

Phase separation and crystallization of La₂O₃ doped ZnO-B₂O₃-SiO₂ glass

WANG, M., FANG, L., LI, M., LIU, Z., HU, Y., ZHANG, X., DENG, Wei and DONGOL, R.

Available from Sheffield Hallam University Research Archive (SHURA) at:

<http://shura.shu.ac.uk/24387/>

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

Published version

WANG, M., FANG, L., LI, M., LIU, Z., HU, Y., ZHANG, X., DENG, Wei and DONGOL, R. (2019). Phase separation and crystallization of La₂O₃ doped ZnO-B₂O₃-SiO₂ glass. *Journal of Rare Earths*.

Copyright and re-use policy

See <http://shura.shu.ac.uk/information.html>

Manuscript Details

Manuscript number	JRE_2018_425_R1
Title	Phase separation and crystallization of La ₂ O ₃ doped ZnO-B ₂ O ₃ -SiO ₂ glass
Article type	Full Length Article

Abstract

In order to investigate the effect of the La₂O₃ on the phase separation and crystallization of ZnO-B₂O₃-SiO₂ glass, after occur of the phase separation and crystallization of glasses by heat treatment, the microstructure morphology and distribution of elements in the different sample areas were characterized by the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS); the non-isothermal crystallization kinetics of the glass samples was studied by using a differential scanning calorimeter (DSC) and the precipitated crystals of crystallized glass were determined by the X-ray diffraction (XRD). The results suggest that the phase separation and crystallization of 60ZnO-30B₂O₃-10SiO₂ glass are occurred at glass surface, and the incorporation of small amount (< 4 mol%) of La₂O₃ significantly inhibits the glass phase separation and consequently improves the thermal stability of glass. Doping of La₂O₃ accelerates the glass crystallization at the elevate temperature (660°C), making the depth of crystal layer thicker and diffraction intensity in XRD patterns stronger. However, due to the precipitation of several crystals occur simultaneously when La₂O₃ doping amount is 4mol%, crystallization of the 60ZnO-30B₂O₃-10SiO₂ glass is obviously depressed, the crystallization activation energy E_c and the relative crystallinity X_c of the glass reaches the maximum and the minimum values respectively. Although transition from one-dimensional growth of crystals to two-dimensional growth of crystals results from La₂O₃ addition, the one-dimensional growth of crystals remains dominant in crystallization process. This work can provide some useful information for preparing glass ceramics with nano-crystals precipitated in the glass surface.

Keywords	zinc borosilicate glass; La ₂ O ₃ ; phase separation; crystallization
Manuscript category	Rare earth applications
Corresponding Author	Mitang Wang
Corresponding Author's Institution	Inner Mongolia University of Science and Technology
Order of Authors	Mitang Wang, Long Fang, Mei Li, Zhaogang Liu, Yanhong Hu, Xiaowei Zhang, Wei Deng, Ruhil Dongol
Suggested reviewers	Peijing Tian, Hiroshi Kobayashi

Submission Files Included in this PDF

File Name [File Type]

cover letter.doc [Cover Letter]

Response to editors and reviewers.docx [Response to Reviewers]

TOC.docx [Graphical Abstract]

425.docx [Manuscript File]

Declarations of interest.docx [Supporting File]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Dear Editor,

We submit our manuscript entitled "**Phase separation and crystallization of La₂O₃ doped ZnO-B₂O₃-SiO₂ glass**" to **Journal of Rare Earths** for publication. This paper has not been submitted to any other journals for publication.

This work is a part of our ongoing project to investigate the thermal stability, structure and properties of 60ZnO30B₂O₃10SiO₂ glasses doped with La₂O₃/Y₂O₃. In this work, glass crystallization kinetics, phase separation and crystallization behavior of La₂O₃ doped 60ZnO-30B₂O₃-10SiO₂ glass with high content of ZnO up to 60 mol% are firstly studied by our group. The results are helpful for preparing structural and thermal stable zinc borosilicate glass with high content of ZnO, and the phase separation phenomenon and crystallization behavior occurred at glass surface provide some useful information for preparing glass ceramics with micro- or nano-crystals in surface, and the results may interest the readers of Journal of Rare Earths.

All authors have seen the manuscript and approved to submit to your journal.

Thank you very much for your attention and consideration.

Sincerely yours,

Mitang Wang

Professor of inorganic nonmetallic materials

Key Laboratory of Green Extraction & Efficient Utilization of Light Rare-Earth Resources, Ministry of Education, Baotou 014010, China.

Email: btwmt@126.com

Fax: 086-0472-5951572

REPLY TO THE REVIEWERS

Journal of Rare Earths

Ref: JRE_2018_425

Title: Phase separation and crystallization of La_2O_3 doped $\text{ZnO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ glass

Authors: Mitang Wang, Long Fang, Mei Li, Zhaogang Liu, Yanhong Hu, Xiaowei Zhang, Wei Deng, Ruhil Dongol

1) 对于审稿意见 "The authors should focus on the elucidation of the underlying mechanism for the thickness-dependent phase separation and crystallization behavior. Why does it occur near surface instead of across the bulk?" 作者并没有在文章中进行解释修改

答：该审稿意见已在文章的 3.2 和 3.4 节中进行了描述。

2) 请作者引用 1-2 篇本刊 17-18 年已发表文章，关于玻璃的文章本刊应该发表了很多，本文没有一篇引用

答：已引用 3 篇贵刊出版的与玻璃相关文献。

3) 参考文献，作者如果超过 6 个，请保留 6 个,然后用 et al 表示.

