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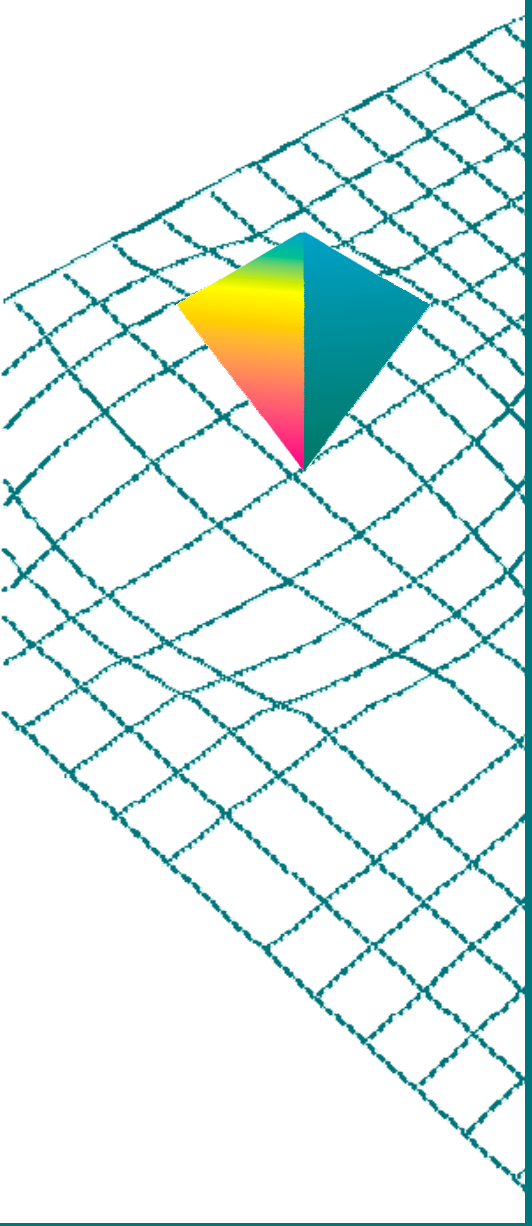

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50. Internationales Wissenschaftliches Kolloquium
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CRYSTALLIZATION KINETICS OF Li_2O . 2 SiO_2 . n RO_2 (R = Ti, Zr) GLASSES

ABSTRACT

For evaluation of the thermal stability of glasses against crystallization, various criteria have been used. Dietzel [1] introduced the first simple criterion, $\Delta T = T_x - T_g$ (T_x is the crystallization onset temperature, T_g is the glass transition temperature). Hrubý [2] proposed the H_r criterion, where $H_r = (T_x - T_g)(T_x - T_g) / T_g$. Some authors [3-6] suggested that the crystallization activation energy (E) and crystallization rate constants, $k(T)$, could also be used to evaluate the glass stability [7].

In this paper, activation energy have been applied for the $Li_2O.2SiO_2$. n RO_2 system (R = Ti, Zr) [8]. It was found, that the characteristic temperatures (maximum peak temperature, T_p, and inflection point temperature, T_f) increase with the increasing heating rates. On the basis values of activation energy the system $Li_2O.2SiO_2.0{,}03\ ZrO_2$ is the most stable.

INTRODUCTION

Glass ceramic materials are polycrystalline solids containing a residual glassy phase prepared by melting glass and forming in into products that are subjected is controlled crystallization such that they posses a valuable combination of the favorable properties of both glasses and ceramics. Consequently these polycrystalline materials produced via the controlled crystallization of glasses are finding many applications as engineering materials and as domestic ware.

Glasses in the Li_2O . 2 SiO_2 system crystallize easily at temperatures at which their viscosity is still high enough to retain the shape of a formed article and consequently this system has been used as a basis of a number of glass-ceramics or crystallized glasses [9, 10]. There have been published many papers concerning the effect of addition of different oxides on thermal stability of $Li_2O.2SiO_2$ glasses. Studies of the influence of P_2O_5 [11], TiO_2 [12], NiO and

V_2O_5 [13] on the crystallization process showed that these components acted as nucleating agents.

