

EFFECT OF ADDED TiO₂ AND ZrO₂ ON THE CRYSTALLIZATION OF Li₂O - SiO₂ GLASSES: THERMAL AND DIFFRACTION PROPERTIES

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Submitted November 7, 2008; accepted February 20, 2009

Keywords: Crystallization of Li₂O - SiO₂ glasses, Thermal properties, Diffraction analysis

Five glasses with the composition of Li₂O - 2 SiO₂ (a), Li₂O - 2 SiO₂ - 0.03 TiO₂ - 0.03 ZrO₂ (b), Li₂O - 2 SiO₂ - 0.05 TiO₂ - 0.05 ZrO₂ (c), Li₂O - 2 SiO₂ - 0.075 TiO₂ - 0.075 ZrO₂ (d), Li₂O - 2 SiO₂ - 0.1 TiO₂ - 0.1 ZrO₂ (e) were prepared and the relationship between structural and kinetic parameters of thermal stability vs. crystallization has been studied. The XRD patterns proved of the presence of lithium metasilicate as a favoured crystallization phase. The order of thermal stability vs. crystallization of studied glass systems based on the values of activation energy is $a \approx b < c < d < e$. It has been shown that the values of activation energy obtained from the Ozawa and Kissinger are equivalent.

INTRODUCTION

Features of nucleation and crystallization processes are basic importance in the control of glass formation in technological application where the formation of nuclei and subsequent crystal growth must be avoided [1]. 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 glass ceramics [2].

Therefore, it is very important to evaluate the thermal stability of glasses against crystallization and their phase analysis. Many authors based the evaluate on glass stability employing the characteristic temperatures of DTA and DSC curves [3-5], crystallization activation energy [6,7] or crystallization rate constants [8,9]. Unfortunately, these stability criteria are not fixed physical parameters, since they mostly depend on the heating rate and temperature.

In our previous papers, several criteria of glass stability have been reviewed and tested [10-12]. In this paper, we study the thermal stability and phase analysis of glasses Li₂O - SiO₂ - n TiO₂ - n ZrO₂ where $n = 0, 0.03, 0.05, 0.075$ and 0.1 .

EXPERIMENTAL

Preparation of glasses

Analytical grade reagents of Li₂CO₃, SiO₂, TiO₂ and ZrSiO₄ were well mixed by ball-milling and then melted in a platinum crucible at 1400°C for 2 hours. The melts

were quenched by pouring them into a cold steel mold.

The 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 of 0.10-0.16 mm and heating rates of 5, 10, 15, 20 and 25°C/min were used.

The glass samples will be further denoted as follows:

- (a) Li₂O - 2SiO₂
- (b) Li₂O - 2SiO₂ - 0.030 TiO₂ - 0.030 ZrO₂
- (c) Li₂O - 2SiO₂ - 0.050 TiO₂ - 0.050 ZrO₂
- (d) Li₂O - 2SiO₂ - 0.075 TiO₂ - 0.075ZrO₂
- (e) Li₂O - 2SiO₂ - 0.100 TiO₂ - 0.100 ZrO₂

RESULTS AND DISCUSSION

Diffraction data of the studied glass systems heated at 595°C [11] are summarized in Table 1. Although lithium disilicate has been also formed, the lithium metasilicate Li₂SiO₃ was the kinetically favoured crystalline phase. The peaks at $2\theta = 21.93^\circ$ and 31.35° are characteristic for Li₂SiO₃ (Table 1). The intensity increase in the order $a < b < c < d < e$.

The exothermic DTA peaks having the maximum at about 612–795°C (Table 2) arise due to the crystallization process which is related to the formation of crystalline phase of lithium metasilicate as dominant component, as detected in the X-ray diffraction measurements. To determine the activation energy associated with the crystallization process, the Kissinger and Ozawa methods, expressed by Equations (1) and (2), were applied [10]:

$$\ln(T_p^2/\beta) = -E(T_p)/RT_p - \ln E/R + \ln A \quad (1)$$

Paper presented at the Czech and Slovak Conference on Glass, Luhačovice, November 5-7, 2008.

Table 1. Diffraction data of the studied glass systems heated at 595°C for 2 hours.

(a)		(b)		(c)		(d)		(e)	
2 θ (°)	d (Å)	2 Θ (°)	d (Å)	2 Θ (°)	d (Å)	2 θ (°)	d (Å)	2 Θ (°)	d (Å)
14.15	7.262	14.11	7.283						
19.12	5.386	19.02	5.414	18.96	5.432				
		21.94	4.701	21.93	4.703	21.95	4.698	21.91	4.707
27.79	3.725	27.74	3.731	27.72	3.734	27.73	3.733		
28.41	3.645	28.36	3.649	28.41	3.645	28.4	3.646		
29.04	3.568	28.93	3.581	28.87	3.588	28.89	3.586		
		31.35	3.311	31.33	3.313	31.34	3.312	31.31	3.315
35.47	2.936								
35.89	2.903	35.8	2.91	35.65	2.922				
		38.48	2.714	38.46	2.716	38.46	2.716	38.41	2.719
44.1	2.382	43.95	2.39	43.97	2.399	43.95	2.39		
44.8	2.347					45.11	2.332	45.09	2.333
46.01	2.289	45.14	2.331	45.1	2.332				
51.73	2.05	51.63	2.054	50.57	2.094	50.57	2.094	50.75	2.087
52.89	2.009	53.98	1.971					51.97	2.042
54.22	1.963	54.23	1.963						
58.06	1.843	58.66	1.832						
59.55	1.801	59.48	1.803	59.42	1.805				
		60.78	1.769	60.78	1.768	60.63	1.772	60.64	1.772

Table 2. Kinetic parameters of studied glass systems.

β (°C/min)	T_p (± 1.4°C) (°C)					$E(T_p)$ (± 8 %) (kJ/mol)	$E(\beta)$ (± 8 %) (kJ/mol)
	5	10	15	20	25		
Glass (a)	612.1	640	658.1	677	682.4	125	140
Glass (b)	656.5	691.5	707.2	727.2	750.8	125	141
Glass (c)	675.3	699.3	723	743.9	761.7	132	149
Glass (d)	696.9	723.1	741.4	760.4	774.5	158	174
Glass (e)	707.6	736.1	760.5	776.8	794.6	159	176

$$\ln \beta = -E(\beta) / RT_p + C \quad (2)$$

where T_p is the maximum peak temperatures on the DTA record, $E(T_p)$ and $E(\beta)$ are the activation energies obtained from Kissinger and Ozawa methods, respectively. The activation energies are given in Table 2. On the basis of their values the resulting order of the stability against crystallization is $a \approx b < c < d < e$, i.e. the increase of the amount of the TiO₂ and ZrO₂ oxides cause the increase of the values of the activation energies. The glasses with TiO₂ and ZrO₂ are more stable against crystallization than the glasses without these components.

CONCLUSIONS

The relation between structural and kinetic parameters of thermal stability vs. crystallization of Li₂O . 2 SiO₂ -n TiO₂ - n ZrO₂ systems (n = 0; 0.03; 0.05; 0.075 and 0.1) has been studied by X-ray diffraction and thermal analysis. The XRD patterns proved the presence of lithium metasilicate as kinetically favoured crystalline phase. The order of thermal stability vs. crystallization of studied glass systems based on the values of activation energy is $a \approx b < c < d < e$. It has been shown that the values of activation energies obtained from the Ozawa and Kissinger method are equivalent.

Acknowledgement

This work has been supported by Slovak Grant Agency VEGA, of Slovak Ministry of Education (grant No 1/3161/006) and AV 4/2014/08.

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