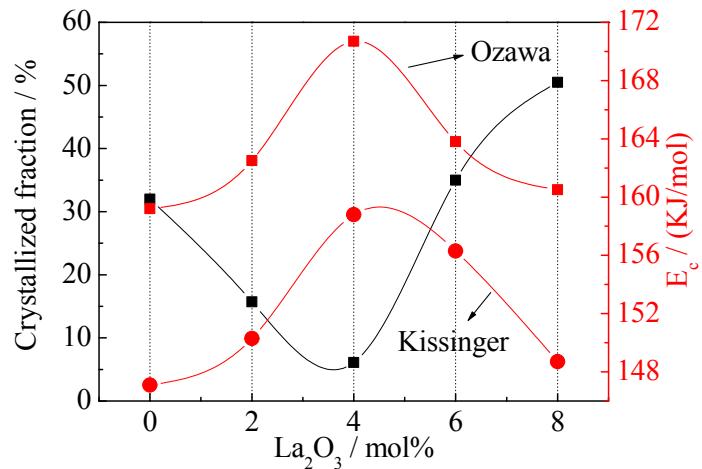
答：已按照要求把全部参考文献修改。

4) 提供 TOC(图加文字)

答：已提供 TOC 图和文字说明。

5) 图 1 和 6 的线条改成彩色

答：已按照要求对图 1 和 6 的线条颜色进行修改。



The dependence of the crystallization activation energy E_c of 60ZnO-30B₂O₃-10SiO₂ glass on the La₂O₃ doping amount is illustrated in Figure, the change trend of E_c values estimated by Ozawa and Kissinger methods is same, as the doping amount of La₂O₃ increases from 0 to 8 mol%, the maximum value of crystallization activation energy E_c appears at 4 mol% of La₂O₃, indicating that the crystallization barrier need to overcome is largest for glass doped with 4 mol% of La₂O₃, as a result, the crystallization of glass is inhibited. This result can be used to control the depth of crystal layer at glass surface, crystallinity and thermal stability of 60ZnO-30B₂O₃-10SiO₂ glass by doping with different content of La₂O₃.

Phase separation and crystallization of La_2O_3 doped $\text{ZnO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ glass

Mitang Wang^{1, 2*}, Long Fang^{1, 2}, Mei Li^{1, 2}, Zhaogang Liu^{1, 2}, Yanhong Hu^{1, 2}, Xiaowei Zhang^{1, 2}, Wei Deng³, Ruhil Dongol⁴

(¹School of Materials and Metallurgy, Inner Mongolia University of Science & Technology, Baotou 014010, China;

²Key Laboratory of Green Extraction & Efficient Utilization of Light Rare-Earth Resources, Ministry of Education, Baotou 014010, China;

³Materials EngineeringMaterials and Engineering Research Institute, Sheffield Hallam University, SheffieldS1 1WB, UK;

⁴New York State College of Ceramics, Alfred University, Alfred, NY, 14802, USA)

Corresponding author: M.T. Wang

Email: btwmt@126.com

Tel: 086-15848255894

Abstract: In order to investigate the effect of the La_2O_3 on the phase separation and crystallization of $\text{ZnO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ glass, after the occurrence of the phase separation and crystallization of glasses by heat treatment, the microstructure morphology and distribution of elements in different sample areas were characterized by the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS); the non-isothermal crystallization kinetics of the glass samples was studied by using a differential scanning calorimeter (DSC) and the precipitated crystals of crystallized glass were determined by the X-ray diffraction (XRD). The results suggest that the phase separation and crystallization of $60\text{ZnO}\text{-}30\text{B}_2\text{O}_3\text{-}10\text{SiO}_2$ glass occur at glass surface, and the incorporation of small amount ($< 4 \text{ mol\%}$) of La_2O_3 significantly inhibits the glass phase separation and consequently improves the thermal stability of glass. Doping of La_2O_3 accelerates the glass crystallization at the elevated temperature (660°C), making the depth of crystal layer thicker and diffraction intensity in XRD patterns stronger. However, due to the precipitation of several crystals that occur simultaneously when La_2O_3 doping amount is 4mol\% , crystallization of the $60\text{ZnO}\text{-}30\text{B}_2\text{O}_3\text{-}10\text{SiO}_2$ glass is obviously depressed, the crystallization activation energy E_c and the relative crystallinity X_c of the glass reach the maximum and the minimum values, respectively. Although transition from one-dimensional growth of crystals to two-dimensional growth of crystals results from La_2O_3 addition, the one-dimensional growth of crystals remains dominant in crystallization process. This work can provide some useful information for preparing glass ceramics with nano-crystals precipitated in the glass surface.

Keywords: zinc borosilicate glass; La_2O_3 ; phase separation; crystallization; rare earths

1. Introduction

ZnO based materials have been extensively applied in the field of optoelectronic devices, gas sensor, catalyst and new energy materials due to the semiconducting properties of zinc oxides [1, 2]. Meanwhile, glasses in the composition of $\text{ZnO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ system have attracted numerous attention in luminescent, optical storage, solid laser and sealing areas because of the excellent optical properties, low thermal expansion coefficient and melting temperature [3, 4]. The properties of glass mainly depend on the structure given by its specific chemical compositions. It is well known that SiO_2 and B_2O_3 are the typical glass network former, silicon atom present in form of $[\text{SiO}_4]$, boron existing in $[\text{BO}_3]$ and $[\text{BO}_4]$, depend on the specific chemical composition of glass. The coordination numbers of zinc in glass could be 4 and 6,

which is named as network intermediate. Zinc oxide has dual role in the glass structure, increases the connectivity of glass structure as zinc exists in $[ZnO_4]$, and provides non-bridging oxygen and makes the glass structure open when coordination number of zinc is 6 [5]. As for optical materials, rare earth elements with abundant of energy levels are commonly incorporated into glass to tailor the luminescent properties of optical materials [6-11]. Rare earth ions always exist in glass as network modifier, and it has higher cationic field strength, which has strong effect on the basic building units in glass structure and makes the order and disorder state of local structure more complicated, consequently results in the occurrence of phase separation and crystallization of glass containing rare earth elements [12]. It was reported that, addition of rare earth oxides such as La_2O_3 , CeO_2 , Nd_2O_3 , Eu_2O_3 and Y_2O_3 has significant impact on the nucleation and crystal growth of $MgO-Al_2O_3-SiO_2$, $Li_2O-Al_2O_3-SiO_2$, $La_2O_3-B_2O_3$ and Li_2O-SiO_2 glasses [13-15]. Apart from the effect of rare earth elements on the microstructure of glass structure, competition of B and Zn for oxygen to satisfy their coordination requirements and different structure between $[BO_3]$ and $[SiO_4]$ units make the phase separation and crystallization of $ZnO-B_2O_3-SiO_2$ system glass much more easy to occur during process [5, 16], as a result, thermal stability and glass forming ability of $ZnO-B_2O_3-SiO_2$ system glass, specially for the glass containing high amount of ZnO and B_2O_3 , are deteriorated seriously [16]. Thereby, it is interesting to explore the effect of rare earth elements on the phase separation and crystallization of $ZnO-B_2O_3-SiO_2$ system glass. In our previous work [16], it shows that different contents of La_2O_3 and Y_2O_3 doping into $ZnO-B_2O_3-SiO_2$ system glass has different influence on the glass forming ability due to their effect on the conversion of $[BO_3]$ and $[BO_4]$, $[ZnO_4]$ and $[ZnO_6]$. Thereby, the objective of this work is to investigate the effect of the La_2O_3 on the phase separation and crystallization of $ZnO-B_2O_3-SiO_2$ glass, the microstructure morphology and the distribution of elements in the different areas after phase separation, and crystallization of glasses heat treated are characterized by SEM equipped with EDS, as well crystallization kinetics of the glass were studied by non-isothermal methods.