Many authors used the so-called Kissinger plot, based on the following equation (1):

$$\ln T_0^2/ß = E/RT_0 + \ln E/R - \ln A \quad (1)$$

(where $ß$ = heating rate, $T_o = T_p, T_f$), or Ozawa plot, based on the equation (2):

$$\ln ß = -E/RT_p + C \quad (2)$$

Only activation energy can be determined by this method.

EXPERIMENTAL

Preparation of glasses

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

Instruments

The thermal stability of glasses was studied with a derivatograph MOM Budapešť. The measurements of DTA curves were carried out in air. Sample masses of about 0,2 - 0,4 g, fraction 0,16 - 0,10 mm and rates of temperature increase of 5,10,15,20 and 25 $^oC.m^{-1}$ were used.

RESULTS AND DISCUSSION

The characteristic temperatures from the DTA curves are summarized in Table 1. The maximum peak temperatures (T_p) were directly determined from DTA curves (Fig.1). The inflection point temperature (T_f) was determined from the maximum peak on the DDTA curve. The characteristic temperatures increase with the increasing heating rates.

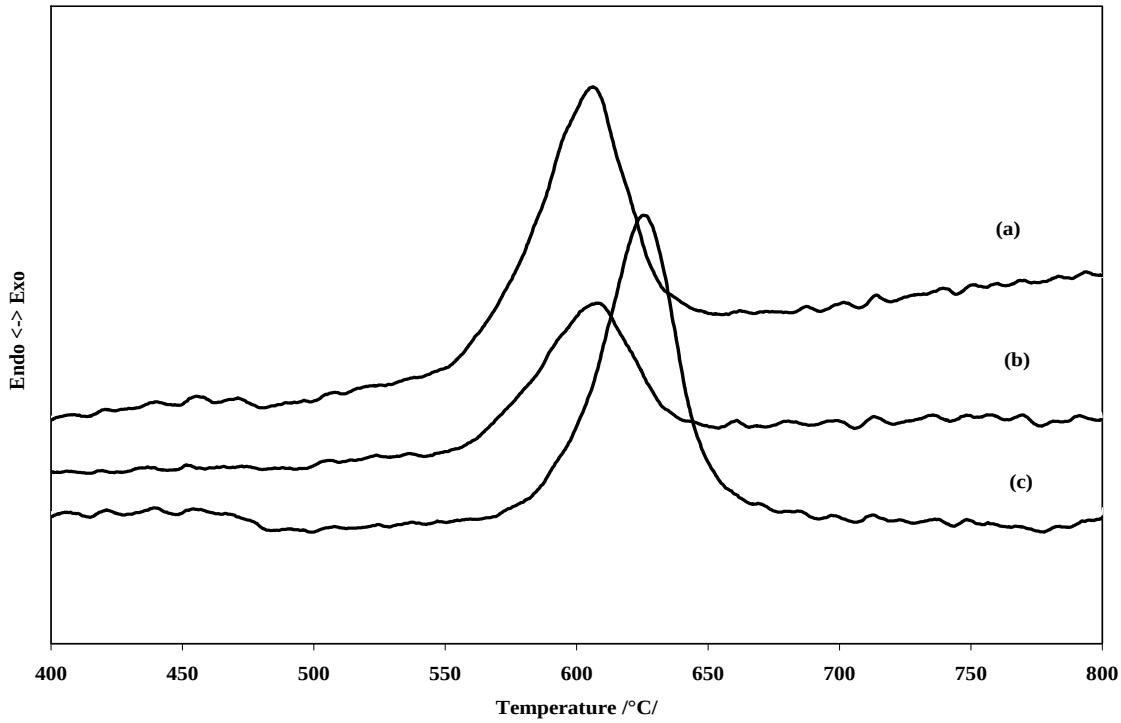

Fig.1: DTA curves of (a) $Li_2O.2SiO_2$, (b) $Li_2O.2SiO_2.0{,}03\ TIO_2$ and (c) $Li_2O.2SiO_2.0{,}03\ ZrO_2$, heating rate 10 °C/min

