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CRYSTALLIZATION STUDY OF Na–Gd PHOSPHATE GLASS USING NON-ISOTHERMAL DTA

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Na–Gd phosphate glasses doped with Ce^{3+} are intensively studied due to their high intensity radioluminescence. Crystallization kinetics of glass with nominal composition of $NaGd(PO_3)_4$ was investigated using non-isothermal DTA at heating rates between 10 and 115 K min^{-1} and evaluated by the Kissinger and Ozawa peak methods. The activation energy for crystallization was determined for heating rates lower than 72 K min^{-1} as 789.91 and 802.77 kJ mol^{-1} by using the Kissinger and Ozawa methods, respectively. Formation of nuclei, their dimensions and movement of the crystallization front were observed using isothermal optical thermomicroscopy.

Keywords: *glass crystallization kinetics, Na-Gd phosphate glasses, optical thermomicroscopy*

Introduction

Thanks to their low cost and high intensity of radioluminescence sodium-gadolinium phosphate glasses doped with Ce^{3+} ions are a potential material for the detection of neutrons, γ- and X-rays for medical and technical applications. High scintillation efficiency in this glass is based on energy transport via the gadolinium sublattice to the emission centres, which are formed in the glass matrix by Ce^{3+} ions [1, 2]. So far preparation method for high quality Na–Gd phosphate glasses was developed and sample with Gd^{3+} concentration between 9 and 89 mol% were prepared and their good chemical durability and high glass forming ability were confirmed. It was found [3, 4] that radioluminiscence efficiency of glass doped by 1 mol% of Ce^{3+} increased sharply with Gd^{3+} concentration and for a glass with Gd concentration of 89 mol% it is almost threefold in comparison to BGO, the most employed scintillator. However, for application of glasses their thermal stability and resistance to phase transformation – origins of the crystalline phase – are of great importance. So crystallization processes in glasses, their kinetics and mechanism are a subject of considerable theoretical and practical interest. From these studies we obtain information about thermal stability of glasses, which is important for their technological application. Thanks to the increasing interest in preparation and application of glassy ceramics, the study of glass crystallization kinetics takes a new impulse. The glass crystallization kinetics is experimentally studied by methods of thermal analysis and by thermomicroscopy under both isothermal and non-isothermal conditions.

The aim of the present work is to study crystallization kinetics of Na–Gd phosphate glass with nominal composition of $NaGd(PO_3)_4$ using non-isothermal DTA and isothermal optical thermomicroscopy, to analyse DTA data and to determine fundamental kinetic parameters by means of the Kissinger and Ozawa peak methods.

Theory

The values of crystallization kinetic parameters can be obtained from thermal data collected at constant temperature by means of DSC or DTA using the Johnson, Mehl and Avrami equation [5]

$$\alpha(\tau)=1-\exp[-k(t)^{\mathrm{n}}] \tag{1}$$

where $\alpha(\tau)$ is the transformed volume fraction, t the time, n the Avrami exponent and k a reaction rate constant given by

$$k=A\exp\left(-\frac{E_{\mathrm{C}}}{RT}\right) \tag{2}$$

E_C being the apparent activation energy for crystallization, A the frequency factor, T the temperature.

The values of n and k can be determined from the logarithmic form of Eq. (1)

$$\ln[-\ln(1-\alpha)]=n\ln k+n\ln(t) \tag{3}$$

when plotting $\ln[-\ln(1-\alpha)]$ *vs.* $\ln(t)$ for different temperatures. In a similar way the activation energy E_C can be obtained from the plot of $\ln k$ *vs.* $1/T$.

Under non-isothermal conditions during collection of thermal data both nucleation and crystalliza-

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tion display a dependence on the heating rate. The thermal effects of transformation scanned at low temperature present sometimes asymmetrical profiles indicating occurrence of two overlapping processes. In spite of this, the crystallization kinetics is studied as if it were a single process. A number of models were developed for these conditions. The Johnson, Mehl and Avrami (JMA), Kissinger and Ozawa models are the most employed ones [6–8].