2 Experimental

2.1 Glass preparation

60 ZnO -30 B_2O_3 -10 SiO_2 glasses doped with different contents of La_2O_3 (2 mol%, 4 mol%, 6 mol% and 8 mol%) were prepared by melt quenching method. The used raw materials were analytical grade reagents including boric acid, ZnO , SiO_2 and La_2O_3 . To be simple, the prepared glass samples were named as B0 for glass doped without La_2O_3 , L1, L2, L3 and L4 for glass doped with La_2O_3 . After mixing thoroughly, 100 g of batch in the platinum crucible was melted in electric furnace at 1100–1300 °C for 1–2 h depending on the glass chemical composition, followed by annealing at 550 °C in a furnace for 1h, and then naturally cooled down to room temperature. Annealed glasses were cut into regular samples of 5 mm×10 mm×20 mm, and heat treated by specific thermal schedule for the study requirements of phase separation and crystallization of glass, and the specific heat treatment schedules were determined on the basis of sample thermal analysis. By cutting and polishing of heat treated glasses the samples for observing phase separation and crystallization behaviors were obtained.

2.2 Characterization

To obtain the glass transition temperature T_g and crystallization temperature T_p of glass, the thermal analysis for grinded glass powder was carried out by a differential scanning calorimeter (DSC, Model STA449C, Germany). The glass powders were heated in nitrogen atmosphere from room temperature to 900 °C with

different heating rates ($\beta=5, 10, 15$ and $20\text{ }^{\circ}\text{C/min}$). The measurement error of T_g and T_p values is $\pm 1\text{ }^{\circ}\text{C}$. To observe the morphology of phase separation occurred and the crystallite phase precipitated in the glass, the measured surfaces of the samples were polished and then eroded in the 4.0 wt% HF acid solution for 10-30s. After cleaning with deionized water and dry in air, the measured surfaces sprayed with a layer of gold were performed by scanning electron microscopy analysis (SEM FEI QUANTA-400 and ZEISS Sigma 500). Meanwhile, the distribution of elements in the different areas after phase separation and crystallization of glasses heat treated were characterized by EDS. The precipitated crystallites of the heat treated specimens were identified by the an X-ray powder diffractometer (XRD, Model QUEST, America), using Cu K α radiation. The XRD patterns were recorded in 2θ range of $10^{\circ}\text{--}80^{\circ}$ at the step size of 0.04. The XRD data were analyzed using Jade software.

3 Results and discussion

3.1 DSC analysis

Fig. 1 illustrates the DSC curves for glass samples B0, L1, L2, L3 and L4 at heating rate of 5, 10, 15 and 20 $^{\circ}\text{C/min}$. It is observed that glass transition temperature T_g and crystallization temperature T_p for all glasses shift to higher temperature with increase of heating rate, which is in agreement with the results reported by other researchers [17-19]. For base glass B0, there are two distinct exothermic peaks T_{p1} and T_{p2} , as shown in Fig. 1(a), T_{p1} is of $725\text{ }^{\circ}\text{C}$ and T_{p2} $760\text{ }^{\circ}\text{C}$ for the DSC curve carried out at heating rate of $10\text{ }^{\circ}\text{C/min}$. Two exothermic peaks present in DCS measurements suggest that there are transformation of crystal form or simultaneous precipitation of different crystal in zinc borosilicate base glass when heat treatment is carried out on it. While there is one exothermic peak for La₂O₃ doped glass as shown in Fig. 1(b-e).

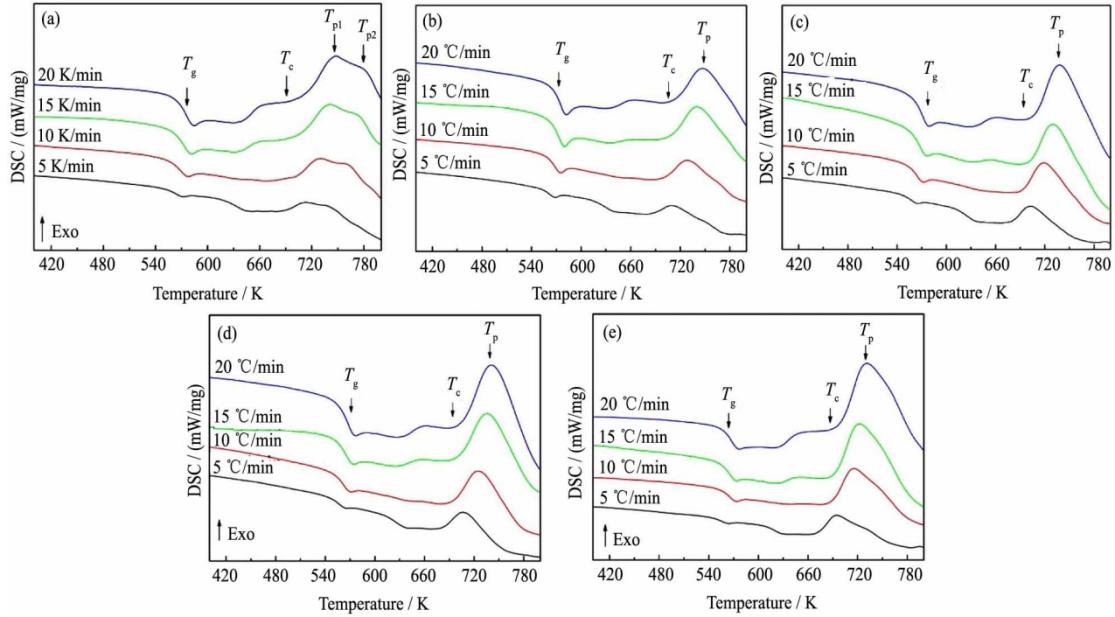


Fig.1 DSC curves of the glasses samples. (a) B0; (b) L1; (c) L2; (d) L3; (e) L4.

