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Crystallization kinetics of superconducting precursor glasses in the Bi–Pb–Sr–Ca–Cu–O system

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Abstract

The crystallization kinetics of Bi,Pb-based superconducting precursor glasses such as $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ (Sample A) with different copper valence states and $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$ (Sample B) with different Ca contents have been examined by differential thermal analysis. The modified Kissinger equation for the nonisothermal crystallization process is used to evaluate the activation energy, E_a, for the crystallization,. The number of crystal nuclei is almost independent of the heating rate in all samples, and the $Bi_2Sr_2CuO_x$ phase appearing first grows three-dimensionally. The values of E_a of Sample A is around 320 kJ mol^{-1}. The values of E_a in Sample B with small Ca contents of y=0.5 and 1.0 are 299 and 287 kJ mol^{-1}, respectively. Compared with Bi-based glasses containing no Pb, Bi,Pb-based glasses tend to have small values of E_a. It is found that the values of E_a of Bi,Pb-based glasses are similar to those in TeO_2-based and fluoride glasses which are known as fragile glass-forming systems.

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1. Introduction

Various compositions in the Bi–Sr–Ca–Cu–O system (Bi-based system) are glass-forming through the quenching of melts, and glasses, i.e. superconducting precursor glasses, are converted into high-T_c superconductors after proper annealing [1,2]. This preparation technique, i.e. glass–ceramic route, is very attractive for the fabrication of dense superconductors with desired shapes, such as fibers. In order to fabricate high-performance superconductors through glass-ceramic processing, it is necessary to clarify the crystallization mechanism in precursor glasses. Further, an in-depth understanding of the structure and various properties of precursor glasses will also shed some important light on glass-ceramic processing.

It has been well established that at least three superconducting phases, $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (n=1, 2 and 3), are presented as stable crystal structures in the Bi-based system. $Bi_2Sr_2CuO_x$ is generally called the 2201 phase (T_c=8–20 K), $Bi_2Sr_2CaCu_2O_x$ is the 2212 or the low-T_c phase (T_c=85–90 K), $Bi_2Sr_2Ca_2Cu_3O_x$ is the 2223 or the high-T_c phase (T_c=105–110 K). It is, therefore, very interesting and important to examine the crystallization mechanism of the samples with the compositions of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$. Further, Bi-based glasses have been prepared by rapid quenching of melts from around 1200°C to room temperature in air, and thus a large amount of copper, i.e. around 70–80%, exists as monovalent Cu^+-ions [2–5]. On the

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other hand, the average copper valences in the superconducting phases are over 2.0, meaning that sufficient oxygen must be supplied into glasses for the formation of superconducting crystals. It is, therefore, intrinsically important to understand the relationship between the copper valence state in precursor glasses and the crystallization mechanism or the formation behaviors of the superconducting crystals.

It has been conformed that the partial substitution of Pb for Bi in the Bi-based system is very effective in increasing the volume of fraction of the high-T_c phase [6]. It is, therefore, important to clarify the glass forming ability and the crystallization mechanism in the Bi–Pb–Sr–Ca–Cu–O (Bi, Pb-based) system. The study on the crystallization behavior of Bi,Pb-based glasses is, however, so far restricted and, hence, the initial crystallization and formation mechanisms of the high-T_c phase are still unclear. Recently, Khaled et al. [7] have proposed a formation mechanism of the high-T_c phase in Bi,Pb-based glasses. In this study, the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses with different Cu valence states and the $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$ glasses with different CaO contents are prepared, and the initial crystallization kinetics clarified. It is known that the glass-forming ability in Bi,Pb-based glasses is low due to the precipitation of CaO crystalline phase [1,2].

2. Experimental

The nominal compositions examined in this study were $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_x$-Cu_3O_z. Commercial powders of *guaranteed reagent* Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO were mixed and calcined at 800°C for 10 h in air. To control the copper valence state in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass, glucose was added to calcined powders and mixed in methanol. The amount of glucose addition was in the 0.5–3 mass% range for batch weight (20 g). The calcined powders with, and without, glucose were melted in an alumina crucible at 1250°C for 12 min in an electric furnace. The melts were poured onto an iron plate and pressed quickly to a thickness of ca. 1 mm. The values of $R(Cu^+)=Cu^+/(Cu^++Cu^{2+})$ in the glasses were estimated by thermogravimetry (TG). The differential thermal analyses (DTA) for bulk samples were carried out at heating rates from 2 to 20 K min^{-1} in air. X-ray diffraction (XRD) analyses at room temperature using CuK_α radiation were performed to examine the phases present in the melt-quenched and heated samples. The microstructure of crystals present in heated samples were observed with a scanning electron microscope (SEM). Electrical resistivities of the heat-treated samples were measured by the four-probe technique with an intensity of electrical current of 10 mA.