Although the JMA equation was derived for isothermal analysis, it can be, under some assumptions, also used for the study of the crystallization kinetics under non-isothermal conditions [9]. By inserting the temperature increase $T=\beta t+T_0$, where β is the heating rate and T_0 the initial temperature, into Eq. (3) the relation below can be obtained

$$\ln[-\ln(1-\alpha)]=n\ln[k(T-T_0)]-n\ln\beta \tag{4}$$

The Avrami exponent n can be calculated from the slope of the plot $\ln[-\ln(1-\alpha)]$ *vs.* $\ln\beta$ [6].

To analyze non-isothermal data Kissinger proposed a following relation

$$\ln\frac{\beta}{T_\mathrm{P}^2}=-\frac{E_\mathrm{C}}{RT_\mathrm{P}}+\ln\frac{AR}{E_\mathrm{C}} \tag{5}$$

where T_P is the crystallization peak temperature. From this the overall activation energy for crystallization E_C and the frequency factor A can be determined. However, a plot $\ln(\beta/T_\mathrm{P}^2)$ *vs.* $1/T_\mathrm{P}$ often yields two parts with different slopes for lower and higher heating rates. Two values of the energy E_C and two values of the frequency factor A can be calculated from the slopes E_C/R and intercepts $\ln(AR/E_\mathrm{C})$.

Ozawa devised another procedure for non-isothermal crystallization. This so-called Ozawa equation is expressed as follows

$$\ln\beta=-1.0516\frac{E_\mathrm{C}}{RT_\mathrm{P}}-\text{const.} \tag{6}$$

and E_C can be calculated from the slope of the plot $\ln\beta$ *vs.* $1/T_\mathrm{P}$.

Experimental

Glass samples with nominal composition of $NaGd(PO_3)_4$ for study of phase transformation were prepared by a direct synthesis using reagent-grade $NaCO_3$, $GdPO_4$ and P_2O_5 from Sigma-Aldrich and Alfa Aesar in the required molar relation. A mixture of these compounds with a small excess of P_2O_5 and doping $CePO_4$ was heated up in air to 1200° C in a quartz crucible and homogenized at this temperature. Then it was cooled by casting into a graphite mould. After short tempering at 280°C the mould with glass ingot was cooled down to the room temperature [3, 4].

The glassy state was determined from X-ray diffraction measurements using a Bruker D8 powder diffractometer.

Crystallization kinetics was studied by non-isothermal DTA using a Setaram Setsys Evolution 16. Glass samples in mass of about 30 mg were measured in an alumina crucible and for every measurement a newly weighed sample was used. The scans were recorded from room temperature to 1100 °C in flowing nitrogen at the following heating rates: 10, 21, 32, 43, 55, 63, 72, 84, 91, 100 and 115 K min^{-1}.

Optical measurements were performed using an Olympus SZX12 microscope and a Linkam THMS 6000 heating stage. Formation of crystalline phase and its growth were observed at temperatures of 470, 490, 500, 510 and 550 °C and were followed by an Olympus Camedia 3040 camera controlled by Quickphoto 2.1 software.

Results and discussion

Glass samples characterization

Prepared glass samples were transparent, colorless, without any cracks and $10\cdot10\cdot25$ mm^3 in size. Their glassy character was confirmed using X-ray diffraction. By this method a $NaGd(PO_3)_4$ compound was also found in devitrified samples [10]. In order to avoid formation of impurities like $(OH)^-$ in these glasses a new preparation method was developed. Phosphorus pentoxide was substituted for ammonium dihydrogen orthophosphate ($NH_4H_2PO_4\cdot2H_2O$) generally used in preparation of phosphate glasses [11]. Thermal properties of the glass with nominal composition of $NaGd(PO_3)_4$ (DTA, heating rate of 10 K min^{-1}) are as follows: glass transition T_G=441°C, crystallization temperature T_C=496°C, melting point T_M=840 °C.

