Non-Isothermal Crystallization Kinetics and Phase Transformation of Bi$_2$O$_3$-SiO$_2$ Glass-Ceramics

H. W. Guo $^{1,2*)}$, X. F. Wang $^{1,2}$, D. N. Gao $^2$

$^1$ School of Materials Science & Engineering, Shaanxi University of Science & Technology, Xi’an 710021, PR China

$^2$ Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry, Ministry of Education, Xi’an 710021, PR China

Abstract:
The Bi$_2$O$_3$-SiO$_2$ (BS) glass-ceramics were prepared by melt-quench technique, and the crystallization kinetics and phase transformation behavior were investigated in accordance with Kissinger and Johson-Mehl-Avrami equation, DSC, XRD and SEM. The results show that in the heat treatment process (or termed as re-crystallizing process) Bi$_5$SiO$_9$ and Bi$_4$Si$_3$O$_{12}$ crystals were found consequently. Respectively, the crystallization activation energies of the two crystals are $E_{p1}=14.8$kJ/mol and $E_{p2}=34.1$kJ/mol. And the average crystallization index of $n_1=1.73$ and $n_2=1.38$ suggested volume nucleation, one-dimensional growth and surface nucleation, one-dimensional growth from surface to the inside respectively. The meta-stable needle-like Bi$_5$SiO$_9$ crystals are easily to be transformed into stable prismatic Bi$_4$Si$_3$O$_{12}$ crystals. By quenching the melt and hold in 850 °C for 1h, the homogenous single Bi$_4$Si$_3$O$_{12}$ crystals were found in the polycrystalline phase of the BS glass-ceramics system.

Keywords: Differential scanning calorimetric; Glass-ceramics; Non-isothermal;

1. Introduction

Glass-ceramics derive particular interest for several end applications, such as thermal, chemical, biological and dielectric ones, because these systems provide great possibilities to manipulate their properties, such as transparency, strength, resistance to abrasion, coefficient of thermal expansion. These properties can be achieved by proper selection of the composition which can control the extent of crystallization, crystal morphology, crystal size and aspect ratio. The ease of fabrication techniques in conjunction with lower production cost offer additional advantages [1].

Bi$_2$O$_3$-SiO$_2$ glass-ceramics are recently known as a new heavy-metallic oxide optical glassy material for their superior infra red transmission, high refractive index, high non-linearity index, high mechanical strength and chemical durability, and fast response to optical signals. And reasonably BS system glass-ceramics have the potential to be widely used in optical communication systems as optical switch and optical signal exchanger [2, 3].

Zhereb et al [4-6] have thoroughly investigated in the glass form zone, melt cooling behavior, and the optical properties of BS system glass-ceramics. From the author’s previous study, the crystallizing characteristic of BS system is complicated. Processed under different
temperatures, Bi$_2$SiO$_5$, Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$, Bi$_2$O$_3$ crystals can be precipitated. The research demonstrates that Bi$_2$SiO$_5$ is a meta-stable phase in BS system and the precipitation of Bi$_4$Si$_3$O$_{12}$ crystals are usually accompanied with meta-stable Bi$_2$SiO$_5$ crystals [7, 8]. To eliminate the effect of meta-stable Bi$_2$SiO$_5$ crystals earned more interest in recent studies [9-11]. However, an extensive literature search shows that the details of the phase transformation and crystallization kinetics of the BS glass system have not been elaborated.

In the present paper, the crystallization kinetics and phase transformation of the BS glass-ceramics have been studied by differential scanning calorimetric (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The purpose of this investigation is to (1) estimate the crystallization kinetics and growth mechanism of Bi$_2$O$_3$-SiO$_2$ glass ceramic, (2) study the morphology of Bi$_2$O$_3$-SiO$_2$ glass ceramic during crystallization and phase transformation, (3) study the crystallizing mechanism of homogeneous single Bi$_4$Si$_3$O$_{12}$ crystals.

2. Experimental procedure

2.1. Preparation of glass sample

The glass with nominal composition Bi$_2$O$_3$: SiO$_2$=2:3 (mol) was made from the powders of technical grade Bi$_2$O$_3$ and SiO$_2$ (purity>99.9%), Homogeneous mixtures of batches (~200g), obtained by ball milling for 2h in acetone medium, were melted in a platinum crucible at 1150°C in an electric furnace for 2, in air. After homogenizing, the melt was cast onto a hot stainless steel plate at 400°C, and transferred to an annealing furnace held at 400°C for 3h. Finally, a clear, transparent, colorless glass was obtained.