3. Results and discussion

3.1. Glass formation

The XRD patterns for some $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses prepared with, and without, glucose addition are shown in Fig. 1. In all samples, the peaks assigned to CaO crystals are observed. But, the peak intensity in the sample with 1.5 mass% glucose addition is small compared with that in the sample without glucose addition. Also, the sample with 3 mass% glucose

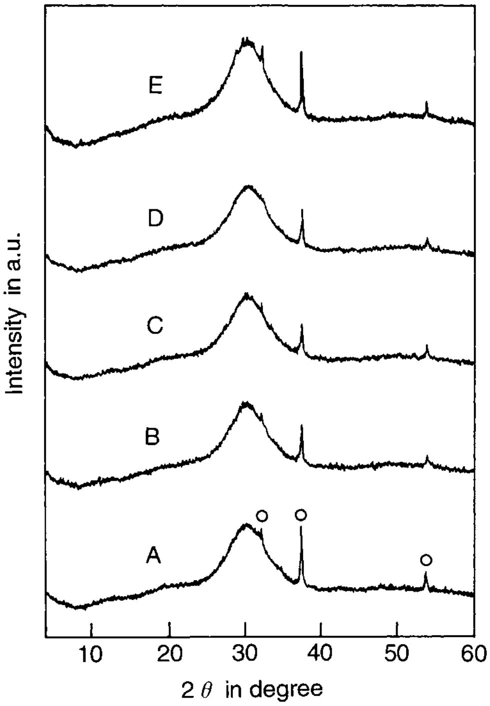

Fig. 1. XRD patterns for the as-quenched samples of $Bi_{1.6}Pb_{0.4}Sr_2$-$Ca_2Cu_3O_y$ added glucose of X mass%. (A) X=0, (B) X=1.0, (C) X=1.5, (D) X=2.0, (E) X=3.0. (○) CaO.

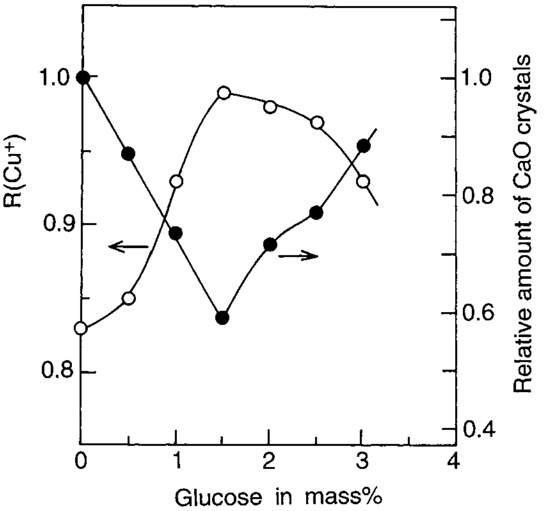

Fig. 2. Values of $R(Cu^+)=Cu^+/(Cu^++Cu^{2+})$ in the as-quenched samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ added glucose of X mass% and relative amounts of precipitated CaO crystals (i.e. I(CaO at X=0)/ I(CaO at X)) evaluated from the peak intensity in XRD patterns.

addition has relatively strong peaks due to CaO. The relative amount of CaO crystals precipitated in as-quenched samples was estimated from the calibration curve (i.e. the relative peak intensity between the amounts of CaO and MgO) used MgO as inner standard compound in XRD analyses. The results are shown in Fig. 2, where the amount of CaO crystals was normalized for the amount of CaO crystals in the as-quenched sample with no glucose. It is clear that the precipitated amount of CaO crystals in the samples prepared by 1.5 mass% glucose addition is small. These results shown in Figs. 1 and 2 indicate that a perfect glass of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$, which has no crystalline peak in XRD pattern, cannot be prepared by the addition of glucose, but some addition of glucose is effective in improving the glass formation in the Bi,Pb-based system.

The ratio of Cu^+ and Cu^{2+} in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses, i.e. $R(Cu^+)=Cu^+/(Cu^++Cu^{2+})$, which was determined from TG measurements, is shown in Fig. 2 as a function of glucose content. We tried to analyze the $R(Cu^+)$ ratio using cerate titration technique [4], but the end point could not be determined clearly in the Bi,Pb-based glasses. Sato et al. [4] reported that the values of $R(Cu^+)$, determined by the cerate titration method in $Bi_2Sr_2CaCu_2O_x$ glasses with various glucose additions, are consistent with those estimated by the TG method. Considering the Ellingham diagram for oxides, Cu-ion is seen to be reduced prior to the Pb ion. It is seen from Fig. 2 that the value of $R(Cu^+)$ increases with increasing glucose content, and Cu ions in the glass with the glucose content of 1.5 mass% exist almost as monovalent Cu^+ ions. The results, therefore, indicate that glucose addition up to around two mass% is effective in changing the copper valence state even in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses. Further addition causes the slight decrease in $R(Cu^+)$, although its reason is unclear at this moment. It was found that the thermal stability, which was estimated from the difference between the glass transition temperature T_g and crystallization temperature T_x, i.e. $\Delta T=T_x-T_g$, increases slightly with increasing $R(Cu^+)$. For examples, ΔT=59°C for a glucose content of X=0, ΔT=63°C for X=0.5, ΔT=69°C for X=1.0, ΔT=67°C for X=2.0 and ΔT=65°C for X=3.0. It has been reported that the thermal stability in $Bi_2Sr_2CaCu_2O_x$ and $Bi_4Sr_3Ca_3Cu_xO_y$ glasses containing no Pb ions increases with increasing $R(Cu^+)$ content [4,5]. Compared with the previous reports [4,5], the improvement in the thermal stability due to the increase in $R(Cu^+)$ in the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses is very small. It is considered that the precipitated CaO crystals suppress the effect of $R(Cu^+)$ on the thermal stability of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses.

