

EFFECT OF P₂O₅ AND V₂O₅ ON THE THERMAL STABILITY OF Li₂O·2SiO₂ GLASSES

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The evaluation of the thermal stability of lithium silicate glasses containing P₂O₅ and V₂O₅ against the crystallisation criteria based on the characteristic temperatures, activation energy values, and the length of the crystallisation induction period was conducted. Five glasses having the composition of Li₂O·2SiO₂, Li₂O·2SiO₂·0.05P₂O₅, Li₂O·2SiO₂·0.1P₂O₅, Li₂O·2SiO₂·0.05V₂O₅, Li₂O·2SiO₂·0.1V₂O₅ were prepared and the validity of the criterion was tested by applying it to the glasses. It was found that the thermal stability of oxide glasses decreases with an increasing P₂O₅ and V₂O₅ content, where the essential system of Li₂O·2SiO₂ proved to be the most stable.

INTRODUCTION

Glasses in the Li₂O·SiO₂ system crystallise easily at temperatures at which their viscosity is still high and consequently this system has been used as the basis of a number of glass-ceramics as crystallised glasses [1]. Many studies exist concerning the effect of the addition of oxide glasses on the crystallisation of Li₂O·SiO₂ glasses. The mechanism of nucleation in the glass containing V₂O₅ may be similar to that in the glass containing P₂O₅, which tends to form some stoichiometric compounds with Li₂O before the Li₂O·SiO₂ crystals are formed in the glass [1]. Infrared spectroscopy (IR) is an important tool for understanding the structure and dynamics of amorphous materials. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping. The spectra of many solid variables can affect the absorption peaks, and the assignment of the vibration peaks of the atoms is very difficult. Usually, the method of repeated occurrence is followed by analysing the IR spectrum of solid materials [2].

On the other hand, those glasses that serve as an intermediate product for fabricating glass-ceramics are expected to possess thermal stability. Therefore, it is very important to appropriate evaluate the thermal stability of glasses vs. the crystallisation [3, 4].

Many authors have based their evaluation of the glass stability employing the characteristic temperature of differential thermal analysis (DTA)

and differential scanning calorimetry (DSC) curves [5], crystallisation activation energy [6,7] or crystallisation rate constants. Cheng [8] evaluated the criterion:

$$k_f(T) = A \cdot \exp \left[\frac{-E}{RT} (T_p - T_f) \right] \quad (1)$$

where T_f is the inflection point temperature, T_p is the maximum peak temperature on the DTA curve and A is the frequency factor and E stands for the activation energy. These stability criteria are not fixed physical parameters since they depend on the heating rate and temperature.

In our previous papers, several thermal stability criteria of glasses have been tested and applied to the Li₂O·2SiO₂·xTiO₂ and Li₂O·2SiO₂·xZrO₂ glasses [9-13], in which the criterion of the thermal stability of the glass systems were based on the induction period of crystallisation. The order of the stabilities evaluated by the new criterion is in agreement with the order based on the characteristic temperatures and values of the activation energy. The results indicate that the new criterion enables one to discriminate among the thermal stabilities of the silicate glass samples. It can be expected that it can be generally employed for the assessment of the thermal stability of any glass against the crystallisation, including metal and organic glasses [9,10,13]. A spectral analysis, the activation energies and the induction period were used to characterise the Li₂O·2SiO₂·xP₂O₅ (x = 0, 0.05 and 0.1) and Li₂O·2SiO₂·xV₂O₅ systems (x = 0.05 and 0.1).

The number of particles precipitated in the glass containing P_2O_5 and V_2O_5 was so large and their size was so small that any observation under an optical microscope was impossible [1].

EXPERIMENTAL

Preparation of the glasses

Analytical grade reagents Li_2CO_3 , SiO_2 and P_2O_5 or V_2O_5 were mixed by ball-milling and melted in a platinum crucible at $1400\text{ }^\circ\text{C}$ for 2 h. The melts were quenched by pouring them into a cold steel mould.

Instruments

The thermal stability of the glasses was studied using a Mettler Toledo TGA/DSC 2 STAR^e System. The DSC curves were measured in nitrogen using a corundum ceramic crucible. About 10 – 20 mg of the powdered samples with a particle size of 0.16 – 0.10 mm with a heating rate of 10, 15, 20 and $25\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ were used. The calibration of the temperature and enthalpy scales was conducted using pure indium (In).

