Vitrification and Crystallization Processes of High- T_c Superconducting Oxides in the System Bi-Ca-Sr-Cu-O

Noboru TOHGE, Shinzo TSUBOI, Yoshinori AKAMATSU,
Masahiro TATSUMISAGO and Tsutomu MINAMI

(Department of Applied Chemistry, University of Osaka Prefecture, Mozu-Umemachi, Sakai-shi, Osaka 591)

Bi-Ca-Sr-Cu-O 系高温超伝導酸化物のガラス化および結晶化過程

峠 登・坪井真三・赤松佳則・辰巳砂昌弘・南 努
(大阪府立大学工学部応用化学科, 591 堺市百舌鳥梅町4丁)

High- T_c superconducting oxides in the pseudo-ternary system $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}\text{-CuO}$, $\text{CaO/SrO}=1$, were vitrified by a rapid-quenching technique, and the properties and crystallization process of the glasses obtained have been studied. The glassy samples were obtained in a relatively wide region including the compositions of interest, such as $\text{BiCaSrCu}_2\text{O}_x$ and $\text{Bi}_2\text{Ca}_x\text{Sr}_2\text{Cu}_3\text{O}_x$. The glass transition temperature in this system was found to be mainly dependent on the $\text{BiO}_{3/2}$ content, with a maximum of 390°C at around 20 mol% $\text{BiO}_{3/2}$. The glasses were crystallized by heat-treatment in various phases, depending on their composition. The crystallization of the glasses of proper compositions produced superconductors which have a critical temperature over 80 K.

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1. Introduction

High- T_c superconducting oxides in the system Bi-Ca-Sr-Cu-O, which has first been reported by Maeda et al.,¹⁾ have the following features, compared with the previously known system Y-Ba-Cu-O: (1) higher superconducting transition temperature, over 100 K, (2) higher chemical durability, and (3) containing no rare-earth elements. Moreover, the vitrification has recently been reported for several compositions in this system successively by Komatsu et al.,²⁾ the present authors,³⁾ and other researchers.⁴⁾⁻⁶⁾ The glass formation of these superconducting oxides has possibilities of fiber-drawing and casting into various shapes such as rods and plates, which are essential for the application of these superconducting materials.

For the vitrification in this system, various quenching techniques have been employed: iron-pressing,^{2),6)} single-roller spinning,⁴⁾ drawing into glass capillaries,⁵⁾ and twin-roller quenching used by the present authors.³⁾ One of the problems encountered when dealing with the melts in this system is a chemical reaction of the melts with a crucible, which results in the contamination of the glasses obtained. In this sense, the twin-roller quenching, combined with melting with a thermal image-furnace, has an advantage that the

starting materials can be melted without a crucible, in addition to a very high cooling rate (over 10^6 K/s).⁷⁾

In a previous paper, the composition $\text{BiCaSrCu}_2\text{O}_x$ was only vitrified.³⁾ The glass-forming region in this Bi-Ca-Sr-Cu-O system, the properties of the glasses obtained, and their crystallization behavior are very interesting from the viewpoint of glass science, as well as for the formation of superconducting ceramics with high performance. The present paper describes the glass-forming region, the properties of the glasses obtained, and their crystallization process in the pseudo-ternary system $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}\text{-CuO}$, $\text{CaO/SrO}=1$.

2. Experimental

The samples of different compositions in the pseudo-ternary system $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}\text{-CuO}$ were prepared in the same manner as that described previously.³⁾ The composition of the samples is represented by the mole ratio $\text{BiO}_{3/2}/(\text{CaO}\cdot\text{SrO})_{1/2}/\text{CuO}$ through the present paper. Special grade nitrates of each metal, $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, were used as starting materials. The mixtures of these raw materials of appropriate compositions were calcined for 20 h at tempera-

tures about 20°C below the melting temperature for each composition. The resultant oxides were ground and pressed into a rectangular rod (3×3×45 mm). The rod was then sintered for 2 h at the same temperature as the calcination process. The sintered rod was hung with Pt wire in a thermal image-furnace and melted from the end of the rod without contact with any vessel. The droplet of melt was rapidly quenched by a twin-roller rotating at about 3000 rpm.

It was judged from the X-ray diffraction patterns whether the quenched samples were glassy or crystalline. The thermal properties such as glass transition temperatures and crystallization temperatures were investigated by thermal analysis (DTA/TG). The X-ray diffraction ($\text{CuK}\alpha$) was also used to identify the crystalline phases deposited. The temperature dependence of resistivity of the crystallized samples was measured by the conventional four-probe method.