It is known that the glass-forming ability in Bi-based glasses increases with increasing Bi_2O_3 content and $R(Cu^+)$ ratio [1,2,4,5] and the coordination number of Cu^+ ions in $Bi_2Sr_2CaCu_2O_x$ glass is two [8]. Recently, Komatsu et al. [5] proposed the network structure model in Bi-based glasses as follows: BiO_6 octahedra are connected to other BiO_6 octahedra through two-coordinated Cu^+. The present results demonstrate that monovalent Cu ions are effective in decreasing the precipitation of CaO crystals during glass preparation process and in improving the thermal stability against crystallization even in the Bi,Pb-based superconducting precursor glasses. It is, therefore, considered that even in the Bi,Pb-based glasses Cu^+ plays an important role in the glass network structure.

The XRD patterns for some $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$ glasses are shown in Fig. 3. Any peaks assigned to

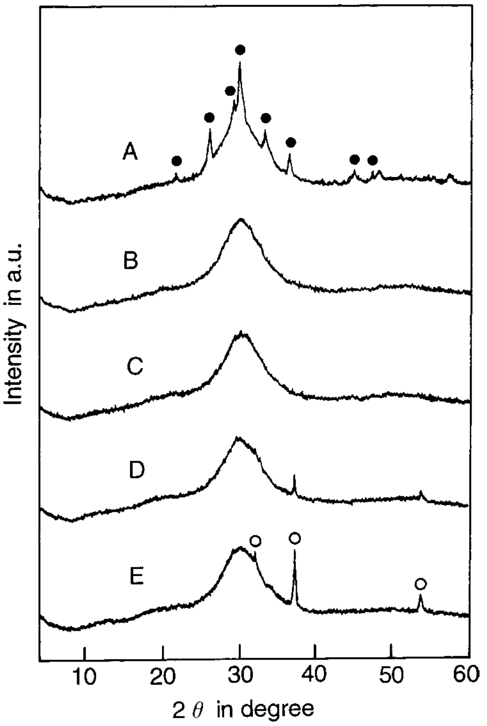

Fig. 3. XRD patterns for the as-quenched samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$. (A) x=0, (B) x=0.5, (C) x=1.0, (D) x=1.5, (E) x=2.0. (○), CaO, and (●), $Bi_2Sr_2CuO_x$.

CaO crystals are not observed in the samples with Ca contents of 0.5 and 1.0. In the sample with no Ca content, the peaks assigned to the 2201 phase appeared. The DTA patterns taken at the heating rate of 20 K min^{-1} in air for the bulk glasses are shown in Fig. 4. It is seen that the crystallization temperature decreases with decreasing Ca content and the values of $\Delta T=T_x-T_g$ also decrease. The results shown in Figs. 3 and 4 indicate that the thermal stability against crystallization decreases with decreasing Ca content, although the glass forming ability in $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_y$ increases with decreasing Ca content.

The crystallization process in $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ glasses has been extensively studied, and the formation behavior of the high-T_c phases is becoming gradually clear. As a general feature of the crystallization of Bi,Pb-based glasses, the first crystalline phase appearing during thermal treatment at around 500°C is the 2201 phase, and then the low-T_c phase appears by annealing at around 800–850°C and, finally, the high-T_c phase is formed through prolonged annealing at around 840–860°C [1,2,7,9,10]. In the Bi,Pb-based glasses examined in this study, we confirmed from XRD analyses that the first crystalline phase is also the 2201 phase, i.e. $Bi_2Sr_2CuO_x$, in which the copper valence is basically two and Ca is not included. It is, therefore, expected that the presence of Cu^+ and Ca^{2+} would suppress the growth rate of the 2201 phase, being consistent with the results shown in Figs. 3 and 4.