Tab.1: Characteristic temperatures of studied glasses

Glass	T_f / °C /					T_p / °C /				
	β / °C/min /					β / °C /min/				
	5	10	15	20	25	5	10	15	20	25
Li_2O . 2 SiO_2	580,4	588,3	601,6	603,6	611,8	595,9	605,4	614,3	617,8	625,7
Li_2O . 2 SiO_2 . 0,03 ZrO_2	603,6	611,5	620,3	621,8	625,6	615,6	625,9	628,9	635,6	638,6
Li_2O . 2 SiO_2 . 0,062 ZrO_2	628,4	652,9	653,4	6661,0	668,5	647,6	667,9	673,6	676,4	682,5
Li_2O . 2 SiO_2 . 0,1 ZrO_2	654,8	672,8	682,9	683,3	687,9	672,4	690,5	696,7	697,8	707,0
Li_2O . 2 SiO_2 . 0,03 TiO_2	581,7	592,9	609,6	610,4	612,6	597,1	606,4	617,0	627,3	628,2
Li_2O . 2 SiO_2 . 0,062 TiO_2	591,6	603,7	610,6	616,5	620,1	609,1	618,1	623,7	628,6	632,9
Li_2O . 2 SiO_2 . 0,1 TiO_2	596,5	608,7	612,7	619,4	622,6	616,7	620,7	625,8	630,6	638,8

For determining the activation energy, we used the Kissinger plot, equation (1) and Ozawa plot, equation (2) (Tab.2). Obviously a plot of (ln T_o^2 / β) versus $1/T_o$ and plot of (ln β) versus $1/T_p$, would be linear and activation energy can be easily determined from the slope and the interception of the plot.

Tab.2: Activation energies of studied glasses

Glass	$E(T_f)$ /kJ/mol/	$E(T_p)$ /kJ/mol/	$E(\beta)$ /kJ/mol/
Li_2O . 2 SiO_2	295,2	339,8	354,5
Li_2O . 2 SiO_2 . 0,03 ZrO_2	447,9	457,0	471,9
Li_2O . 2 SiO_2 . 0,062 ZrO_2	272,1	324,7	340,2
Li_2O . 2 SiO_2 . 0,1 ZrO_2	332,1	356,1	372,1
Li_2O . 2 SiO_2 . 0,03 TiO_2	254,2	288,7	303,4
Li_2O . 2 SiO_2 . 0,062 TiO_2	346,1	438,1	453,0
Li_2O . 2 SiO_2 . 0,1 TiO_2	342,3	452,2	467,1

The results indicate that the glass $Li_2O.2SiO_2.0{,}03\ ZrO_2$ is the most stable vs. crystallization from studied samples and values of activation energy increases with small amount ZrO_2, and degreases with small amount TiO_2.

The initial crystallization of the lithium metasilicate can by explained since the activation energy for its crystallization is much less than that for crystallization of lithium disilicate. The addition of TiO_2 to $Li_2O.2SiO_2$ system results in a successive transformation of Li_2SiO_3 to $Li_2Si_2O_5$. But addition of ZrO_2 results in a successive transformation of $Li_2Si_2O_5$ to Li_2SiO_3. It was confirmed by X-ray diffraction at powdered samples heated at 595 °C.

From the literature it is namely known that the bulk nucleation is usually dominant in $Li_2O.2SiO_2$ glass. In the glass containing TiO_2 and ZrO_2 the surface crystallization is dominant [16]. Thus, the results obtained can also be affected by different nucleation mechanisms, which depends on the TiO_2 and ZrO_2 content.

CONCLUSIONS

The thermal stability of $Li_2O.2SiO_2.n\ RO_2$ (R = Ti, Zr) glasses was studied using differential thermal analysis. For evaluating the thermal (kinetic) stability of studied glasses vs. crystallization the values of activation energies have been used. On the basis of these parameters the glass $Li_2O.2SiO_2.0{,}03ZrO_2$ is the most stable against crystallization.

The exothermic peaks having the maximum at about 600 – 700 °C are due to the crystallization process which is related to the formation of crystalline phase of lithium metasilicate and/or lithium disilicate as dominant components, detected in the X-ray diffraction measurements.

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