3. Results and discussion

3.1 Glass-forming region

In the present $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}-\text{CuO}$ system, glasses were obtained in a relatively wide region. Figure 1 shows the glass-forming region (a broken line) which was determined in this study. Double circles in the region mean that the samples are completely glassy to X-ray, as shown in Fig. 2 (c) for the sample 20/30/50. On the other hand, for the samples represented by single circles, weak crystalline peaks due to CaO are observed on halo patterns; typical patterns of these samples are shown in Fig. 2 (a) for the sample 20/40/40 (corresponding to the composition $\text{BiCaSrCu}_2\text{O}_x$), and in Fig. 2 (b) for the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$). These samples were also included in the present glass-forming region, since the glass transition temper-

ature was observed on the thermal analysis even for these samples, as described below. Solid circles indicate that the samples are crystalline; the crystalline phases deposited were CuO, CaO, Bi_2O_3 , CuBi_2O_4 , and/or other unknown compounds, depending on the compositions. A solid square means the sample was decomposed; the decomposition was implied by the observation of gas evolution during the melting. The presence of a relatively wide glass-forming region is very interesting from the viewpoint of glass science, because the present system includes no oxides

Fig. 2. X-ray diffraction patterns of melt-quenched samples; (a) 20/40/40 ($\text{BiCaSrCu}_2\text{O}_x$), (b) 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$), and (c) 20/30/50; x: CaO. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2}\cdot y(\text{CaO}\cdot\text{SrO})_{1/2}\cdot z\text{CuO}$ in mol percent.

Fig. 1. Glass-forming region of the pseudo-ternary system $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}-\text{CuO}$, $\text{CaO}/\text{SrO}=1$; samples (a) and (b) correspond to $\text{BiCaSrCu}_2\text{O}_x$ and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$, respectively.

Fig. 3. DTA and TG curves of the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$); the inset shows a part of DTA curve enlarged. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2}\cdot y(\text{CaO}\cdot\text{SrO})_{1/2}\cdot z\text{CuO}$, in mol percent.

so-called the "network former".

3.2 Thermal properties of the glasses

Typical DTA and TG curves for the glasses are shown in Fig. 3: the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) was taken as an example. In the DTA curve there is a sharp exothermic peak due to crystallization at 440°C , below which the glass transition temperature, T_g , is observable, as shown in an inset. The presence of T_g shows most part of this sample is glassy, though a very small amount of CaO was detected in the X-ray diffraction patterns (Fig. 2 (b)). The similar result has been already reported for the sample 20/40/40 ($\text{BiCaSrCu}_2\text{O}_x$), in which CaO was also observed.³⁾ The sharp exothermic peak is followed by several broad exothermic peaks up to 700°C . Over this temperature, there are no appreciable thermal changes except the endothermic peak due to melting at about 880°C . In the TG curve, there is a slight increase in weight in a temperature range of 400°C to 700°C ; the cause of this weight increase is not clear at the present stage.

Figure 4 shows the isotherms of T_g in the present glasses. It is seen that T_g depends mainly on the $\text{BiO}_{3/2}$ content and has a maximum of about 390°C at around 20 mol% $\text{BiO}_{3/2}$. It should be now noted that the glasses of the special compositions such as $\text{BiCaSrCu}_2\text{O}_x$ (a) and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$ (b) are located in a region of the highest T_g in this system. The above behavior of glass transition temperature should be discussed in relation to the glass structure, which is now under study.

3.3 Crystallization process

The X-ray diffraction patterns of the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) heat-treated at different temperatures for 4 h are shown in Fig. 5, as an example of the crystallization process of the glasses in the present system. For the sample

Fig. 4. Isotherms of glass transition temperature; samples (a) and (b) correspond to $\text{BiCaSrCu}_2\text{O}_x$ and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$, respectively.

heat-treated at 500°C , slightly higher than crystallization temperature T_x in DTA curve, crystalline peaks are already observable. As the heat-treatment temperature is increased, the intensity of these crystalline peaks is increased. Most of the crystalline peaks observed for the sample heat-treated at 860°C can be assigned to the low- T_c (80 K) phase (represented by open circles), with a small amount of unknown phase (solid circles).⁸⁾ The crystalline peaks of the samples heat-treated below this temperature are ascribable to the phases observed for the sample at 860°C , though the peaks become broader with decreasing heat-treatment temperature. From above findings it can be concluded that the low- T_c (80 K) superconducting phase deposits from the early stage of crystallization process and grows gra-

Fig. 5. X-ray diffraction patterns of the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) heat-treated at different temperatures for 4 h; ○ : low- T_c (80 K) phase; × : CaO, and ● : unknown phase. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2} \cdot y(\text{CaO} \cdot \text{SrO})_{1/2} \cdot z\text{CuO}$ in mol percent.