2.2. Differential scanning calorimeter (DSC)

Differential scanning calorimeter (DSC) with a 200mg sample (67.48µm in size) at various heating rates from 10 to 20K/min in air was conducted with a NETZSCH STA - 409. Powdered Al$_2$O$_3$ was used as a reference material. During all runs the sample chamber was purged with dry nitrogen. The uncertainty in glass transition temperature is ±1°C.

2.3. X-ray diffraction (XRD)

The crystalline phases were identified by XRD with CuKα radiation and a Ni filter operated at 40kV, 20mA and a scanning rate of 0.25°/min (Model Rad & A, Rigaku, Tokyo, Japan).

2.4. Environmental scanning electron microscopy (ESEM)

The micro-structural characterization of BS glass-ceramic is investigated by Quanta 200 ESEM produced by Philips- FEI Corporation. The samples were etched with a solution of give parts HF, two parts HCl and 93 parts H$_2$O, and coated with a thin gold film.
3. Results and discussion
3.1. Crystallization analysis

Fig. 1. DSC curves of different heating rates

$T_\text{g}$ is the glass transition temperature; $T_{p1}$ is the crystallization exothermic peak of the first precipitates; $T_{p2}$ is the crystallization exothermic peak of the second precipitates.

The DSC curves of the as-quenched BS glass-ceramics samples at a heating rate of 10, 15, 20 °C/min are shown in Fig.1. Fig.1 reveals two apparent crystallization exothermic peaks, $T_\text{g}$ is the glass transition temperature and $T_{p1}$ and $T_{p2}$ are the crystallization exothermic peaks of the 1$^{st}$ precipitates and the 2$^{nd}$ precipitates in the heating of BS glass-ceramics. In accordance of previous work [7, 8], using the moderate DSC heating rate of 15 °C/min, $484$ °C is the glass transition temperature and the two identical crystallization exothermic peaks were at $632$ °C and $818$ °C. After annealing, the specimens were cut into rectangles of 50mm×10 mm×10 mm and heated at a rate of 5 °C/min to the crystallization temperature for 2h. Finally, the crystallized sample was cooled to room temperature at a rate of 2 °C/min. The crystalline phases were identified by XRD with Cu$\kappa$ radiation.

Fig.2 is the XRD pattern of the sample. In p0, the BS glasses, no characteristic peaks were found and the homogenous non-crystalline phase was proved. Comparison to typical pattern card # of 36-0287, 33-0215 and 27-0051, the main phase of crystallization peak $T_{p1}$ is $\text{Bi}_2\text{SiO}_5$, and the main phase of crystallization peak $T_{p2}$ is $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (small amount of $\text{Bi}_2\text{O}_3$ crystals).

Fig. 2. XRD patterns of BS glass-ceramics under different heating rates
p0: BS glasses; p1: 632 °C, 2h; p2: 818 °C, 2h
3.2. Non-isothermal analysis

The kinetic parameters of the glass-crystallization transformation were determined under non-isothermal conditions applying Kissinger and Ozawa equation\[12-18\]. The temperature of crystallization exothermic peak \( T_p \) can be a function of the heating rate of DSC \( \alpha \). Moderate heating rate offers enough transformation time and lower \( T_p \), reflected in the curve as a gentle curve. As a contrast, at high heating rate of DSC the transformation is delayed and shows a sharp slope (high instantaneous transformation rate) in the curve \[12\]. Commonly, easy transformation to glasses shows a good stability. Based on these characters and by applying the Johnson-Mehl-Avrami (JMA) equation, DSC can be applicable to the analysis of glass-crystallization kinetics and the calculation of kinetic parameter \[12-14\]. And the kinetic parameters are significantly important to the evaluation of glass stability and crystallizing rate.

Under non-isothermal condition \[15-24\], the solid-state transformation kinetics equation is:

\[
\frac{dx}{dt} = K(1-x)^n \quad (1)
\]

\( n \) represents the reaction order, also the crystallization index; \( x \) is the phase transition point; \( K \) is the crystallization kinetics parameter.