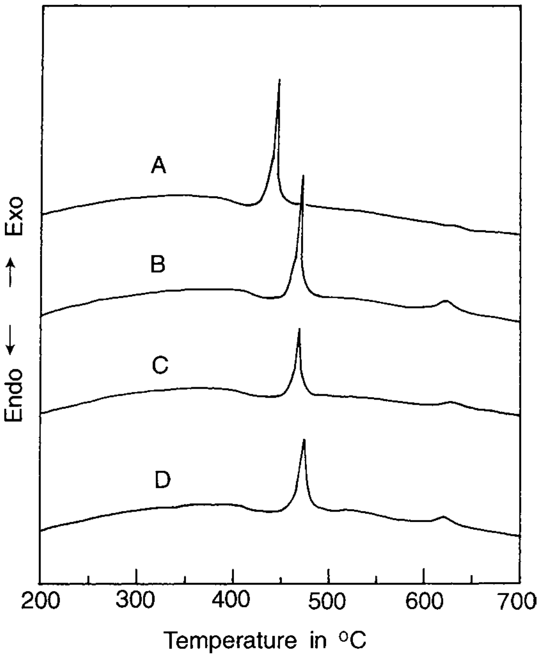

Fig. 4. DTA curves in air for the as-quenched samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$. (A) x=0.5, (B) x=1.0, (C) x=1.5, (D) x=2.0. Heating rate, 10 K min^{-1}.

3.2. Crystallization kinetics

The crystallization kinetics of superconducting precursor Bi-based glasses has been examined by DTA or differential scanning calorimetry (DSC) measurements by several authors [9,11–15]. Zheng and Mackenzie [13] examined the initial crystallization kinetics of $Bi_4Sr_3Ca_3Cu_4O_x$ glasses using DSC measurements and reported that the crystallization of the glasses follows the Avrami equation with the Avrami exponent n=3. They also reported that the activation energies for the crystallization, E_a, estimated from an isothermal method are almost the same as those

Table 1
Activation energies, E_a, for initial crystal growth of bulk Bi-based glasses evaluated by nonisothermal DSC or DTA experiments

Glass	E_a (kJ mol^{-1})	Ref.
$Bi_2Sr_2CaCu_2O_x$		
R(Cu^+)=0.82	428	[13]
R(Cu^+)=0.99	353	[13]
$Bi_{1.5}SrCaCu_2O_y$	412–437	[9]
	347	[10]
$Bi_{2.7}SrCaCu_2O_x$	375–391	[9]
$Bi_4Sr_3Ca_3Cu_4O_x$		
R(Cu^+)=0.66	432	[11]
R(Cu^+)=0.80	417	[11]
$Bi_2Sr_2Ca_2Cu_3O_x$	340	[12]
$Bi_4Sr_3Ca_3Cu_4O_x$	332	[12]
$Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_y$	292	[8]

estimated from a nonisothermal method. The values of E_a for various Bi-based glasses reported so far are summarized in Table 1.

In a nonisothermal method, which was used in this study, various equations for data analyses have been proposed. Komatsu et al. [15] evaluated the value of E_a for $Bi_2Sr_2CaCu_2O_x$ glasses with different copper valence states using several nonisothermal equations, such as the modified Kissinger equation [16] and the equation proposed by Bansal et al. [17]. They confirmed that the type of equation used is not critical, at least for the determination of E_a of the Bi-based glasses in which the number of crystal nuclei was almost independent of the heating rate, but for the Bi-based glasses in which the number of crystal nuclei varies significantly with heating rate, the numerical factors which depend on the crystallization mechanism must be considered. They also found that the values of E_a estimated from the modified Kissinger equation for $Bi_2Sr_2CaCu_2O_x$ glasses are almost the same as those estimated from the modified Ozawa equation [18]. In this paper, we estimated E_a for various Bi,Pb-based glasses using the modified Kissinger equation [16] including the numerical factors,

$$\ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mE_a}{RT_p} + \text{const.} \qquad (1)$$

where α is the heating rate, T_p the crystallization peak temperature, R the gas constant, and n and m numerical factors which depend on the crystallization mechanism. The values of n and m for various crystallization mechanisms are summarized elsewhere [16,17,19].

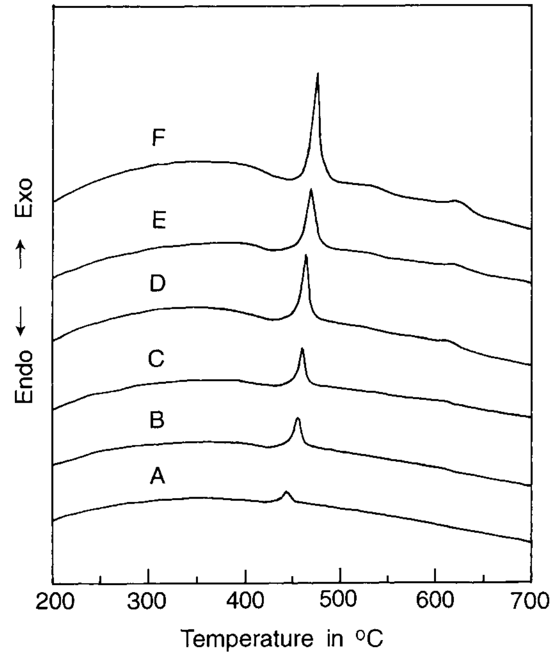

Fig. 5. DTA curves taken at various heating rates, α (K min^{-1}), in air for the as-quenched bulk samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ added glucose of 0.5 mass%. (A) α=2, (B) α=5, (C) α=7, (D) α=10, (E) α=15, (D) α=20.