Study of crystallization kinetics

DTA scans for $NaGd(PO_3)_4$ glass recorded at all heating rates are characterized by 3 effects corresponding to the temperatures of glass transition, crystallization and melting. The scans of exothermic effects representing glass crystallization for heating rates of 10, 32, 43, 72, 100 and 115 K min^{-1} are shown in Fig. 1. Their areas, maximum effects temperatures T_P as well as onset of crystallization temperatures T_0 increase with rise in heating rate until it reaches 72 K min^{-1}. At higher rates (84–115 K min^{-1}) the peak temperatures are approximately the same, about 591°C.

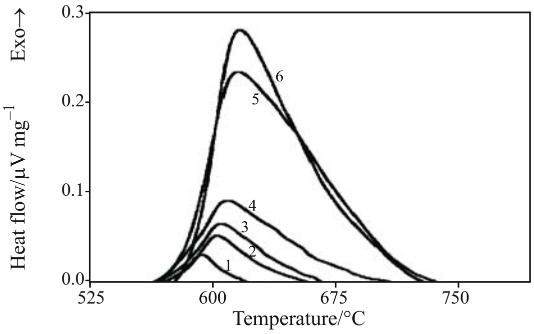

Fig. 1 Non-isothermal DTA traces for crystallization of $NaGd(PO_3)_4$ glass at heating rates of 1 – 10, 2 – 32, 3 – 43, 4 – 72, 5 – 100 and 6 – 115 K min^{-1}

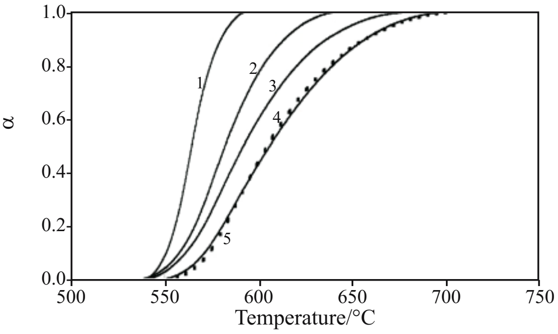

Fig. 2 Plots of crystallized volume fraction α as a function of temperature for heating rates of 1 – 10, 2 – 43, 3 – 72, 4 – 91 and 5 – 115 K min^{-1}

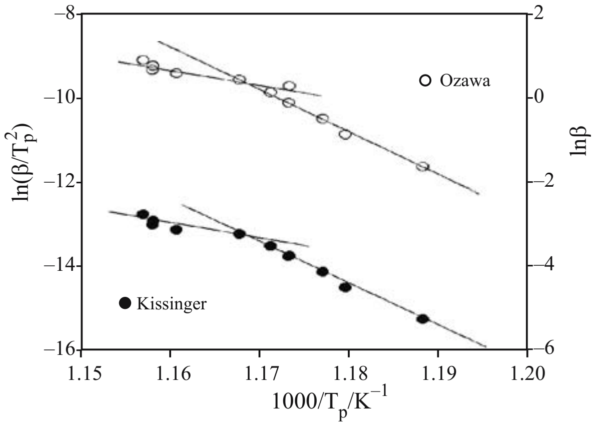

Fig. 3 Kissinger peak method of $\ln(\beta/T_P^2)$ *vs.* $1000/T_P$ and Ozawa plot of lnβ *vs.* $1000/T_P$ for crystallization of $NaGd(PO_3)_4$ glass

Transformed volume fraction α also depends on heating rate and temperature of thermal treatment. Figure 2 shows the plots of α *vs.* temperature for heating rates of 10, 43, 72, 91 and 115 K min^{-1}. They have a characteristic sigmoid shape, which changes depending on heating rate. Transformation temperature gradually increases with heating rate and on the contrary transformation time decreases. Crystallization at the lowest heating rate of 10 K min^{-1} realizes during about 8 min at a temperature range of 75 K, while at 115 K min^{-1} it takes hardly 2 min. Nevertheless, for heating rates higher than about 72 K min^{-1}, the shapes of α plots are identical and independent of heating rate. It means that such heating rates do not influence the rate of glass transformation any more.