Kissinger proved \( K \) obeys the Arrenhius equation \[17-20, 24\]:

\[
K = K_0 \exp \left( -\frac{E}{RT} \right) \quad (2)
\]

\( K_0 \) is the effective frequency factor; \( E \) is the crystallization activation energy; \( R \) is the gas constant; \( T \) represents Kelvin.

The exothermic peak temperatures \( (T_p) \) of the DSC curves at various heating rates for BS glasses are listed in Fig.1. The following relation is derived from the Johnson-Mehl-Avrami (JMA) equation\[1,13-14\]:

\[
\ln \left( \frac{T_p^2}{\alpha} \right) = \frac{E}{RT_p} + \ln \left( \frac{E}{R} \right) - \ln K_0 \quad (3)
\]

Where \( \alpha \) is the heating rate, \( E \) is the apparent activation energy for crystallization and \( R \) denotes the gas constant. Straight line is obtained in the plotting of \( \ln(T_p^2/\alpha) \) versus \( 1/T_p \), as illustrated in our previous paper \[25\]. The apparent activation energy is calculated from the slope of these straight lines, and is given in Fig.3. \( E, K_0 \), and \( K \) can be calculated respectively.

Crystallization process will be induced with certain amount of activation energy to overcome the energy barrier of rearrangement. With the low energy barrier, the less energy is required to crystallizing behavior and shows a higher probability to crystallize. From the activation energy evaluation perspective, the activation energy can reflect the capacity to crystallize \[22-24\]. From Fig.3, the activation energies to the precipitation of the two kind of crystals are \( E_{p1}=14.8kJ/mol \) and \( E_{p2}=34.1kJ/mol \) respectively. Comparison of the activation energies goes to that in the 1st crystallization exothermic peak the \( Bi_2SiO_5 \) crystals are easy to precipitation, while in the 2nd peak the crystallization capacity of \( Bi_2Si_3O_12 \) is relatively small.
It is well known that the crystal nucleation rate in glasses reaches its maximum at a temperature somewhat higher than the glass transition temperature, and then decreases rapidly with increasing temperature, while the crystal growth rate reaches its maximum at a temperature much higher than the temperature at which the rate of nucleation is the highest [1]. Hence, as the glass is heated at constant rate, \(dT/dt=\alpha\), there are two types of crystallization which take place in glasses, based on bulk and surface nucleation[26-29]. Moo-Chin Wang [1] and S.W.Yung [30] derived the crystallization index equation with E as constant:

\[
\ln \Delta T = -\frac{nE}{RT_p} + C
\]  

(4)

\(T_p\) is temperature respective to a point in the crystallization exothermic peak curve, \(\Delta T\) is the temperature difference between the sample and the comparing sample, and C is a constant [1]. Plot \(1/T_p\) as the function of \(\ln \Delta T\), a linear with slope of \(-nE/R\) is derived. According to the E, the crystallization index can be calculated from Eq.(4) shown as Fig.4 (a) and (b).

Crystallization activation energy and crystallization index are considered as the most important parameters to characterize the crystallization behavior. The activation energy, or termed as the energy barrier, can reflect the complexity of crystallization. The crystallization index show the nucleating and growing pattern of the crystals [1,21]. Yinnon et al. [31-35] have shown that \(n\) may be 4, 3, 2, or 1, which are related to different glass-crystal
transformation mechanism $s=4$, volume nucleation, three-dimensional growth; $n=3$, volume nucleation, two-dimensional growth, $n=2$, volume nucleation, one-dimensional growth; $n=1$, surface nucleation, one-dimensional growth from surface to the inside. Tab. I is the crystallization index of BS glasses under different heating rates. Creveals the average crystallization indexes of the two types of crystals are $n_1=1.73$ and $n_2=1.38$ respectively, according to solid state transformation theory, the crystals precipitated are volume nucleation, grow in one-dimension and surface nucleation, one-dimensional growth from surface to the inside respectively [32-35].