The DTA patterns taken at various heating rates in air for the bulk $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glass with the glucose addition of 0.5 mass% and for the bulk $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$ glass are shown in Figs. 5 and 6, as examples. The values of T_p are obtained from these patterns as a function of heating rate. In order to obtain meaningful activation energies for crystal growth, information on crystal nucleation is a prerequisite. It is necessary to determine whether the number of crystal nuclei during heating varies or is constant. Fig. 7 shows the SEM photograph for the fracture surface of the bulk $Bi_{1.6}Pb_{0.4}Sr_2Ca_{0.5}Cu_3O_z$ sample heated to the temperature of crystallization onset at a heating rate of 15 K min^{-1} in air. It is seen that sphere-like particles with diameters of ca. 0.2–0.3 µm precipitate randomly in the interior of the sample. The morphology of spherical particles in other samples was the same, irrespective of heating rate, Cu^+/Cu^{2+} ratio and CaO content. Since the spherical

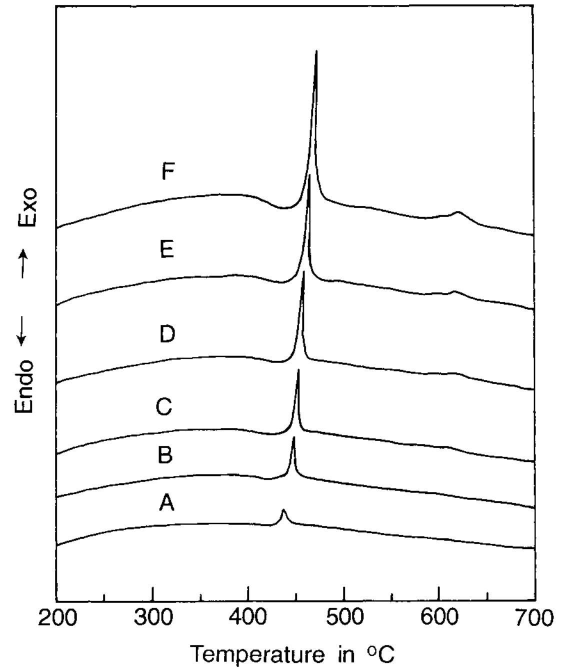

Fig. 6. DTA curves taken at various heating rates, α (K min^{-1}), in air for the as-quenched bulk samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$. (A) α=2, (B) α=5, (C) α=7, (D) α=10, (E) α=15, (D) α=20.

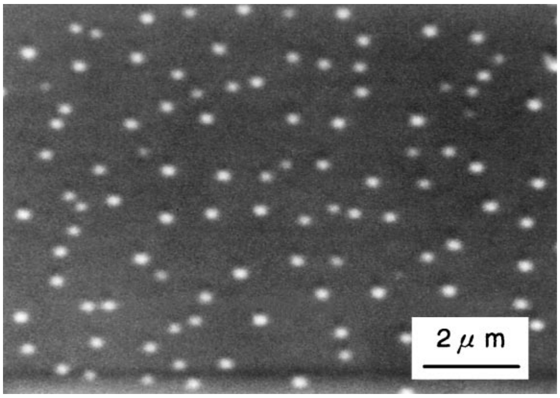

Fig. 7. SEM photograph of the fracture surface of bulk $Bi_{1.6}Pb_{0.4}Sr_2Ca_{0.5}Cu_3O_z$ glass obtained by heating to the crystallization onset temperature at a rate of 15 K min^{-1} in air.

crystallites are observed even in the interior of the samples, it is concluded that the crystal growth in Bi,Pb-based glasses occurs three-dimensionally. This growth dimension in Bi,Pb-based glasses is the same as that in $Bi_2Sr_2CaCu_2O_x$ glasses [15].

