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THERMAL PROPERTIES OF OXIDE GLASSES
Part III. Thermal stability of $Li_2O{\cdot}2SiO_2{\cdot}n\mathrm{MeO}_2$ glasses (M=Ti, Zr)

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Glasses with the composition $Li_2O{\cdot}2SiO_2{\cdot}nTiO_2$ and $Li_2O{\cdot}2SiO_2{\cdot}nZrO_2$, where n=0, 0.03, 0.062, 0.1, were prepared and the onset and peak temperatures have been determined by DTA. From these characteristic temperatures, the kinetic parameters describing the nucleation and crystal growth have been obtained by isoconversional methods. The kinetic parameters have been used for the calculation of nucleation and crystal growth times for individual glasses so determining the order of glass stability at reheating. The stability of glasses increases with the content of TiO_2 or ZrO_2 where the increase is higher for ZrO_2. Within the concentration range under study, the increase of both times with the metal oxide concentration is quadratic. It has been discussed that the crystallization kinetics does not obey the Arrhenius law and, therefore, when using the evaluation methods based on this law, the results should not be extrapolated outside the temperature range of the measurements.

Keywords: *crystal growth, crystallization, induction period, non-Arrhenius kinetics, nucleation, stability of glass*

Introduction

Features of the nucleation and crystallization processes are of basic importance in the control of glass formability in technological applications where the formation of nuclei and the subsequent crystal growth should be avoided [1–3]. On the other hand, the formation of nuclei and crystal growth by controlled crystallization can give rise to polycrystalline solids containing residual glass phase called the glass ceramics [4]. Therefore, it is very important to evaluate the thermal stability of glasses *vs.* crystallization [5, 6]. Many authors based the evaluation of glass stability employing the characteristic temperatures of DTA or DSC curves [7–10], crystallization activation energy [11–13] or crystallization rate constants [14, 15]. Unfortunately, these stability criteria are not fixed physical parameters, since they mostly depend on the heating rate and temperature [16]. A very good review of glass stability criteria can be found in [17].

In our previous papers, several criteria of glass stability have been reviewed and tested [18–20]. In another paper, a new criterion for evaluating the thermal stability of glasses based on the induction period of crystallization was suggested and applied to $Li_2O{\cdot}2SiO_2{\cdot}nTiO_2$ systems. It has been discussed that the induction period corresponds to the nucleation stage of crystallization. Comparisons were also made between the new criterion and some existing criteria [21]. Later, the criterion has been applied for the crystallization of metal glasses [22]. In this paper, we study the stability of glasses $Li_2O{\cdot}2SiO_2{\cdot}nTiO_2$ and $Li_2O{\cdot}2SiO_2{\cdot}nZrO_2$ where n=0, 0.03, 0.062 and 0.1. The kinetics of the nucleation stage will be assessed from the onset temperatures of crystallization using the new criterion [21]. The rate of crystal growth will be evaluated using the incremental isoconversional method [23].

Theoretical

Processes occurring in the condensed phase often exhibit an induction period. During the induction period, the technique used registers no signal so that the sample seemingly remains unchanged. As a matter of fact, the induction period is a preparatory stage where the species and intermediates necessary for the occurrence of the main stage of the process are formed. Formation of these intermediates could be detected by another technique [24]. The end of induction period is determined as a sudden increase in the rate of the process under study, i.e. it is determined as the onset time for isothermal measurements or the onset temperature for measurement with linear heating. At the end of induction period, also a sudden change in material characteristics mostly takes place so that the length of induction period is often considered a relative measure of material stability [24].