3.2 Phase separation of parent glass

It is well known that the occurrence of glass phase separation can be observed by heat treating the glass at the temperature close to glass transition temperature T_g ^[20]. Glass transition temperature of 60ZnO-30B₂O₃-10SiO₂ parent glass is about $570\text{ }^{\circ}\text{C}$ when the heating rate is $10\text{ }^{\circ}\text{C/min}$, as shown in Fig. 1(a). Thereby, the parent glass B0 were heat treated at temperatures of 620 and $640\text{ }^{\circ}\text{C}$, respectively for 5 or 10 h ,

and the phase separation of glass B0 are given in Fig. 2. It is found that the phase separation of glass B0 occurs at the glass surface, and the morphology of phase separation is mainly wormlike along with a few of isolated droplets. Comparing the glass B0 heat treated at 620 °C for 5 h (Fig. 2(a)) with glass B0 at 640 °C for 5 h (Fig. 2(b)), the phase separation becomes more severe with the increase of heat treatment temperature from 620 to 640 °C when keep the duration of heat treatment constant, which is mainly due to the easier structure rearrangement caused by the open glass structure as the temperature increases. When keeping the heat treatment temperature at 640 °C, the phase separation of glass B0 gets more serious with prolonging the heat treatment time from 5 to 10 h, as shown in Fig. 2(b) and (c). Besides, a few crystals are precipitated as illustrated in framed area in Fig. 2(c), in order to obtain the detail information about crystallization behavior, the magnified view of the framed region in Fig. 2(c) is given in Fig. 2(d). It suggests that the crystal growth along with the interfaces between the two phases caused by heat treatment, orients to the inside of glass and extends to the inner walls of phases. The way of crystal nucleation and growth mainly correlates with two factors. On the one hand, the larger surface area of interface caused by phase separation makes the nucleation occur easier at the interface, on the other hand the components in one phase is really similar with the components of crystal precipitated in the interface between two phases, as a result decreasing the nucleation activation energy and facilitating the nucleation and crystal growth [21]. Due to the larger surface area and more structure defect near glass surface, and there is no nucleating agent in glass chemical compositions, the phase separation easier occurred near glass surface rather than glass bulk, and phase separation facilitates the crystallization.

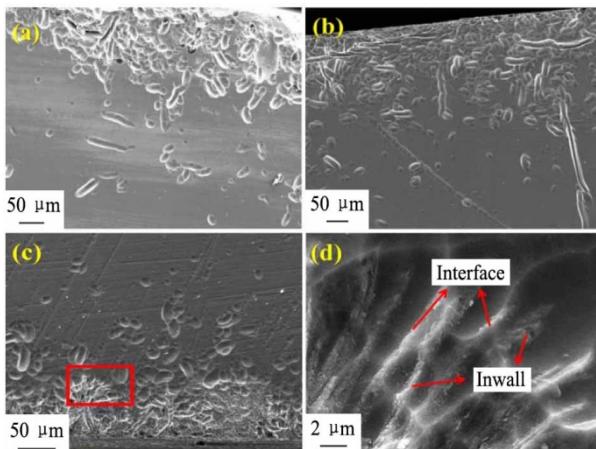


Fig. 2 The SEM images of phase separated B0 glass. (a) Glass B0 heat treated at 620 °C for 5 h; (b) Glass B0 at 640 °C for 5 h; (c) Glass B0 at 640 °C for 10 h; (d) The enlarged view of the red region in fig(c).

3.3 Phase separation and crystallization of La_2O_3 containing glass

60ZnO-30B₂O₃-10SiO₂ glasses doped with different contents of La_2O_3 were heat treated at 620 °C for 5 h to observe the variation of phase separation of glass. As shown in Fig. 3, comparing with Fig. 2, phase separation of glass is significantly inhibited as doping content of La_2O_3 is less than 4 mol% (Fig. 3 (a) and (b)), while more than 4 mol%, the phase separation becomes serious, and is accompanied with precipitation of crystals (Fig. 3(c) and (d)). It is obvious that the extent of crystallization increases with increase of La_2O_3 doping content in parent glass when

comparing Fig. 3(c) with (d). Additionally, the phase separation and crystallization keep occurring at the glass surface, indicating that the addition of La_2O_3 into glass has slight influence on the mechanism of phase separation and crystallization of 60ZnO-30B₂O₃-10SiO₂parent glass, and it can be concluded that phase separation of 60ZnO-30B₂O₃-10SiO₂glass can be depressed when a small amount of La_2O_3 (< 4 mol%) is added into glass, in turn improves the thermal stability of glass which has been reported in our previous study [16], while the doping content of La_2O_3 is more than 4 mol%, the crystallization of 60ZnO-30B₂O₃-10SiO₂glass can be accelerated maybe because La_2O_3 acts as nucleating agent in glass, thereby the thermal stability of glass deteriorates [13,14].

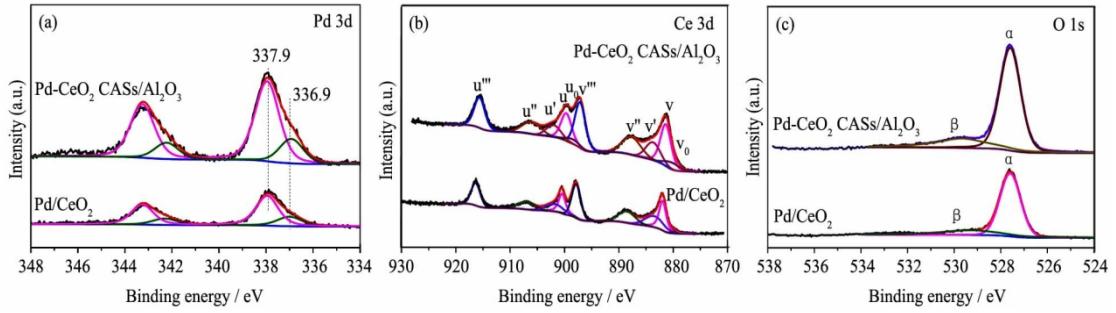


Fig. 3 SEM micrographs showing the surface microstructure of the glass doped with La_2O_3 heat treated at 620 °C for 5 h.