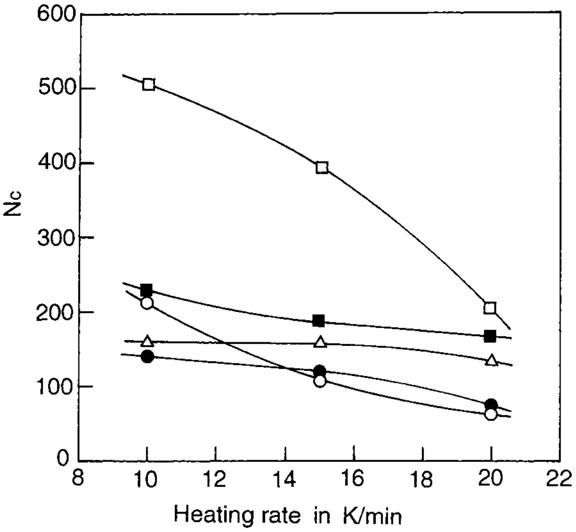

Fig. 8. Numbers of crystallites Nc in the area of 100 μm^2 of the fracture surface of bulk samples: (○), $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$; (●), $Bi_{1.6}Pb_{0.4}Sr_2Ca_{0.5}Cu_3O_z$; (△), $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ with glucose of two mass%. The data for $Bi_2Sr_2CaCu_2O_x$ glasses are taken from Ref. [15], i.e. (■) for R(Cu^+)=0.79 and (□) for R(Cu^+)=0.99.

The number of particles present in a 100 μm^2 area of fracture surface was counted. A mean value for five different areas in each sample was taken as a datum. The results for some samples are shown in Fig. 8. The data for the $Bi_2Sr_2CaCu_2O_x$ glass are also shown in Fig. 8 [15]. In all the samples, the number of crystalline particles in 100 μm^2 at the heating rates of 10–20 K min^{-1} is around 150. In all the samples, except $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$ glass, the number of crystallites are almost constant, irrespective of the heating rate. This means that the number of crystal nuclei does not vary with the heating rate. On the other hand, only in $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$ glass, the number of spherical crystallites decreases slightly with increasing heating rate, and thus there is a weak dependence of heating rate on the number of crystal nuclei. From the results shown in Figs. 7 and 8, it is concluded that the values of numerical parameters, depending on the crystallization mechanism, are n=3 and m=3 for Bi,Pb-based glasses with different copper valence states and different Ca contents.

The activation energy for crystal growth were evaluated using Eq. (1). The plots of $\ln(\alpha^n/T_p^2)$ against m/T_p for some samples are shown in Figs. 9 and 10.

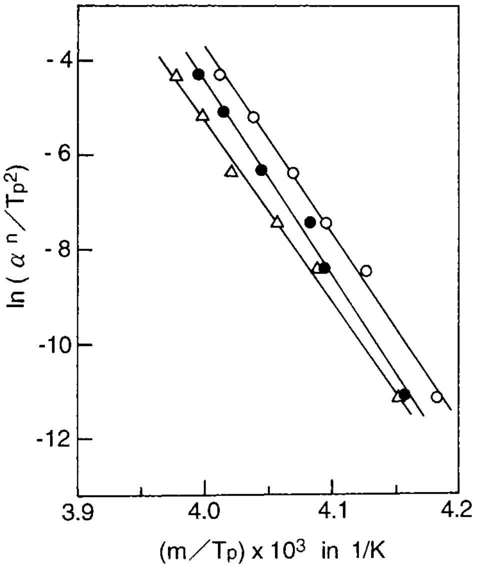

Fig. 9. Plots of $\ln(\alpha^n/T_p^2)$ against m/T_p for the as-quenched bulk samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ added glucose of X mass%. (○) X=1.0; (●), X=2.0. (△) X=3.0.

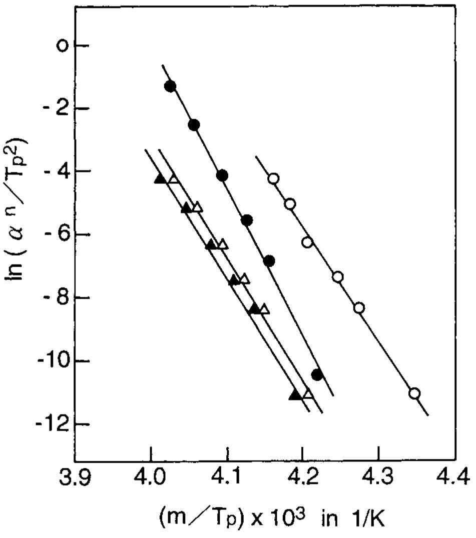

Fig. 10. Plots of $\ln(\alpha^n/T_p^2)$ against m/T_p for the as-quenched bulk samples of $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$. (○) x=0.5; (●) x=1.0; (△) x=1.5; (▲) x=2.0.