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It is discussed in [21] that the end of the induction period of crystallization should correspond to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts, i.e. the end of induction period corresponds to completion of the nucleation stage of crystallization. If it is assumed that the crystallization obeys the Arrhenius kinetics, for a given constant temperature the length of induction period can be expressed by an Arrhenius-like relationship [21, 24]:

$$t_\mathrm{n} = A_\mathrm{n} \exp\left[{}^{B_\mathrm{n}}\!/_{T}\right] \tag{1}$$

where t_n is the length of induction period corresponding to the nucleation time, A_n and B_n are constants and T is the absolute temperature. In the case the measurements are carried out at linear increase of temperature, the parameters A_n and B_n occurring in Eq. (1) can be obtained from Eq. (2):

$$\beta = \int_0^{T_\mathrm{x}} \frac{\mathrm{d}T}{A_\mathrm{n} \exp\left[{}^{B_\mathrm{n}}\!/_{T}\right]} \tag{2}$$

where T_x is the onset temperature of the crystallization peak and β stands for the heating rate.

The crystal growth is accompanied with the evolution of heat. The peak maximum of DTA record corresponds to the maximum rate of the crystal growth, i.e. to the moment when the growing crystals start to interconnect. Considering that conversion of the crystallization does not depend on the heating rate, the kinetic parameters of the crystal growth can be obtained by the incremental isoconversional method [23] where the integration is carried out between T_x and T_p, where T_p stands for the maximum peak temperature:

$$\beta = \int_{T_\mathrm{x}}^{T_\mathrm{p}} \frac{\mathrm{d}T}{A_\mathrm{g} \exp\left[{}^{B_\mathrm{g}}\!/_{T}\right]} \tag{3}$$

Duration of the growth can be calculated using an equation analogical to Eq. (1):

$$t_\mathrm{g} = A_\mathrm{g} \exp\left[{}^{B_\mathrm{g}}\!/_{T}\right] \tag{4}$$

From the linear-heating measurements, the parameters A_n and B_n in Eq. (2), or the parameters A_g and B_g in Eq. (3), are obtained by minimising the sum of squares between experimental and theoretical values of temperature using the simplex method [25]. The integration indicated in Eqs (2) and (3) is carried out by the Simpson method.

Experimental

Preparation of glasses

Analytical grade reagents of Li_2CO_3, SiO_2 and TiO_2 ($ZrSiO_4$) were mixed by ball-milling and then melted in a platinum crucible at 1400°C (1500°C) for 2 h. The melts were quenched by pouring into a cold steel mold. The amorphous nature of the as-quenched glasses was confirmed by X-ray diffraction.

Instruments

Thermal stability of glasses was studied using a computerized Derivatograph OD 102 (MOM, Hungary). DTA measurements were carried out in a platinum crucible, the purge gas was air. About 200 mg of powdered samples with a particle size 0.10–0.16 mm and heating rates of 5, 10, 15, 20 and 25°C min^{-1} were used.

Results and discussion

Examples of DTA records for $Li_2O{\cdot}2SiO_2{\cdot}nTiO_2$ glasses can be found in [21]. The DTA curves of $Li_2O{\cdot}2SiO_2{\cdot}nZrO_2$ glasses at heating rate 10 K min^{-1} are shown in Fig. 1. As seen in Fig. 1, as the crystallization proceeds, an exothermic peak is observed since the crystallization is accompanied by heat evolution. The composition of glasses and the characteristic temperatures, i.e. the onset temperatures and the maximum peak temperatures, are summarised in Table 1. All these temperatures increase with increasing the content of both TiO_2 and ZrO_2 where the increase is higher for ZrO_2. The characteristic temperatures increase also with increasing the heating rate.

The kinetic parameters A_n and B_n describing the nucleation stage have been calculated from the values of T_x by Eq. (2) and the isothermal nucleation times have been calculated by Eq. (1). The parameters A_g and B_g describing the crystal growth stage have been calculated from the values of T_x and T_p by Eq. (3) and the crystal growth times have been calculated by Eq. (4). The kinetic parameters are listed in Table 2. The nucleation times and crystal growth times are