The infrared spectra were recorded at room temperature with an SFT Fourier Transform Infrared spectrometer in the range of 500 to 4000 cm^{-1} by the KBR disc technique.

RESULTS AND DISCUSSION

To evaluate the thermal stability of the $Li_2O\cdot 2SiO_2\cdot xP_2O_5$ ($x = 0, 0.05$ and 0.1) and $Li_2O\cdot 2SiO_2\cdot xV_2O_5$ ($x = 0.05$ and 0.1) glasses, a criterion based on the induction period of the crystallisation and activation energies was used. It is discussed in [10] that the end of the induction period of the crystallisation should correspond to the moment where the crystallisation nuclei have already been formed and the intense growth of the crystals starts, i.e., the end of the induction period corresponds to the completion of the nucleation stage of crystallisation. If it is assumed that the crystallisation obeys Arrhenius kinetics, for a given constant temperature, the length of the induction period can be expressed by an Arrhenius-like relationship [11].

$$t_i = A_i \exp[B_i/T] \quad (2)$$

where t_i is length of the induction period corresponding to the nucleation time, A_i and B_i are constants and T is the absolute temperature. In the case where

the measurements are carried out with a linear increase in the temperature, the parameters A_i and B_i occurring in Equation 2 can be obtained from Equation 3:

$$\beta = \int_0^{T_x} \frac{dT}{A_i \exp[B_i/T]} \quad (3)$$

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

Typical DSC curves of $Li_2O\cdot 2SiO_2\cdot xP_2O_5$ and $Li_2O\cdot 2SiO_2\cdot xV_2O_5$ ($x = 0, 0.05$ and 0.1) glasses at the heating rate $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ are shown in Figure 1.

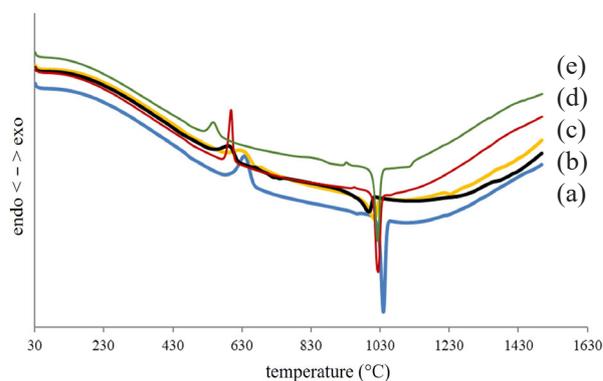


Figure 1. DSC curves of: (a) $Li_2O\cdot 2SiO_2$, (b) $Li_2O\cdot 2SiO_2\cdot 0.1V_2O_5$, (c) $Li_2O\cdot 2SiO_2\cdot 0.05V_2O_5$, (d) $Li_2O\cdot 2SiO_2\cdot 0.05P_2O_5$, (e) $Li_2O\cdot 2SiO_2\cdot 0.1P_2O_5$ glasses at a heating rate $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

The exothermic DSC peaks having a maximum at about $500 - 600\text{ }^\circ\text{C}$ arise due to the crystallisation process which is related to the transformation of the crystalline phase of lithium metasilicate and/or lithium disilicate and/or phosphor disilicate as the dominant components. The onset temperatures T_x were directly determined from the DSC curves and are summarised in Table 1.

Table 1. Onset temperatures of the oxide glasses $Li_2O\cdot 2SiO_2$, $Li_2O\cdot 2SiO_2\cdot 0.1V_2O_5$, $Li_2O\cdot 2SiO_2\cdot 0.05V_2O_5$, $Li_2O\cdot 2SiO_2\cdot 0.05P_2O_5$ and $Li_2O\cdot 2SiO_2\cdot 0.1P_2O_5$.