Table 2
Activation energies, E_a, for initial crystal growth of bulk Bi,Pb-based glasses evaluated by using the modified Kissinger equation

Sample	E_a (kJ mol^{-1})
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ added glucose of X mass%	
X=0 (n=m=3)	317
X=1.0 (n=m=3)	328
X=1.5 (n=m=3)	324
X=2.0 (n=m=3)	345
X=3.0 (n=m=3)	315
$Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$	
x=0.5 (n=m=3)	299
x=1.0 (n=4, m=3)	383
(n=m=3)	287
x=1.5 (n=m=3)	323

The values of E_a, evaluated by using linear least-squares fittings, are summarized in Table 2. In the $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$ glass, the activation energy was evaluated for two cases, namely n=m=3 and n=4, m=3, because the number of spherical crystallites changes slightly with the heating rate. Since the first crystalline phase in Bi,Pb-based glasses is the 2201 phases, the values of E_a obtained in the present study correspond to the activation energy for the crystal growth of the $Bi_2Sr_2CuO_x$ phase containing no Cu^+ and Ca^{2+}. It is seen that the values of E_a in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses with different glucose contents are around 320 kJ mol^{-1}, apparently irrespective of the copper valence state. Compared with the activation energy of Bi-based glasses containing neither Pb and nor CaO precipitation (Table 1), it seems that the activation energies of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2$-Cu_3O_y glasses with CaO crystallites are small. It is considered that CaO crystallites, present in the interior of the glasses, might lower the activation energy of the crystal growth of the $Bi_2Sr_2CuO_x$ phase.

In the case of $Bi_{1.6}Pb_{0.4}Sr_2Ca_xCu_3O_z$ glasses, the sample with x=1.5 containing CaO crystallites (Fig. 3) has E_a=323 kJ mol^{-1}, which is similar to those of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ glasses with CaO crystallites. As seen in Table 2, the value of the activation energy of the glass with x=1.0 depends strongly on the numerical parameters n and m. Considering the value of E_a=299 kJ mol^{-1} for the glass with x=0.5 and the small change in the number of crystallites with changing heating rates (Fig. 3), the numerical parameters n=m=3 might be more reasonable than n=4 and m=3. If we take the parameters n=m=3, the value of E_a=287 kJ mol^{-1} is obtained. Since $Bi_2Sr_2CuO_x$ crystals do not contain Ca element,

Table 3
Activation energies, E_a, for initial crystal growth of various glasses evaluated by nonisothermal DTA or DSC experiments

Glass	E_a (kJ mol^{-1})	Ref.
Li_2O–$2SiO_2$	267	[16]
Na_2O–CaO–$3SiO_2$	370	[20]
2MgO–$2Al_2O_3$–$5SiO_2$	640	[21]
BaO–Al_2O_3–$2SiO_2$	565	[22]
2CaO–Al_2O_3–SiO_2	740	[23]
48BaO–$48B_2O_3$–$4SiO_2$	716	[24]
$30Li_2O$–$70TeO_2$	423	[25]
$16.7Na_2O$–$83.3TeO_2$	$\sim$280	[26]
$28.18TeO_2$–$71.82P_2O_5$	114	[27]
$62ZrF_4$–$33BaF_2$–$5LaF_3$	315	[17]
$36InF_3$–60(Ba,Sr,Zn)F_2–$4GaF_3$	259	[28]
$Bi_5Ge_{20}Se_{75}$	110	[29]

the lowering in E_a in the glasses with x=0.5 and 1.0 containing small amounts of Ca would be expected.

The known values of E_a for initial crystal growth of various glasses evaluated by nonisothermal DTA or DSC experiments (Kissinger, modified Kissinger or Ozawa equations) are presented in Table 3 [16,17,20–29]. It is seen that the values of E_a of aluminosilicate or borosilicate glasses containing no alkali metal ions are large, maybe due to rigid glass structure. The values of E_a of Bi,Pb-based glasses given in Table 2 are very close to those of tellurite glasses such as $16.7Na_2O$–$83.3TeO_2$ and fluoride glasses such as $62ZrF_4$–$33BaF_2$–$5LaF_3$. According to the strong and fragile concept proposed by Angell [30], TeO_2-based and fluoride glasses belong to the category of the fragile glass-forming systems [31–33]. That is, in these glasses a rapid breakdown of their configurational structure occurs with increasing temperatures ($>T_g$). In such glasses, it is expected that atomic rearrangements, i.e. diffusions of ions, to form crystalline phase in fragile glass-forming systems would be easy. At this moment, we have no data on viscosity of Bi,Pb-based glasses, and such data will be necessary to understand the physical meaning of the activation energy for crystal growth more clearly.