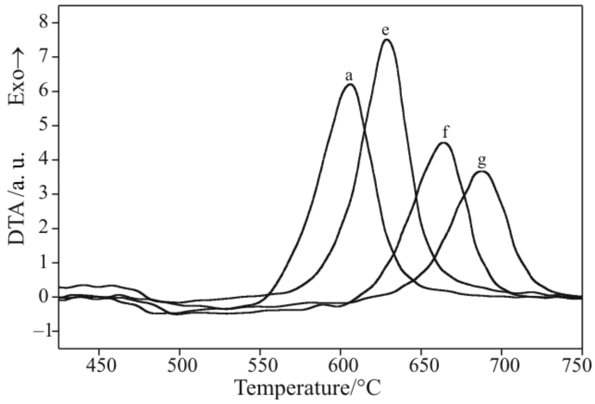

Fig. 1 DTA records of a – $Li_2O{\cdot}2SiO_2$, e – $Li_2O{\cdot}2SiO_2{\cdot}0.03ZrO_2$, f – $Li_2O{\cdot}2SiO_2{\cdot}0.062ZrO_2$ and g – $Li_2O{\cdot}2SiO_2{\cdot}0.1ZrO_2$ glass at heating rate 10 K min^{-1}

Table 1 Onset and peak temperatures for the glasses under study

Glass	T_x/°C					T_p/°C				
	β/°C min^{-1}					β/°C min^{-1}				
	5	10	15	20	25	5	10	15	20	25
a $Li_2O·2SiO_2$	556.7	562.6	572.3	577.9	580.7	595.9	605.4	614.3	617.8	625.7
b $Li_2O·2SiO_2·0.03TiO_2$	559.3	563.1	572.7	574.1	585.3	597.1	606.4	617.0	627.3	628.2
c $Li_2O·2SiO_2·0.062TiO_2$	561.9	581.9	583.3	586.3	589.9	609.1	618.1	623.7	628.6	632.9
d $Li_2O·2SiO_2·0.1TiO_2$	587.8	589.9	584.9	597.8	600.9	616.7	620.7	625.8	630.6	638.8
e $Li_2O·2SiO_2·0.03ZrO_2$	580.9	592.2	597.8	604.3	607.9	615.6	625.9	628.9	635.6	638.6
f $Li_2O·2SiO_2·0.062ZrO_2$	609.8	618.2	632.3	639.1	645.2	647.6	667.9	673.6	676.4	682.5
g $Li_2O·2SiO_2·0.1ZrO_2$	633.1	647.7	657.6	660.9	665.8	672.4	690.5	696.7	697.8	707.0

shown in Figs 2–5. The range of temperatures for the calculation of the nucleation and crystal growth times was chosen from the interval where the characteristic temperatures have been observed. Hence, it can be expected that the values of calculated times are quite realistic since no extrapolation outside the temperature region of the measurement has been carried out.

For the $Li_2O·2SiO_2·nTiO_2$ glasses, the isothermal nucleation times are shown in Fig. 2. It can be seen that the nucleation times of the glasses a and b are practically the same. For n=0.062 (glass c) the nucleation time increases and for n=0.1 (glass d) the increase is quite high. The nucleation times are thus in the order a≈b<c<d. Approximately the same order is seen from Fig. 3 for the crystal growth time. The increase of both nucleation and crystal growth times with increasing content of TiO_2 is not linear, it is much steeper. For the $Li_2O·2SiO_2·nZrO_2$ glasses, the isothermal nucleation times and crystal growth times are shown in Figs 4 and 5. It can be seen that both the nucleation times and the crystal growth times increase with the content of ZrO_2 where the increase of both times with increasing content of ZrO_2 is again steep. The order of both times is a<e<f<<g. Table 3 shows the values of t_n for 550°C and t_g for 575°C. It can be seen that the increase of both times with increasing content of TiO_2/ZrO_2 is quadratic within the concentration range under study.