Tab. I Crystallization index of BS glass-ceramics under different heating rates

<table>
<thead>
<tr>
<th>Heating rate/ (K.min$^{-1}$)</th>
<th>$n_1$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.83</td>
<td>1.38</td>
</tr>
<tr>
<td>15</td>
<td>1.62</td>
<td>1.42</td>
</tr>
<tr>
<td>20</td>
<td>1.73</td>
<td>1.33</td>
</tr>
<tr>
<td>Average crystallization index</td>
<td>1.73</td>
<td>1.38</td>
</tr>
</tbody>
</table>

3.3 Morphology of Crystals

Fei.Y.D et al [3-5] found that the meta-stable were precipitated in the Bi$_2$O$_3$-SiO$_2$ system. Using Fig.5, the XRD patterns held at 650 °C and 850 °C for 6h, with comparison to the typical PDF card the precipitated crystals can be determined. Comparing to PDF card # 36-0287 and 33-0215, the main phase transformation (650 °C, 6h) follows the equation form meta-stable Bi$_2$SiO$_3$ to stable Bi$_4$Si$_3$O$_{12}$:

$$
3 \text{Bi}_2\text{SiO}_3 \rightarrow \text{Bi}_4\text{Si}_3\text{O}_{12} + \text{Bi}_2\text{O}_3
$$

Fig.6 (a) and (b) are the surface SEM micrographs of the sample. Needle-like Bi$_4$Si$_3$O$_{12}$ crystals were precipitated on the surface, and with the low temperature and high viscosity the crystals cannot grow sufficiently. Fig.6 (c) and (d) are the cross-sectional SEM micrographs of the sample, no inerratic crystals were found. Fig.6 (e) and (f) are the cross-sectional SEM micrographs of the sample held at 850 °C for 6h, prismatic Bi$_4$Si$_3$O$_{12}$ homogenous distributed polycrystalline phase (the length varies from 3 to 5 µm). Erratic crystals were also found, because of high temperature induced Eq.(5).
Fig. 6. SEM micrographs of the BS glass-ceramics samples for different heat treatment: (a) surface 650 °C, 6h; (b), (c) cross-section 650 °C, 6h; (d) Surface 850 °C, 6h; (e), (f) cross-section 850 °C, 6h.

The crystallization behavior in Bi₂O₃-SiO₂ system and the meta-stable Bi₂SiO₅ phase balance follows the experimental result of Zhereb [4, 5]. Based on the density and viscosity test of BS system melt, the liquids condition of the melt system has been put into 3 categories: low temperature zone A, moderate temperature zone B, and high temperature zone C. And the crystallization temperature and the formed phase structure have great dependency on the cooling temperature started zone. At B zone, the melt is basically constituted of [SiO₄] tetrahedron chains and [Bi₂O₂] layers. The over under cooling of f meta-stable crystallization were caused by the massive heat to decompose of the [SiO₄] tetrahedron. SiO₂ rich melt structure is similar to the meta-stable Bi₄[O₄][Si₂O₆] of Bi₂SiO₅, so easier crystallization of the Bi₂SiO₅ and the dropsied texture were found ([SiO₄] tetrahedron was separated by [Bi₂O₂] layers. δ phase (δ- Bi₂O₃ and SiO₂ solid solution) were formed by the transformed [Bi₂O₅] when oxygen atom occupied face center of cubic crystal lattice. So high purity Bi₄Si₃O₁₂ polycrystalline phase cannot be seen from normal heat treatment, but in the sample massive Bi₂O₃ phase were found as suggested by the crystalline phase transformation in Eq.(5).

Fig. 7 illustrates the room temperature XRD patterns recorded for the powders (Bi₂O₃:SiO₂=2:3, melt at 1200 °C for 1h, held at 900 °C for 4h) using CuKα radiation. All peaks can be indexed with the space group I₄₃d and unit cell parameters a=10.27 Å, V =1083.21 Å³ and Z= 4, refined by the least-squares method, and confirmed the powder to be pure phase.