Differences in shapes of transformation effects and α plots depending on heating rates can be explained as follows: At low heating rates the glass crystallizes in a narrow temperature range and the conditions are similar to those at isothermal method. At high heating rates the glass crystallizes over a wide temperature range and because both nucleation and growth rates are temperature dependent, the shapes of transformation effects and α plots are changed.

To determine the overall activation energy E_C and the frequency factor A for crystallization of $NaGd(PO_3)_4$ glass according to the Kissinger peak method, the term $\ln(\beta/T_P^2)$ was plotted *vs.* $1/T_P$. The plots are shown in Fig. 3. From the heating rates ranging between 10 and 72 K min^{-1} and respective peaks temperature a straight line was constructed and the values of E_C and A were determined as 789.91 kJ mol^{-1} and 8.81E+10 s^{-1}, respectively. Another straight line was plotted from respective peak temperatures and heating rates greater than 84 K min^{-1}. However, these temperatures are approximately identical, between 590–592°C, and independent of heating rate. So the determined values of E_C=296.17 kJ mol^{-1} and A=1.44E+42 s^{-1} are not reliable enough. A heating rate of 72 K min^{-1} seems to be the critical heating rate.

When applying the so-called Ozawa plot of lnβ *vs.* $1/T_P$ results similar to those by the Kissinger peak method were obtained. Two straight lines were also constructed (Fig. 3) and the values of E_C were determined as 802.77 and 288.59 kJ mol^{-1} for lower heating rates up to 72 K min^{-1} and for higher ones above this value, respectively.

Microscopic observation

Optical microscopy is a very efficient method for study of crystallization of transparent glassy samples. Using this method the formation of nuclei, their dimensions and movement of the crystallization front can be directly observed, recorded and analyzed. Optical measurements were performed on thin polished glass plates of 2·2 mm^2 in magnitude and 0.3 and 0.7 mm in thickness. In these plates nucleation started at edges and on both polished faces after some time of annealing above the glass transition temperature. This time – time lag of crystallization – depends on the annealing temperature and at 530°C it was 58 h. The number of forming nuclei also depends on temperature and after two weeks annealing at 465°C about

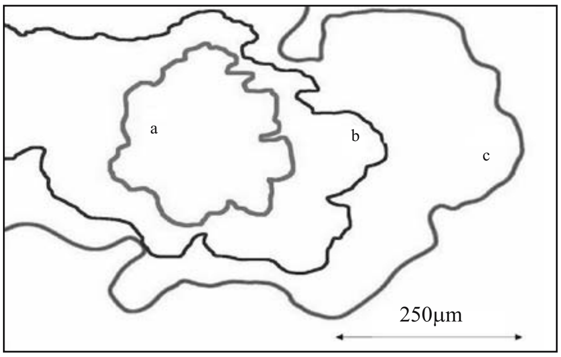

Fig. 4 Position of crystallization front after a – 26, b – 92.5 and c – 259 h

30 nuclei on 1 mm^2 in average were found in the tested sample.

The forming nuclei are round at the very beginning but they are not single crystalline and their growth does not proceed uniformly in all directions. The progress of the crystallization front during annealing at 490°C is shown in Fig. 4. Individual positions are depicted after 26, 92.5 and 259 h since a nucleus has been registered for the first time.

Conclusions

The paper deals with the crystallization study of glass with nominal composition of $NaGd(PO_3)_4$ using non-isothermal DTA and isothermal optical thermomicroscopy. The DTA traces were scanned over a wide range of heating rates between 10 and 115 K min^{-1} and the data obtained were evaluated by the Kissinger and Ozawa plots. The activation energy for crystallization was determined for both lower and higher ranges of heating rates divided by a critical heating rate. Using optical thermomicroscopy, information about formation of nuclei and their growth rates was obtained.

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