To determine the distribution of glass components such as La and other elements after phase separation and crystallization, backscattered scanning and energy dispersive spectroscopy for glass L4 subjected heat treatment at 640 °C for 5 h, polishing and gold sputtering, was carried out and the results are illustrated in Fig. 4. It can be seen from Fig. 4(a) that slight phase separation and obvious dendritic crystal are formed at the glass surface, suggesting that distribution of glass components in the dark and slight grey regions is different. Fig. 4(c) and (d) give the EDS results for A (dark grey region) and B (slight grey region) areas in Fig. 4(b), and the specific distribution of glass components are listed in Table 1. Comparing the elements contents in A and B regions, B region is mainly rich in La and Si, while A region is mainly rich in Zn, and according to XRD results (next section) the B also aggregates in dark grey region, which suggests that regions rich in La and Si as well as Zn and B are formed in 60ZnO-30B₂O₃-10SiO₂glass by phase separation and crystallization.

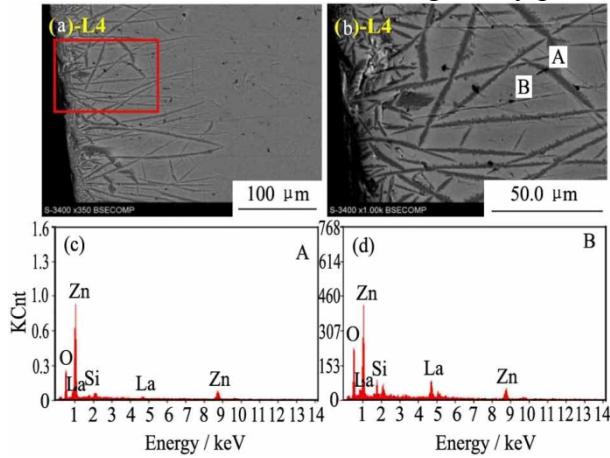


Fig.4 The backscattered electron scanning images of samples L4 heat treated at 640 °C for 5 h. (a) The microscopic appearance of glass samples; (b) The amplification of Fig. (a); (c and d) EDS patterns of marked areas A and B

Table 1 Distribution of element content of different region caused by phase separation

Element	Mass fraction		Atom fraction	
	A	B	A	B
O	17.14	13.43	46.28	42.85
Si	2.29	5.16	3.52	9.37
La	8.9	38.17	2.71	14.02
Zn	71.86	43.23	47.49	33.75

It has been demonstrated that the crystallization occurs for the 60ZnO-30B₂O₃-10SiO₂ glass doped with more than 4 mol% La₂O₃ when heat treatment was done at 620 °C for 5 h. To further investigate the effect of La₂O₃ content on the crystallization of 60ZnO-30B₂O₃-10SiO₂ glass, glasses doped with different contents of La₂O₃ were heat treated at elevated temperature (660 °C for 5 h), the variation of crystallization behavior performed at the glass surface. Fig. 5 shows the surface microstructure of the glass samples heat treated at 660 °C for 5 h. Crystallization for all glasses occurs at their surface and precipitated crystals are dendritic and orient inside of glass, incorporation of La₂O₃ accelerates the crystallization of glass and makes the precipitated crystals more fine and close when comparing with the glass B0. Additionally, the depth of crystal layer precipitated at the glass surface increases from about 172.4 μm for B0 to 1111 μm for L4 as the doping amount of La₂O₃ increases from 0 to 8 mol%, indicating that except glass L2 as shown in Fig. 5(c), crystal layer depth increases with increase of La₂O₃ content. Fig. 6 presents the XRD patterns of all glasses heat treated at 660 °C for 5 h. It shows that the diffraction intensity in XRD patterns increases with the increase in La₂O₃ amount, however, the diffraction intensity in XRD patterns for sample L2 is not increased obviously, which is in agreement with the results depth of crystal layer at glass surface. From the XRD patterns, one can also find that the main crystallite phase is Zn₃B₂O₆ for glass B0, as doping content of La₂O₃ in parent glass increases up to 4 mol%, the crystallites LaBO₃ and Zn₂SiO₄ begin to precipitate simultaneously with Zn₃B₂O₆, this might be the reason for slight decrease of crystal layer depth and diffraction intensity for glass L2 comparing with other glass doped with La₂O₃, potential barrier for crystallization for glass L2 becomes larger due to several crystals precipitated simultaneously, nucleation and crystal growth consequently are inhibited [13,14, 22].

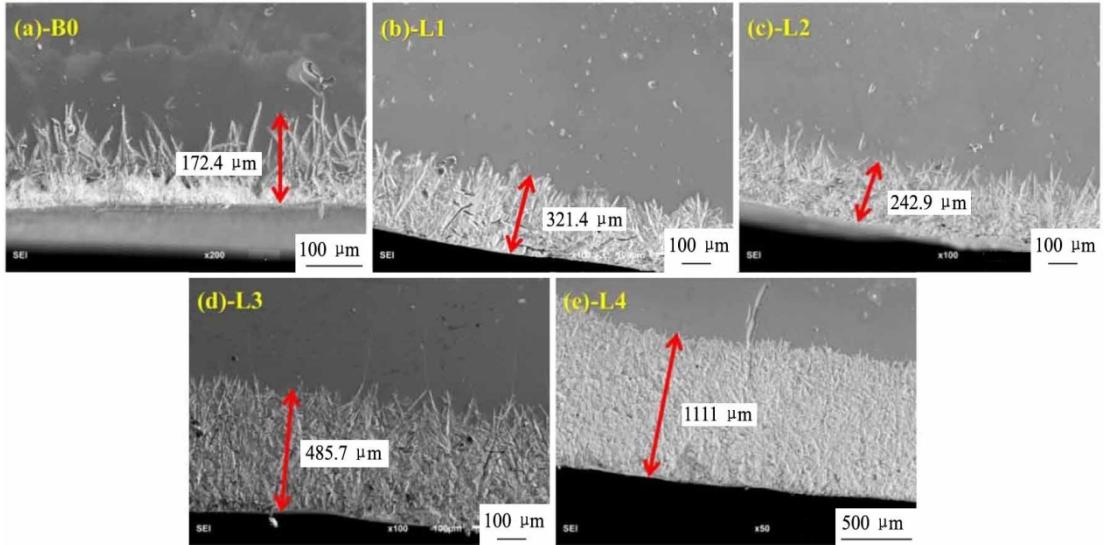


Fig.5 SEM micrographs showing the surface microstructure of the glass samples heat treated at 660 °C for 5 h.