Fig. 7. Polycrystalline Bi₄Si₃O₁₂ XRD pattern (900°C, 4h)
Previous study [8] found that when heated to 850 °C the materials have been densified with the presence of Bi$_4$Si$_3$O$_{12}$ crystals. Continuing the sintering process, solid state reaction is surveyed and Bi$_4$Si$_3$O$_{12}$ crystal particles are sintered. Later, abnormal growth of Bi$_4$Si$_3$O$_{12}$ crystals and the regular size of other crystals were observed, which are caused by the chemical instability of microscopic structure. In the abnormal growth, grain boundaries escaped from the drag of vacancies and the solvent and have freely directional motion. The kinetics of the growth cannot follow the G$^3$-t relationship, while the regular growth probably follows the G-t relationship [7,8]. Kinetics of the Bi$_4$Si$_3$O$_{12}$ cannot be simply generalized as a kinetic relationship, because small proportion of the Bi$_4$Si$_3$O$_{12}$ crystals transited from continuous growth to non-continuous growth. Suggested by several publications, the abnormal growth of Bi$_4$Si$_3$O$_{12}$ crystals is cited as non-continuous growth, see Fig.8.

![Fig. 8. SEM micrographs of the samples (Surface 900C, 4h)](image)

From Fig.8, the system surface is characterized by little vacancies, densified system structure, and cubic crystals. In accordance with Fig.7, the low viscosity of the melt and the long and high heating induced the sufficient propagation of Bi$_4$Si$_3$O$_{12}$ and the single crystal cleavage structure. Commonly, high energy in the boundary can cause the growth of crystals in order to lower the grain boundary interface energy. Approaching the eutectic point, liquid present at the system, probably with several atomic layers covered the crystals. In the densification process, the porosity is lowered, more liquid layers covered the crystals, and the high energy solid-solid interfaces were replaced by low energy liquid-solid interfaces [4-8]. Hence, the driving force of crystal growth is greatly lowered and the abnormal growth is found in the system. The prepared Bi$_4$Si$_3$O$_{12}$ crystals can be used as sputtering target materials for Bi$_4$Si$_3$O$_{12}$ thin films and the high purity Bi$_4$Si$_3$O$_{12}$ bulk crystals [5-8].

4. Conclusions

The Bi$_2$O$_3$-SiO$_2$ system were prepared by melt-quench technique, in the heat treatment process two main crystalline phases Bi$_2$SiO$_5$ and Bi$_4$Si$_3$O$_{12}$ were precipitated with two apparent crystallization exothermic peak in the DSC curve. The crystallizations of $E_p$=14.8kJ/mol, $E_p$=34.1kJ/mol were calculated by Kissinger equation, with the crystallization index of $n_1$=1.73 and $n_2$=1.38 respectively (volume nucleation, one-dimensional growth). Low T precipitated needle-like Bi$_2$SiO$_5$ are easily transformed into stable prismatic Bi$_4$Si$_3$O$_{12}$. Cooling the high T melt into 900 °C for 4h, the single Bi$_4$Si$_3$O$_{12}$ crystals were found in the polycrystalline phase.

Acknowledgements

The authors gratefully acknowledge the financial support of the Natural Science
Foundation of China (No.50972087) and Scientific Technology Research Project of Shaanxi Province (No.2010JM6019).

References

18. Ozawa T, Therm Anal.12(970)301.

Садржај: Bi$_2$O$_3$-SiO$_2$ (BS) керамика је припремљена техником топљење-квенчовање, а кинетика кристализације и фазних трансформација праћена је методама рендгенске
дифракције, СЕМ и ДСЦ и израчунавана једначинама Кисинђера и Јонсон-Мел-Аврамија. Резултати показују да се током зглобања кристали Bi₂SiO₅ и Bi₄Si₃O₁₂ појављују један за другим. Енергије активације износе $E_{p1}=14,8$ kJ/mol и $E_{p2}=34,1$ kJ/mol, истим редом. Средњи индекс кристализације $n_1=1,73$ и $n_2=1,38$ указује на запреминску нуклеацију, једнодимензионални раст и површинску нуклеацију, једнодимензионални раст од површине ка унутрашњости, истим редом. Метастабилни игличасти кристали Bi₂SiO₅ лако прелазе у стабилне призматичне кристале Bi₄Si₃O₁₂. Квенчовање истопљене фазе и држање на 850°C 1h води до стварања хомогеног једнофазног кристала Bi₄Si₃O₁₂ унутар поликристалне фазе BS система.

**Кључне речи:** Диференцијална скањујућа калориметрија; стакло; кинетика кристализације