Glass	T_x ($^\circ\text{C}$)			
	β ($^\circ\text{C}\cdot\text{min}^{-1}$)			
	10	15	20	25
$Li_2O\cdot 2SiO_2$	600.6	610.2	623.1	622.2
$Li_2O\cdot 2SiO_2\cdot 0.05P_2O_5$	585.2	598.7	603.8	610.1
$Li_2O\cdot 2SiO_2\cdot 0.1P_2O_5$	524.9	531.0	532.8	536.9
$Li_2O\cdot 2SiO_2\cdot 0.05V_2O_5$	558.6	592.1	601.3	605.7
$Li_2O\cdot 2SiO_2\cdot 0.1V_2O_5$	551.1	562.8	571.7	573.6

In our previous papers [10–13], it was found that the criterion (induction period of the crystallisation) is in agreement with the order based on the characteristic temperatures. Therefore, this criterion was applied to the Li₂O·2SiO₂·xP₂O₅ and Li₂O·2SiO₂·xV₂O₅ glass system. From the linear-heating measurements, the parameters A_i and B_i in Equation 3 were obtained by minimising the sum of squares between the experimental and theoretical values of the temperature using the simplex method. The integration indicated in Equation 3 is carried out by the Simpson method. The resulting values are listed in Table 2.

Table 2. The parameters A and B and the values of the induction period t_i of the oxide glasses Li₂O·2SiO₂, Li₂O·2SiO₂·0.1V₂O₅, Li₂O·2SiO₂·0.05V₂O₅, Li₂O·2SiO₂·0.05P₂O₅ and Li₂O·2SiO₂·0.1P₂O₅.

Glass	A (min)	B (K)	t_i (min ⁻¹)
Li ₂ O·2SiO ₂	$0.5999 \cdot 10^{-13}$	27440	204.7
Li ₂ O·2SiO ₂ ·0.05P ₂ O ₅	$0.1375 \cdot 10^{-16}$	34100	157.9
Li ₂ O·2SiO ₂ ·0.1P ₂ O ₅	$0.4594 \cdot 10^{-18}$	34040	4.1
Li ₂ O·2SiO ₂ ·0.05V ₂ O ₅	$0.2814 \cdot 10^{-17}$	35290	13.8
Li ₂ O·2SiO ₂ ·0.1V ₂ O ₅	$0.9626 \cdot 10^{-19}$	36780	2.1

The temperature dependence of the lengths of the induction period for the individual glasses is shown in Figure 2. It can be seen that the thermal stability of the studied glasses against the crystallisation is in the order Li₂O·2SiO₂·0.1P₂O₅ < Li₂O·2SiO₂·0.05P₂O₅ < Li₂O·2SiO₂, i.e., the system Li₂O·2SiO₂ is the most stable against the crystallisation.

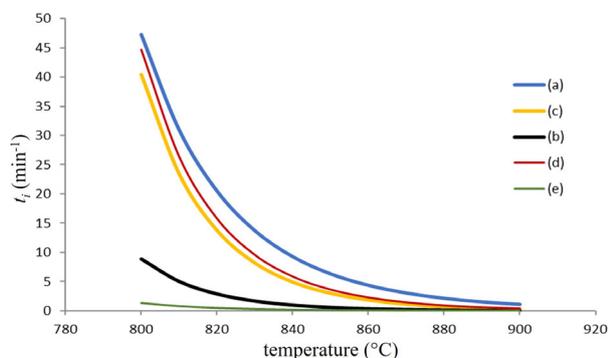


Figure 2. Induction period as a function of the temperature of (a) Li₂O·2SiO₂, (b) Li₂O·2SiO₂·0.1V₂O₅, (c) Li₂O·2SiO₂·0.05V₂O₅, (d) Li₂O·2SiO₂·0.05P₂O₅, (e) Li₂O·2SiO₂·0.1P₂O₅ glasses.

To determine the activation energies $E(T_p)$ and $E(\beta)$, many authors [14, 9, 15, 16] have used the Kissinger plot:

$$\ln(T_p^2/\beta) = E(T_p)/RT_p + \ln E(T_p)/R - \ln A \quad (4)$$

where: β is the heating rate, or the Ozawa plot [17], based on Equation 5:

$$\ln(\beta) = -E(\beta)/RT_p + C \quad (5)$$

or the Flynn–Wall–Ozawa (FWO) method [18, 19], which is based on the Doyle approximation for heterogeneous chemical reactions – Equation 6:

$$\log(\beta) = \log\left(\frac{AEa}{Rg(\alpha)}\right) - 2.315 - 0.4567 \frac{Ea}{RT} \quad (6)$$

where: $g(\alpha)$ is a conversional function, E_a is the activation energy, R is the gas constant, and A is a pre-exponential factor. The values of the activation energy of the glasses for the different heating rates at a constant degree of conversion were evaluated by the software STAR^e SW 13.00 and are summarised in Table 3.