Fig. 6. X-ray diffraction patterns of the crystallized samples of different compositions ; (a) 20/40/40 ($\text{BiCaSrCu}_2\text{O}_x$), (b) 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$), and (c) 20/30/50, which were crystallized for 4 h at 850°, 860°, and 850°C, respectively ; $\circ$: low- T_c (80 K) phase ; $\star$: CuO, and $\bullet$, $\blacktriangledown$: unknown phases. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2} \cdot y(\text{CaO} \cdot \text{SrO})_{1/2} \cdot z\text{CuO}$ in mol percent.

dually with increasing heat-treatment temperature.

The X-ray diffraction patterns of the crystallized samples of different compositions are compared in Fig. 6 : sample 20/40/40 ($\text{BiCaSrCu}_2\text{O}_x$), (a), sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$), (b), and sample 20/30/50, (c), which were crystallized for 4 h at 850°, 860°, and 850°C, respectively. For the samples 20/40/40 and 22/44/34, the crystalline peaks are due to the low- T_c phase (represented by open circles) and unknown phase (solid circles). For the sample 20/30/50, however, CuO phase (stars) and other unknown phases (triangles), which is absent in the other two samples, are observed, in addition to the low- T_c phase and the unknown phase which is present on the other two samples. The deposition of CuO phase probably arises from higher CuO content than the other two samples.

Fig. 7. Temperature dependence of resistivity for the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) crystallized at 700°C and 860°C for 4 h. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2} \cdot y(\text{CaO} \cdot \text{SrO})_{1/2} \cdot z\text{CuO}$ in mol percent.

Fig. 8. Temperature dependence of resistivity for the samples 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$), and 20/30/50 crystallized for 4 h at 860° and 850°C, respectively. The notation $x/y/z$ represents the composition $x\text{BiO}_{3/2} \cdot y(\text{CaO} \cdot \text{SrO})_{1/2} \cdot z\text{CuO}$ in mol percent.

3.4 Superconducting characteristics

Figure 7 shows the temperature dependence of resistivity for the sample 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$), crystallized at different temperatures for 4 h. The resistivity of the sample heat-treated at 700°C increases with decreasing temperature, indicating that this sample is still a semiconductor. In contrast to this, the sample heat-treated at 860°C exhibits a metallic behavior and a lower resistivity at room temperature by several tenth than the sample heat-treated at 700°C. The resistivity of this sample begins to decrease sharply at around 90 K and finally becomes zero at 86 K. The above change of resistivity with the heat-treatment reflects the gradual growth of the superconducting phase, as shown in Fig. 5. The sample 20/40/40 ($\text{BiCaSrCu}_2\text{O}_x$) also exhibited the similar superconducting characteristics.

The temperature dependence of resistivity for the crystallized samples 22/44/34 ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) and 20/30/50 is compared in Fig. 8. For the sample 20/30/50 the onset temperature of superconducting transition shifts to lower temperature than that of the sample 22/44/34

($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$) and the resistivity does not show zero within the temperature range in the present study (above 77 K). This decrease in transition temperature probably results from the presence of the CuO phase (Fig. 6 (c)).

4. Summary

In a relatively wide region of the pseudo-ternary system $\text{BiO}_{3/2}-(\text{CaO}\cdot\text{SrO})_{1/2}-\text{CuO}$, $\text{CaO}/\text{SrO}=1$, glassy samples have been obtained by the rapid-quenching technique. The glass transition temperature in this system was found to be mainly dependent on the $\text{BiO}_{3/2}$ content, with a maximum of 390°C at around 20 mol % $\text{BiO}_{3/2}$. The crystallization of the glasses of proper compositions such as $\text{BiCaSrCu}_2\text{O}_x$ and $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$ produced superconductors consisting mainly of the low- T_c (80 K) phase; this superconducting phase grew gradually with increasing heat-treatment temperature. The critical temperature $T_c(\text{zero})$ was 86 K for $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x$, whereas it can be expected to be increased by optimizing the heat-treatment condi-

tions and/or using appropriate additives.

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