pattern seen for the Pb-compound observed in the sample of  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . The XRD pattern for  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$  is shown in Fig. 3. The XRD patterns clearly show that the Pb-compound is assigned to  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$ , but not to  $\text{Ca}_2\text{PbO}_4$ . From the present study, therefore, we propose that the Pb-com-

pound formed by annealing of  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  glassy samples is  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$ .

### 3.2. Formation of Pb-containing 2212 phase

It has been clarified that the 2212 phase forms at around  $780^\circ\text{C}$  in samples prepared by a melting method and that a liquid phase, formed at around  $760^\circ\text{C}$ , enormously enhances the growth of the 2212 phase by easing oxidation of  $\text{Cu}^+$  into  $\text{Cu}^{2+}$  and by easing diffusion of  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  entities toward the 2212 phase [11]. As is well known, the substitution of Pb for Bi is essential for the formation of the high- $T_c$  phase, but the role of Pb remains unclear. As shown in Fig. 2, the Pb-compound, i.e.  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$ , is formed then disappears, accompanied by formation and growth of the 2212 phase, implying that the Pb-compound might have some effect on the growth of the 2212 phase. We therefore examined the role of Pb-compound on the growth of the 2212 phase before checking the formation mechanism of the high- $T_c$  phase. To our knowledge, such a study has not been reported so far.

The intensity of the peaks ( $2\theta = 17.8^\circ$  and  $31.0^\circ$ ) of  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$  decreases with increasing annealing temperature and completely vanishes at  $850^\circ\text{C}$ , as shown in Fig. 2. The remaining phases in the sample annealed at  $850^\circ\text{C}$  are the 2212 phase and  $\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_5\text{O}_x$ ; precipitation of other Pb-compounds has not been observed in the XRD pattern. These results strongly suggest that Pb released from the decomposition of  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$  may be present at grain boundaries or may diffuse into the 2212 phase and/or  $\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_5\text{O}_x$ . Fig. 4 shows the peak at  $2\theta = 33.2^\circ$  attributed to the 2212 phase. Fig. 4a, for the Pb-containing sample, shows that the peak at  $2\theta = 33.2^\circ$  begins to deform at above  $820^\circ\text{C}$ . The peak deformation is enhanced with increasing annealing temperature and at  $850^\circ\text{C}$  it becomes very clear. Such peak deformation has not been observed in the samples with the composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  containing no Pb, as shown in Fig. 4b. The peak at  $2\theta = 33.2^\circ$  represents the (200) and (020) planes of the 2212 phase, so the peak deformation shown in Fig. 4a indicates that the lengths of  $a$ - and  $b$ -axes of the 2212 phase are no longer equal after annealing above  $820^\circ\text{C}$ . The peaks at  $2\theta = 33.2^\circ$  are separated by computer simulation using Lorentz curve profiles, and the values of the  $a$ - and  $b$ -axes are given in Fig. 5, together with the  $c$ -axis length, determined from the  $(00\bar{1}0)$  plane. The  $a$ -axis length is almost constant irrespective of annealing temperature. The  $b$ - and  $c$ -axis lengths, however, decrease with increasing annealing temperature. The changes in the lattice parameters shown in Fig. 5 strongly suggest the formation of the 2212 phase containing Pb, i.e.  $(\text{Bi, Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  [18]. The diffusion of  $\text{Pb}^{2+}$  into  $\text{Bi}^{3+}$  is expected to be accompanied with a release of oxygen that is believed to be a cause of the decrease in lattice parameters. From the above