3.3. Superconducting properties of crystallized glasses

Although the purpose of the present study is not to examine superconducting properties of heat-treated samples, i.e. superconducting glass-ceramics, we checked the formation of the high-T_c phase, i.e. $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$, and the temperature dependence of electrical resistivity. The XRD patterns for some samples obtained by heat-treatment at 850°C for 48 h in air are shown in Fig. 11. It is known that 850°C is one of the optimum heat-treatment temperatures for the formation of the high-T_c phase [7]. It is seen that the intensity of the peaks attributable to the high-T_c phase in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ sample with glucose addition of one mass% is large in comparison with the sample with no glucose addition. It was found that the peak intensities for both, the low-T_c phase and the high-T_c phase in the sample with glucose addition of three mass% are weak (not shown in Fig. 11). Therefore, an addition of a large amount of glucose in the glass-preparation process is not adequate for the formation of the high-T_c phase. The formation of the high-T_c phase was not detected in the $Bi_{1.6}Pb_{0.4}Sr_2$-

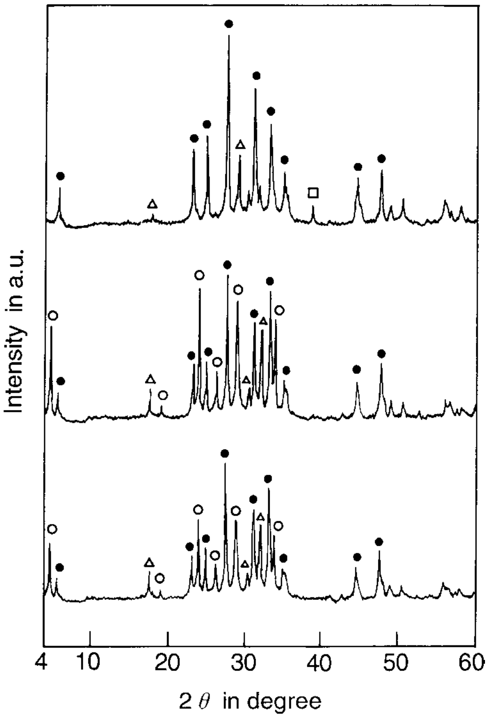

Fig. 11. XRD patterns for the heat-treated (850°C, 48 h in air) samples. (A) $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ with no glucose addition, (B) $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ with glucose addition of one mass%, (C) $Bi_{1.6}Pb_{0.4}Sr_2Ca_1Cu_3O_z$; (●) $Bi_2Sr_2CaCu_2O_x$ phase; (○) $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ phase. (△) Pb-compound, and (□) CuO.

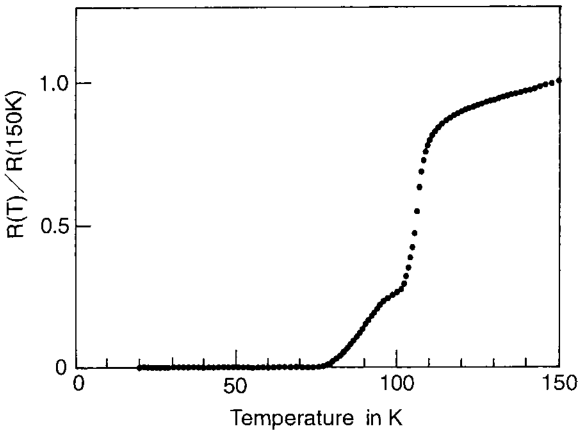

Fig. 12. Temperature dependence of resistivity for the heat-treated (850°C, 48 h, in air) sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ with glucose addition of one mass%.

$Ca_xCu_3O_z$ samples with $y=0$, 0.5 and 1.0. In the sample with $y=1.5$, the high-T_c phase was formed. The present study strongly suggests that it is extremely difficult to improve both, the glass-forming ability and the formation of the high-T_c phase in the Bi,Pb-based system. The temperature dependence of resistivity for the heat-treated (850°C, 48 h) sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_y$ with glucose addition of one mass% is shown in Fig. 12, as an example. Similar results were obtained in other samples with different glucose additions. The results shown in Fig. 12 indicate that a prolonged heat-treatment will be necessary to obtain Bi,Pb-based superconducting glass-ceramics with T_c >100 K, even in the samples with glucose addition.

4. Conclusions

The crystallization kinetics of various Bi,Pb-based superconducting precursor glasses with different copper valence states and with different Ca contents were examined by using differential thermal analysis. The relation between the heating rate and the crystallization peak temperature obtained from DTA patterns was analyzed using the modified Kissinger equation. The activation energies for crystallization, E_a, are in the range from 287 to 345 kJ mol^{-1}. Since the number of crystal nuclei is almost independent of the heating rate in all samples, it has been suggested that crystal nuclei are already present in the precursor glasses which were prepared by rapid quenching of melts. It was found that the values of E_a in Bi, Pb-based glasses are similar to those in TeO_2-based and fluoride glasses which are known as fragile glass-forming systems. Recently, nonlinear optical properties of Bi_2O_3-based glasses have been extensively studied [34,35]. But, information on the crystallization process of such optical functional Bi_2O_3-based glasses is totally lacking. It would be of interest to compare the crystallization mechanism and kinetics in various Bi_2O_3-based glasses, including superconducting precursor glasses.

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