Table 2 Kinetic parameters of the nucleation and crystal growth for studied glasses

Glass	T_x		T_p–T_x	
	A/min	B/K	A/min	B/K
a	8.077E-22	41150	2.821E-19	38050
b	3.661E-20	38030	3.184E-19	38110
c	5.855E-20	38090	3.600E-24	48460
d	7.808E-27	52080	4.968E-26	52540
e	4.111E-23	45010	1.468E-25	51610
f	2.364E-17	35010	1.905E-18	38800
g	3.059E-20	41990	3.235E-22	48030

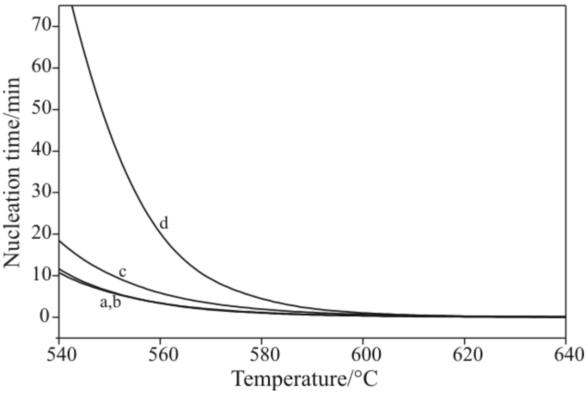

Fig. 2 Nucleation time as a function of temperature for the $Li_2O·2SiO_2·nTiO_2$ glasses

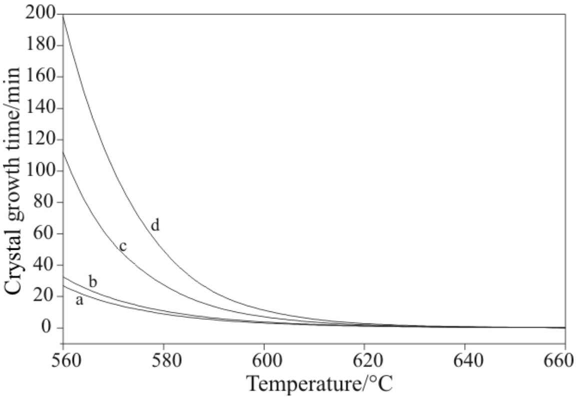

Fig. 3 Crystal growth time as a function of temperature for the $Li_2O·2\ SiO_2·nTiO_2$ glasses

The longer are the nucleation/crystal growth times, the greater is the resistance of a given glass against nucleation/crystal growth upon reheating. Hence, both times define the glass stability. As can be seen from Table 3, the order of stabilities is a≈b<c<d for the $Li_2O·2SiO_2·nTiO_2$ glasses and a<e<f<<g for the $Li_2O·2SiO_2·nZrO_2$ glasses. As seen from Table 2, this order of stabilities cannot be derived from criteria comprising just the activation energy (the relation between the parameter B and the activation energy is

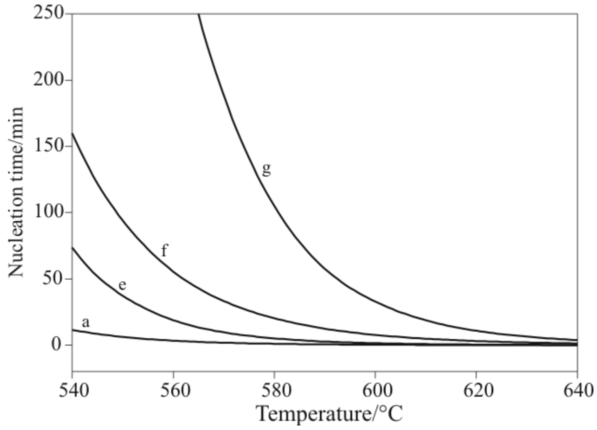

Fig. 4 Nucleation time as a function of temperature for the $Li_2O{\cdot}2SiO_2{\cdot}nZrO_2$ glasses