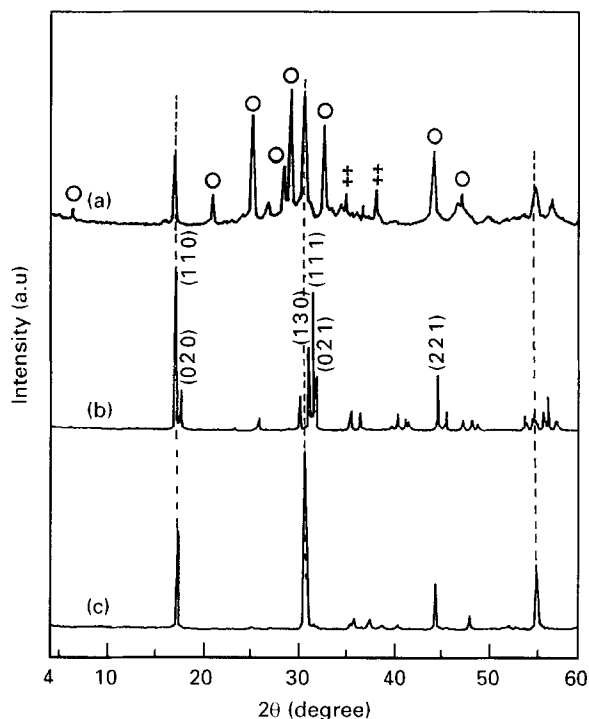


Figure 3 (a) X-ray diffraction pattern for  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  annealed at  $650^\circ\text{C}$  for 48 h in air; (b) X-ray diffraction pattern for  $\text{Ca}_2\text{PbO}_4$ ; (c) X-ray diffraction pattern for  $\text{Pb}_2\text{Sr}_{1.2}\text{Ca}_{1.8}\text{CuO}_y$  ( $x = 1.8$ ) annealed at  $850^\circ\text{C}$  for 24 h in air; (○) 2201 phase and (+ + +)  $\text{CuO}$ .

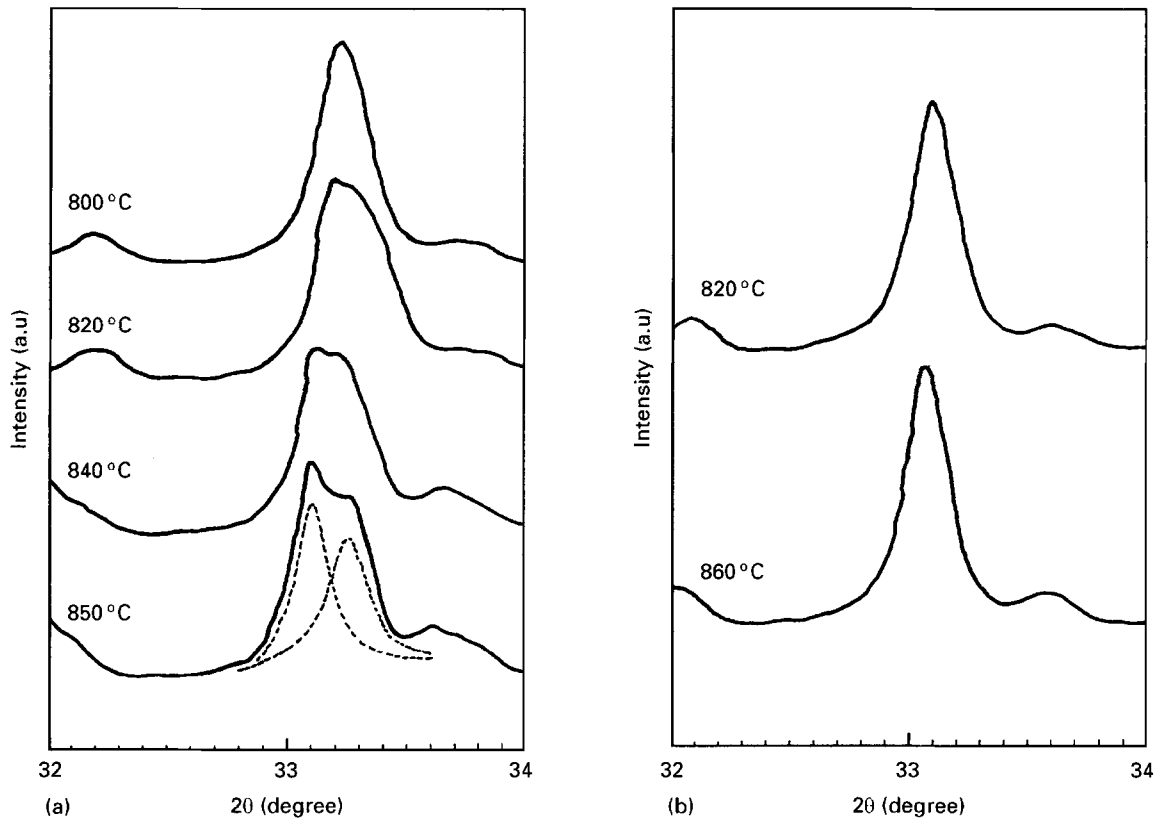


Figure 4 Temperature dependence of the peak at 33.2° in XRD powder patterns for 2212 phase: (a)  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  and (b)  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ .

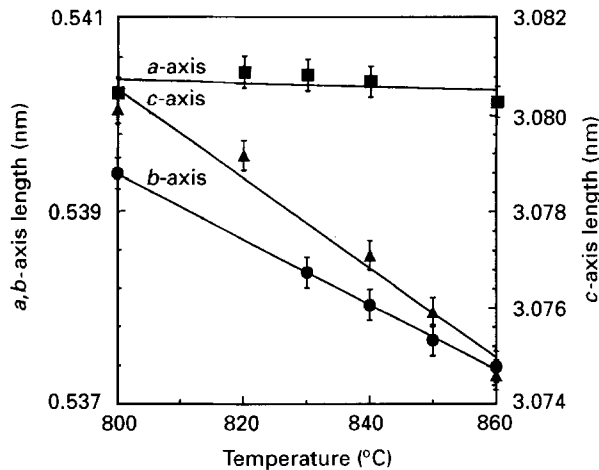
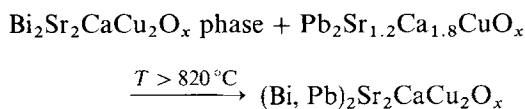


Figure 5 Annealing temperature dependence of lattice parameters of 2212 phase in  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ .