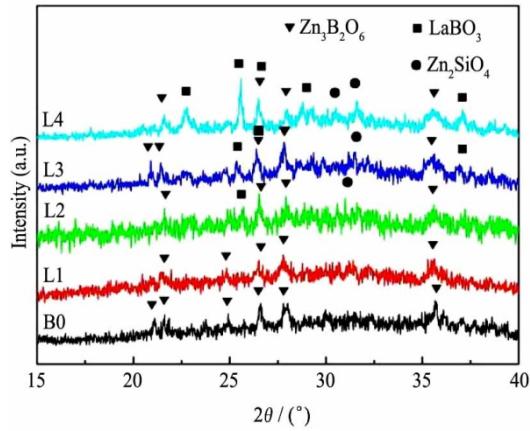


Fig.6 XRD patterns of different amount of La_2O_3 doped glass samples

To quantitatively characterize the effect of La_2O_3 on the crystallization degree of 60ZnO-30B₂O₃-10SiO₂ glass, crystallinity X_c defined as the ratio of precipitated crystals volume to original volume of glass is calculated by following expression on the basis of XRD data [23,24].

$$X_c = \frac{I_c}{I_a + I_c} \times 100\% \quad (1)$$

where I_a is integral sum of all diffuse peak, I_c is integral sum of all crystal peak in XRD patterns. I_a , I_c and X_c are values calculated on the basis of XRD results as shown in Fig. 6 are listed in Table 2. The dependence of glass crystallinity on the La_2O_3 doping amount is given in Fig. 7, the crystallinity of glass decreases firstly and then increases with increasing of La_2O_3 content from 0 to 8 mol%, minimum value for glass crystallinity appears at glass L2 doped with 4 mol% La_2O_3 . This is mainly due to the variation of potential barrier for glass nucleation and crystal growth caused by the incorporation La_2O_3 in 60ZnO-30B₂O₃-10SiO₂ glass, which will be discussed in next section.

Table 2 The I_a , I_c and X_c values of glasses calculated from the XRD pattern

Glass	$T/^\circ\text{C}$	t/h	I_a (a.u.)	I_c (a.u.)	$X_c/\%$
B0	660	5	11687	5528	32.0
L1	660	5	10157	1888	15.7
L2	660	5	15827	1030	6.1
L3	660	5	5149	2771	35.0
L4	660	5	3705	3775	50.5

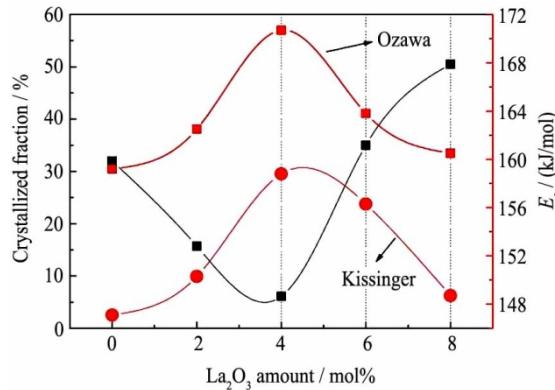


Fig. 7 The crystallinity and crystallization activation energy of La₂O₃ doped glass samples

3.4 Crystallization kinetics

The difficulty of glass crystallization can be characterized by the crystallization activation energy, glass structure rearrangement when glass transforms into crystals needs to overcome the crystallization barrier which is defined as crystallization activation energy E_c . The larger the crystallization activation energy, the higher the crystallization barrier needs to overcome; nucleation and crystal growth rates become slowly, consequently the crystallization of glass is depressed [25,26]. To quantitatively explore the effect of La₂O₃ doping amount on the crystallization activation energy E_c of 60ZnO-30B₂O₃-10SiO₂ glass, two expressions were used to estimate the E_c value. One is the Kissinger equation [26,27],

$$\ln(\beta/T_p^2) = \text{cons} \tan t - E_c / RT_p \quad (2)$$

The other is Ozawa expression [28] as following,

$$\ln\beta = \text{cons} \tan t - E_c / RT_p \quad (3)$$

Where β is heating rate, T_p crystallization peak temperature, R gas constant. And according to the specific experimental data, the $\ln(\beta/T_p^2)$ versus $1000/T_p$ and $\ln\beta$ versus $1000/T_p$ plots (as shown in Fig. 8) for parent and La₂O₃ doped sample at different heating rates are fitted on the basis of Kissinger (Fig. 8(a)) and Ozawa (Fig. 8 (b)) equations, the crystallization activation energy can be obtained from the slope E_c/R of lines and summarized in Table 3. For comparison, the dependence of the crystallization activation energy E_c of 60ZnO-30B₂O₃-10SiO₂ glass on the La₂O₃ doping amount is illustrated in Fig. 7, the value of E_c obtained by Ozawa method is larger than that by Kissinger, but the change trend of E_c values estimated by two different methods is the same, E_c values increase firstly from 147.1 to 158.8 kJ/mol and then decreases to 148.7 kJ/mol for Kissinger method, 159.2 to 170.7 then to 160.5 kJ/mol for Ozawa method as the doping amount of La₂O₃ increases from 0 to 8 mol%, the maximum value of crystallization activation energy E_c appears at 4 mol% La₂O₃,

indicating that the crystallization barrier that needs to overcome is the largest for glass L2, as a result, the crystal nucleation and crystallization in glass L2 is inhibited because the several crystals ($Zn_3B_2O_6$, $LaBO_3$ and Zn_2SiO_4) are precipitated simultaneously as shown in Fig. 6. This can be used to explain variation trends for the depth of crystal layer at glass surface, X-ray diffraction intensity and crystallinity of 60ZnO-30B₂O₃-10SiO₂ glass doped with different contents of La₂O₃. This also suggests that crystallization of glass L2 is the hardest comparing with other La₂O₃ doped glasses, namely its thermal stability is the best, which is in good agreement with our previous results characterized by parameter S ^[16]. It can be concluded that the crystallization and thermal stability of 60ZnO-30B₂O₃-10SiO₂ glass can be depressed and improved by doping less than 4 mol% La₂O₃, while introduction of more than 4 mol% La₂O₃ facilitates the crystallization behavior of this glass.

Table 3 The crystallization activation energy E_c and crystal growth parameter n .