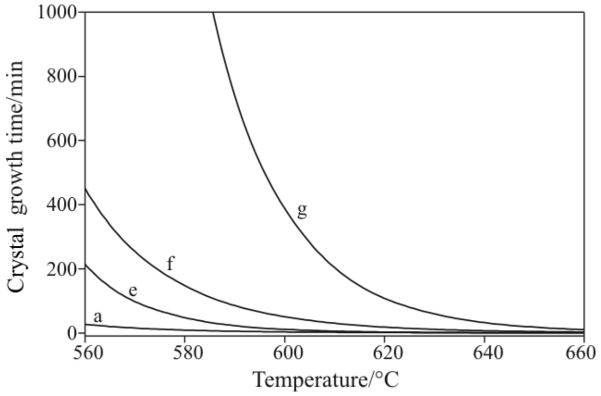

Fig. 5 Crystal growth time as a function of temperature for the $Li_2O{\cdot}2\ SiO_2{\cdot}nZrO_2$ glasses

$B=E/R$ [23, 24]). Within the single-step approximation [26], the activation energy and pre-exponential factor are just parameters without a clear physical meaning. Therefore, greater activation energies may not necessarily be indicative of greater thermal stability. One should be very cautious when using their values for mechanistic or stability considerations. For drawing conclusions, the quantities accessible to measurement should be calculated from the values of kinetic parameters, i.e. reaction rate, temperatures or times. We calculated here the times of isothermal nucleation and crystal growth since these quantities are most illustrative to be compared.

Table 3 Times of nucleation for 550°C and times of crystal growth for 575°C for studied glasses

Glass	t_n (550°C)	t_g (575°C)
a	4.15	8.59
b	4.25	10.4
c	7.31	23.5
d	23.4	39.7
e	23.0	39.2
f	70.0	140
g	436	1270

In general, crystallization proceeds by two elementary processes, i.e., nucleation and growth. The temperature dependences of these processes are different from each other [27]. In this paper we proposed a method to find the kinetic parameters of both processes under the assumption that the rate constants follow the Arrhenius law. Generally, the Arrhenius law does not hold for these processes. For both the processes, the temperature dependences are so complicated that the rate constants decrease beneath the melting temperature with increase of the temperature, and they increase in a lower temperature range with increase of the temperature [27]. Approximated relations for constant rate heating or cooling hitherto used for non-isothermal kinetics of chemical reactions are based on the Arrhenius law. Therefore, these relations cannot generally be applied for non-isothermal kinetics of crystallization [27].

As follows from the Ozawa paper [27], both the nucleation and crystal growth kinetics do not obey the Arrhenius law. Despite this, in the field of thermal analysis, evaluation of the crystallization data is carried out practically exclusively on the methods based on the Arrhenius law. For the crystal growth it has been shown in [28] that the apparent activation energy can be expressed as

$$E_g = E_0 + \frac{\Delta H}{1 - \exp\left[\frac{\Delta H(1-T/T_m)}{RT}\right]}$$

where E_0 is the true acivation energy of the crystal growth, T_m is the crystal melting temperature and ΔH is the enthalpy change of the liquid to crystal phase transformation. T_m is about 1034°C for lithium disilicate [29]. If temperature approaches the melting temperature, the apparent activation energy of the crystal growth is close to infinity. A similarly complicated relationship could be derived from the paper [28] for the apparent activation energy of nucleation. It is necessary to emphasize that the apparent activation energies are obtained from the treatment of experimental data based on the Arrhenius equation. This treatment implicitly involves the assumption that the kinetic data can be approximated by the Arrhenius equation solely within the range of temperatures measured. When using the methods based on the Arrhenius equation, the extrapolation of the results outside the temperature of measurement must not be carried out.

We believe that the approach presented here can be employed generally for the assessment of the stability of any glass against crystallization, including metal and organic glasses. A DOS version of the program KINPAR for the calculation of the kinetic parameters in Eqs (2) and (3) is available on request.

Conclusions

The isothermal times of both nucleation and crystallization are suggested to evaluate the thermal stability of glasses. It is discussed that the completion of nucleation corresponds to the end of the induction period of crystallization and the crystal growth corresponds to the peak of the crystallization DTA record. For the glasses under study, the order of stabilities are not in line with the values of activation energy.

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