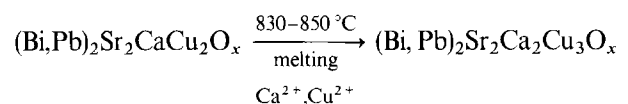
results, we propose the following reaction in which the diffusion of Pb into the Pb-free 2212 phase,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ , leads to the formation of the Pb-containing 2212 phase.



### 3.3. Formation of the high- $T_c$ phase

Fig. 6 shows the DTA curves of the samples obtained by annealing at 850°C for 24h in air with  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  and  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . These

annealed samples consist mainly of the 2212 phase. In the Pb-free sample, the melting starts at around 884°C. But in the Pb-containing sample it begins at around 877°C. In addition, a small but clear endothermic peak is observed at 856°C in the Pb-containing sample. It is well known that the formation temperature of the high- $T_c$  phase in Pb-free samples is much higher than in Pb-containing samples [19]. Chen *et al.* [10] reported that the volume fraction of the high- $T_c$  phase is the highest at 856°C. The volume fraction of the high- $T_c$  phase for the Pb-containing samples was estimated from the a.c. susceptibility data (Fig. 7). It is seen that the volume fraction of the high- $T_c$  phase increases with increasing annealing temperature between 835°C and 850°C, indicating that the high- $T_c$  phase is unstable at 860°C. The above results in our samples are in agreement with those reported by Chen *et al.* [10]. From these results, we propose that the endothermic peak at 856°C shown in Fig. 6 is due to the formation of a certain liquid phase. This liquid phase may be due to the slow melting of the  $(\text{Bi, Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  phase or due to some melting at grain boundaries where  $\text{Pb}^{2+}$  might be present. The formation of this liquid phase is believed to be an origin of the enhancement of the formation of the high- $T_c$  phase. Consequently, the following reaction for the formation of the high- $T_c$  phase is proposed:



The growth kinetics of the high- $T_c$  phase in glass-ceramic processing was also examined. Such a study in

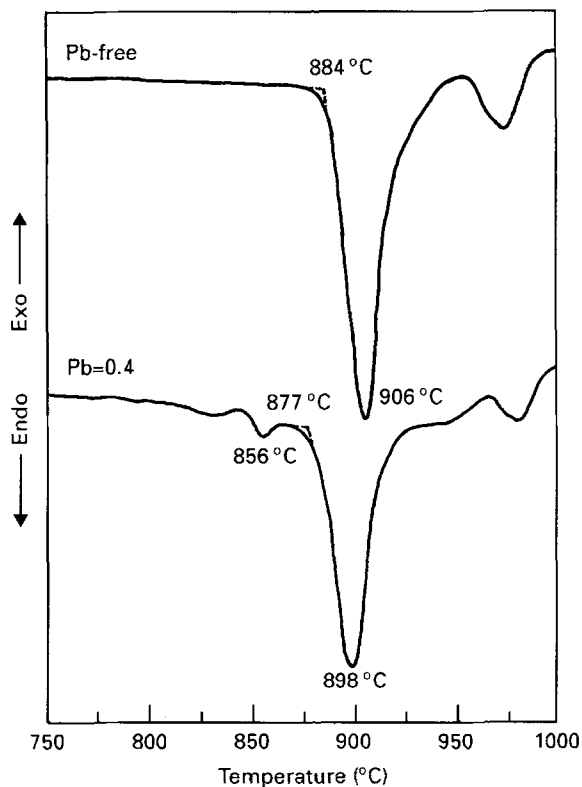


Figure 6 DTA curves for  $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  samples annealed at  $850^\circ\text{C}$  for 24 h in air.