Glass	E_c (kJ/mol)		n	m
	Kissinger	Ozawa		
B0	147.1	159.2	2.00	1
L1	150.3	162.5	2.12	1
L2	158.8	170.7	2.10	1
L3	152.1	163.8	2.08	1
L4	148.7	160.5	2.48	1

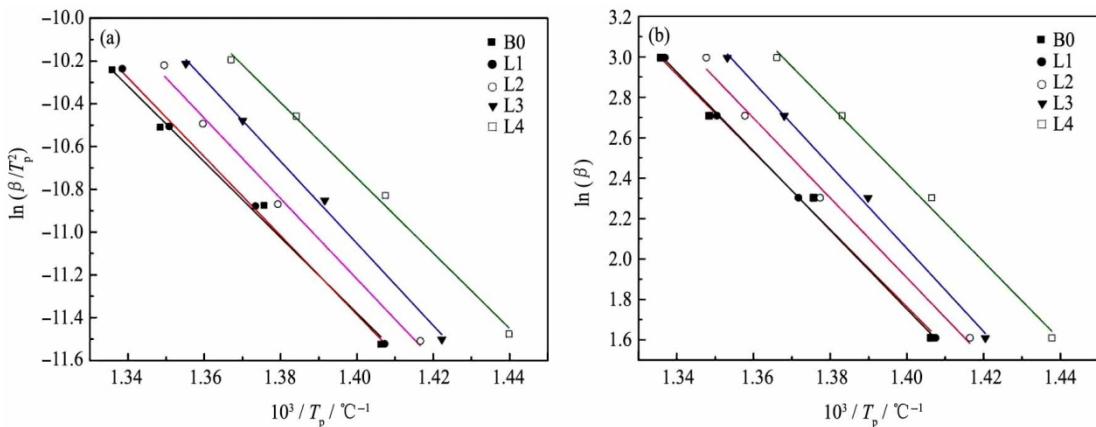


Fig. 8 (a) $\ln(\beta/T_p^2)$ versus $1000/T_p$ plots for B0, L1, L2, L3 and L4 samples at different heating rates; (b) $\ln \beta$ versus $1000/T_p$ plots.

The mechanism for the crystallization of 60ZnO-30B₂O₃-10SiO₂ glass doped with different contents of La₂O₃ is calculated by Augis-Bennett equation^[29],

$$n = \frac{2.5}{\Delta T} \cdot \frac{RT_p^2}{E_c} \quad (4)$$

where n is Avrami index correlated with phase transformation mechanism; ΔT is the full width at half maximum of the exothermical peak in DSC curve. The n values obtained from Kissinger results and specific experimental data are shown in Fig. 1, and m calculated according to n value^[30] is as well listed in Table 3. Values of n and m for parent glass are 2 and 1, indicating that both one-dimensional growth of crystals and surface crystallization mechanisms occur in glassy to crystalline transformation of 60ZnO-30B₂O₃-10SiO₂ parent glass. With incorporation of La₂O₃ into parent glass,

the Avramiexponents n is more than 2, and m approximate to 1, suggesting that transition from one-dimensional growth of crystals to two-dimensional growth of crystals occurs at glass surface, but the one-dimensional growth of crystals remains dominant in crystallization process. These are consistent with the crystallization behavior as shown in Fig. 5.

4 Conclusions

The influence of La_2O_3 on the phase separation and crystallization behavior of 60ZnO-30B₂O₃-10SiO₂ glass was investigated in this work, the phase separation and crystallization of 60ZnO-30B₂O₃-10SiO₂ glass occur at glass surface when glasses are heat treated at about glass transition temperature, and the incorporation of small amount (< 4 mol%) of La_2O_3 significantly inhibits the glass phase separation and thus improves the thermal stability of glass. The depth of crystal layer and diffraction intensity in XRD patterns of all glasses heat treated at 660 °C for 5 h, show that doping of La_2O_3 accelerates the crystallization of parent glass, however, the diffraction intensity in XRD patterns for sample L2 (4 mol% La_2O_3) is not increased obviously due to crystallites LaBO_3 and Zn_2SiO_4 begin to precipitate simultaneously with $\text{Zn}_3\text{B}_2\text{O}_6$. Crystallization kinetics results indicate that as the doping amount of La_2O_3 increases from 0 to 8 mol%, the crystallization activation energy increases firstly and then decreases, the maximum value of crystallization activation energy appears at 4 mol% La_2O_3 , indicating that the crystallization barrier needing to overcome is the largest for glass L2. And transition from one-dimensional growth of crystals to two-dimensional growth of crystals occurs at glass surface, but the one-dimensional growth of crystals remains dominant in crystallization process.

Foundation item: Project supported by National Natural Science Foundation of China (51662033, 51362019) and Natural Science Foundation of the Inner Mongolia Autonomous Region (2016JQ05).

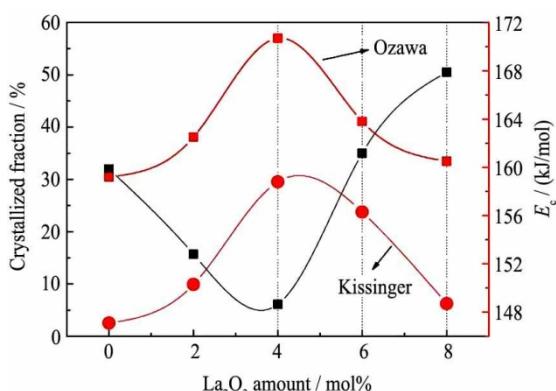
References:

- [1] Masai H, Toda T, Ueno T, Takahashi Y, Fujiwara T. ZnO glass ceramics: An alternative way to produce semiconductor materials. *Appl Phys Lett*. 2009; 94(15): 151908.
- [2] Uma V, Marimuthu K, Muralidharan G. Effect of ZnO on the spectroscopic properties of Dy³⁺ doped zinc telluroborate glasses for white light generation. *J Non-Cryst Solids*. 2018; 498: 386.
- [3] Shen Y, Hou L Y, Zuo G F, Li FF, Meng YZ. Preparation of ZnO-B₂O₃-SiO₂: Mn²⁺ optical-storage glass-ceramics with different ZnF₂ dopant by sol-gel method. *J Sol-Gel Sci Technol*, 2015, 73(1): 192.
- [4] Annapurna K, Dwivedi R N, Kundu P, Buddhudu, S. Blue emission spectrum of Ce³⁺: ZnO-B₂O₃-SiO₂ optical glass. *Mater Lett*. 2004; 58(5): 787.
- [5] Cetinkaya C S, Akyuz I, Atay F. On the dual role of ZnO in zinc borate glasses. *J Non-Cryst Solids*, 2016; 432: 406.
- [6] Zeng P, Cao ZM, Chen YH, Yin M. Investigation of the temperature characteristic in SrB₄O₇:Sm²⁺ phosphor-in-glass by analyzing the lifetime of 684 nm. *J Rare Earths*, 2017; 35(8): 783.
- [7] Wantana N, Kaewjaeng S, Kothan S, Kim HJ, Kaewkhao J. Energy transfer from Gd³⁺ to Sm³⁺ and luminescence characteristics of CaO-Gd₂O₃-SiO₂-B₂O₃ scintillating glasses. *J Lumine*, 2017; 181: 382.