Table 3. The values of the activation energies of the oxide glasses Li₂O·2SiO₂, Li₂O·2SiO₂·0.1V₂O₅, Li₂O·2SiO₂·0.05V₂O₅, Li₂O·2SiO₂·0.05P₂O₅ and Li₂O·2SiO₂·0.1P₂O₅.

sample	$E(T_p)$ (kJ·mol ⁻¹)	$E(\beta)$ (kJ·mol ⁻¹)	$E(\alpha)$ (kJ·mol ⁻¹)
Li ₂ O·2SiO ₂	216.7	231.4	213.2
Li ₂ O·2SiO ₂ ·0.05P ₂ O ₅	218.6	233.02	219.4
Li ₂ O·2SiO ₂ ·0.1P ₂ O ₅	407.16	420.5	407.9
Li ₂ O·2SiO ₂ ·0.05V ₂ O ₅	93.13	107.33	93.56
Li ₂ O·2SiO ₂ ·0.1V ₂ O ₅	206.45	220.34	206.8

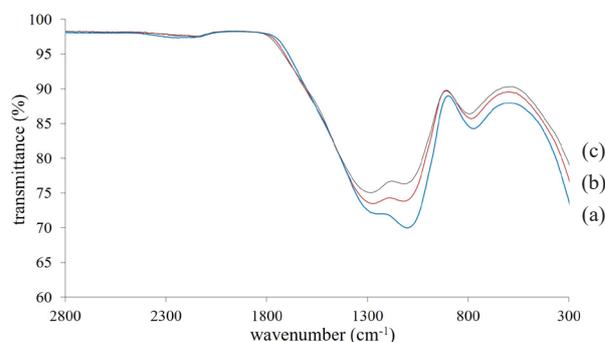


Figure 3. Infrared spectra of (a) the Li₂O·2SiO₂, (b) the Li₂O·2SiO₂·0.05P₂O₅, (c) the Li₂O·2SiO₂·0.1P₂O₅ glasses.

The structural changes that occur in the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glasses during the increase in the P_2O_5 content are manifested in the infrared spectra (Figure 3).

Table 4. Selected absorption maxima of the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$, $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.05\text{P}_2\text{O}_5$ and $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{P}_2\text{O}_5$.

Assignment	Band position (cm^{-1})		
	A	b	c
ν Si-OH+	1019	1011.5	1008
ν Si-O-M	941.7	-	-
$\delta / \nu_{\text{sym}}$ Si-O-Si	783.4	777	772.1
ν_2 Si-O-Si	772.1	-	-

The broad band at $\sim 780 \text{ cm}^{-1}$ corresponds to the ν_{sym} (Si-O-Si) vibration. As Table 4 shows, the addition of P_2O_5 to the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glasses causes one important effect at $\sim 940 \text{ cm}^{-1}$ corresponding to the ν (Si-O-M) vibration.

CONCLUSIONS

It is very important to evaluate the thermal stability of glasses against crystallisation. The criteria based on the activation energy or the crystallisation rate constant do not always fit with the actual experimental observations. Therefore, in this paper, the influence of the added P_2O_5 and V_2O_5 on the thermal stability of the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass system was studied by means of the criteria based on the crystallisation induction period and characteristic temperatures. Parameters A and B are obtained from the dependence of the onset temperature of the crystallisation peak on the heating rate in the non-isothermal DSC measurements. The order of the thermal stability of the studied glasses against crystallisation, on the basis of the induction period and characteristic temperatures, is $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{P}_2\text{O}_5 < \text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{V}_2\text{O}_5 < \text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.05\text{V}_2\text{O}_5 < \text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.05\text{P}_2\text{O}_5 < \text{Li}_2\text{O}\cdot 2\text{SiO}_2$. The addition of P_2O_5 and V_2O_5 to the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass system decreases its thermal stability. On the basis of the activation energies, an opposite order was found. According to Branda [6], devitrification occurs in the temperature range where the number of formed nuclei and the crystal growth frequency factor are high enough so that the crystal growth kinetic barrier is overcome. Therefore, the greater activation energies obtained from DSC should not necessarily be indicative of a greater thermal stability. The addition of small amount P_2O_5 to $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glasses causes one important effect in the infrared spectra at $\sim 940 \text{ cm}^{-1}$ corresponding to the ν (Si-O-M) vibration.

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