$(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  glass-ceramics has not been reported so far. The growth of the high- $T_c$  phase is very slow, so it is controlled by a diffusion process, as mentioned by many authors, and here the following the Johnson-Mehl-Avrami equation is used for the analysis of the growth kinetics:

$$1 - X = \exp(-Kt^n)$$

where  $X$  is the volume fraction of a crystal formed through a reaction controlled by a diffusion process at a time  $t$  and  $n$  is the growth factor which reflects the nucleation rate and/or the growth morphology.  $K$  is a constant related to the activation energy,  $E$ , by  $\ln(K) = -nE/RT + \text{constant}$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. The volume fraction of the high- $T_c$  phase at various temperatures and times was estimated, and the curves of  $\ln(-\ln(1-X))$  versus  $t$  are shown in Fig. 8. The value of  $n$  was estimated from the slope of the curves and was  $1.31 \pm 0.11$ . The value of  $K$  was also estimated from the curves, and the activation energy calculated was  $576 \pm 45 \text{ kJ mol}^{-1}$ . The value of  $n = 1.31$ , close to  $n = 1.5$ , suggests again that the growth of the high- $T_c$  phase is controlled by a diffusion process and therefore the formation of the liquid phase is very important for the formation of the high- $T_c$  phase. Note that the value of  $E = 576 \text{ kJ mol}^{-1}$  is much lower than  $1530 \text{ kJ mol}^{-1}$  for the high- $T_c$  phase formed by the sintering method [20]. This strongly suggests that the glass-ceramic processing, in which the constituent elements are usually well mixed compared with the sintering processing, is a favourable technique for the fabrication of the high- $T_c$  superconductors.

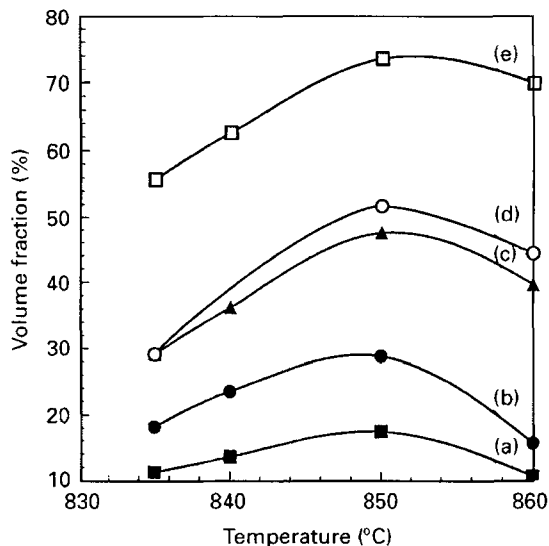


Figure 7 Variation of high- $T_c$  phase volume fraction with annealing time for  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  annealed at different temperatures in air: (a) 30 h, (b) 48 h, (c) 72 h, (d) 96 h, (e) 250 h.

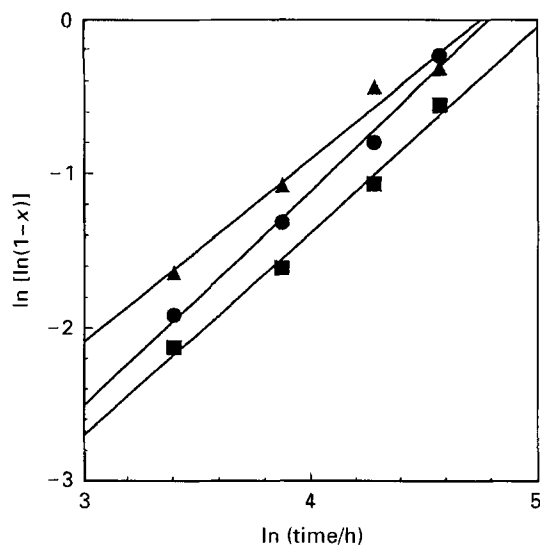


Figure 8 Relation between  $\ln[-\ln(1-x)]$  and  $\ln(\text{time})$  for the volume fraction,  $X$ , of high- $T_c$  phase in  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ : (■)  $835^\circ\text{C}$ , (●)  $840^\circ\text{C}$ , (▲)  $850^\circ\text{C}$ .

#### 4. Conclusion

The formation of the high  $T_c$  phase in the (Bi, Pb)-Sr-Ca-Cu-O system through the glass-ceramic route was studied. It was found that a new Pb-compound  $\text{Pb}_2\text{Sr}_{3-x}\text{Ca}_x\text{CuO}_y$  ( $x = 1.8$ ) precipitates at around  $550^\circ\text{C}$  and is stable up to  $800^\circ\text{C}$ . Above this temperature, it begins to decompose and the released Pb is found to diffuse into the 2212 phase. This leads to the formation of Pb-containing 2212 phase. At  $856^\circ\text{C}$  an endothermic peak related to the melting of Pb-containing 2212 phase or to some melting at grain boundaries containing  $\text{Pb}^{2+}$  is observed. Such a liquid phase is thought to be an origin for the enhancement of the high- $T_c$  phase formation. The activation energy for the formation of the high- $T_c$  phase in the initial stage (shorter than 96 h), determined by using the Johnson-Mehl-Avrami equation, is  $576 \pm 45 \text{ kJ mol}^{-1}$ .

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