- [8] Man XQ, Yu LX, Sun JJ, Li SC, Zhong JL. Synthesis and photoluminescent properties of Eu³⁺/Dy³⁺ doped SrO-Al₂O₃-SiO₂ glass-ceramics. *J Rare Earths*, 2017; 35(5): 446.
- [9] Hu FF, Zhao ZM, Chi FF, Wei XT, Yin M. Structural characterization and temperature-dependent luminescence of CaF₂:Tb³⁺/Eu³⁺ glass ceramics. *J Rare Earths*, 2017; 35(6): 536.
- [10] Kemere M, Sperga J, Rogulis U. Luminescence properties of Eu, RE³⁺ (RE = Dy, Sm, Tb) co-doped oxyfluoride glasses and glass-ceramics. *J Lumin*, 2017; 181: 25.
- [11] Ramachari D, Moorthy L R, Jayasankar C K. Energy transfer and photoluminescence properties of Dy³⁺/Tb³⁺co-doped oxyfluorosilicate glass-ceramics for solid-state white lighting. *Ceram Int*. 2014; 40(7): 11115.
- [12] Elodie N, Sophie S, Frederic A, Charpentier T, Jollivet P, Le Gac A, et al. Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass. *J Non-Cryst Solids*. 2015; 472(3): 120.
- [13] Pytalev DS, Caurant D, Majerus O, Tregouet H, Charpentier T, Mavrin, BN. Structure and crystallization behavior of La₂O₃·3B₂O₃metaborate glasses doped with Nd³⁺ or Eu³⁺ ions. *J Alloys Compd*. 2015; 641: 43.
- [14] Lu P, Zheng Y, Cheng JS, Guo DY. Effect of La₂O₃ addition on crystallization and properties of Li₂O-Al₂O₃-SiO₂ glass-ceramics. *Ceram Int*. 2013; 39(7): 8207.
- [15] Katrin T, Christian R. CeO₂ and Y₂O₃ as nucleation inhibitors in lithium disilicateglasses. *J Mater Sci*. 2016; 51(2): 989.
- [16] Wang MT, Fang L, Li M, Liu ZG, Hu YH, Zhang XW. Effect of rare earth on thermal stability and glass structure of ZnO-B₂O₃-SiO₂ glass. *J Inorg Mater*. 2017; 6(32): 643. (in China.)
- [17] Lopes AAS, Monteiro RCC, Soares RS, Lima MMRA, Fernandes MHV. Crystallization kinetics of a barium-zinc borosilicate glass by a non-isothermal method. *J. Alloys Compd*. 2014; 591(1): 268.
- [18] Aroraa A, Goelb A, Shaaban ER, Singh K, Pandey OP, Ferreira JMF. Crystallization kinetics of BaO-ZnO-Al₂O₃-B₂O₃-SiO₂ glass. *Physica B*. 2008; 403(10–11): 1738.
- [19] Imran MMA. Crystallization kinetics, glass transition kinetics, and thermal stability of Se_{70-x}Ga₃₀In_x ($x=5, 10, 15$, and 20) semiconducting glasses. *Physica B*. 2011; 406(3): 482.
- [20] Rafferty A, Hill R, Kelleher B, ODwyer T. An investigation of amorphous phase separation, leachability and surface area of an ionomer glass system and a sodium-boro-silicate glass system. *J Mater Sci*. 2003; 38(19): 3891.
- [21] Hou ZX, Su CH. Composition, structure and optical properties of transparent glass ceramics. Shenyang: Northeastern University Press, 2008.
- [22] Kullberg ATG, Lopes AAS, Veiga JPB, Lima MMRA, Monteiro RCC. Formation and crystallization of zinc borosilicate glasses: Influence of the ZnO/B₂O₃ ratio. *J Non-Cryst Solids*. 2016; 441: 79.
- [23] Song XL, Hui XH. Fundamentals of Materials Science. Beijing: Chemical Industry Press, 2005.
- [24] Huang J W, Li Z. X-ray Diffraction of Polycrystalline Materials-Experimental Principle, Method and Application. Beijing: Metallurgical Industry Press, 2012.
- [25] Wang F, Liao QL, Zhu H Z, Dai YY, Wang H. Crystallization kinetics and glass transition kinetics of iron borophosphate glass and CeO₂-doped iron borophosphate compounds. *J Alloys Compd*. 2016; 686: 641.
- [26] Kissinger HE. Variation of Peak Temperature With Heating Rate In Differential Thermal Analysis. *J Res National Bureau Standards*. 1956; 57(4): 217.

- [27] Kissinger HE. Reaction kinetics in differential thermal analysis. *Anal Chem*. 1957; 29(11): 1702.
- [28] Ozawa T. Estimation of activation energy by isoconversion methods. *Thermochim Acta*. 1992; 203(2):159.
- [29] Augis JA, Bennett JE. Calculation of the Avrami parameters for heterogeneous solid state reactions using a modification of the Kissinger method. *J Thermal Anal Calorim*. 1978, 13(2): 283.
- [30] Bai Y, Peng L, Zhu QS, Hao ZG. Non-isothermal crystallization kinetics of stoichiometric lithium disilicate-based glasses with Al_2O_3 additives. *J Non-Cryst Solids*. 2016; 445: 116.

Graphic abstract:



The dependence of the crystallization activation energy E_c of 60ZnO-30B₂O₃-10SiO₂ glass on the La₂O₃ doping amount is illustrated in the figure, the change trend of E_c values estimated by Ozawa and Kissinger methods is the same, as the doping amount of La₂O₃ increases from 0 to 8 mol%, the maximum value of crystallization activation energy E_c appears at 4 mol% of La₂O₃, indicating that the crystallization barrier needing to overcome is the largest for the glass doped with 4 mol% La₂O₃, as a result, the crystallization of glass is inhibited. This result can be used to control the depth of crystal layer on glass surface, crystallinity and thermal stability of 60ZnO-30B₂O₃-10SiO₂ glass by doping with different contents of La₂O₃

Declarations of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.