

A STUDY OF VARIOUS ADDITION TITANIUM AND ZIRCONIUM DIOXIDES ON THE THERMAL STABILITY OF LITHIUMSILICATE GLASSES.

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ABSTRACT: The glasses with the composition of $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 \cdot x \text{ZrO}_2 \cdot x \text{TiO}_2$ (where $x = 0; 0,015; 0,031; 0,05; 0,075; 0,1; 0,15; 0,2$) were prepared and the relationship between structural and selected parameters of thermal stability vs. crystallization has been studied by X-ray diffraction, IR spectra and thermal analysis. The order of thermal stability vs. crystallization of studied glass systems based on the results of XRD is increasing with higher addition both oxides. The same order was obtained from the values of activation energy.

KEY WORDS: thermal stability, oxide glasses, activation energy, zirconium, lithium

1. INTRODUCTION

The crystallization kinetics of $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 \cdot x \text{ZrO}_2 \cdot x \text{TiO}_2$ was investigated using DTA, XRD, and IR spectra studies. Moreover, the influence of nucleating agents such as TiO_2 , ZrO_2 oxides, base glasses was elucidated.

Glass ceramic materials are polycrystalline solids containing a residual glassy phase prepared by melting glass and forming it into products that are subjected to controlled crystallization such that they possess a valuable combination of the favourable properties of both glasses and ceramics [1–3]. Consequently these polycrystalline materials produced via the controlled crystallization of glasses are finding many applications as engineering materials and domestic ware. In fact, examined system is technologically important in several areas including glass and glass ceramics containing $\text{Li}_2\text{Si}_2\text{O}_5$ and Li_2SiO_3 , zirconia based refractoriness and enamels containing Li_2ZrO_3 [4, 5]. Glasses in the $\text{Li}_2\text{O} \cdot \text{SiO}_2$ 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 the basis of a number of glass – ceramics or crystallized glasses [6].

One of the first information about glasses is thermal stability vs. crystallization. In order to characterize the tendency of glass to crystallize it can be encountered that, as a criterion, characteristic temperatures from DTA curves, values of activation energy (E_a), combined criteria such as E_a / RT or the crystallization rate constant $k(T)$ are used [7, 8]. In this paper the relation between structural parameters (X-ray diffraction and IR spectral data) and kinetic parameters (the values of activation energy) for $\text{Li}_2\text{O} \cdot 2 \text{SiO}_2 \cdot x \text{ZrO}_2 \cdot x \text{TiO}_2$ systems (where $x = 0; 0,015; 0,031; 0,05; 0,075; 0,1; 0,15; 0,2$) has been studied from the point of view of thermal stability vs. crystallization.

2. EXPERIMENTAL

Preparation of glasses

Analytical grade reagents of Li_2CO_3 , SiO_2 and ZrSiO_4 were well mixed by ball – milling and then melted in a platinum crucible at 1500 °C for 2 h. The melts were quenched by pouring them into

a cold steel mold. The amorphous nature of the as quenched glasses was confirmed by X-ray diffraction.

3. INSTRUMENTS

The thermal stability of glasses was studied using a modified Derivatograph OD 102 (MOM Budapest). The modification of DTA equipment consists of a digitalization of obtained values by means of computer. The measurements of DTA curves were carried out in air using OxAl crucibles. Approximately 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 were used.

Powder diffraction patterns were taken on automatic Brac – Brentano DRON UM-1 diffractometer with Cu K α radiation.

The infrared spectra were recorded at room temperature with a Philips analytical UP 98000 FTIR spectrometer in the range of 4500 – 400 cm $^{-1}$.

4. RESULTS AND DISCUSSION

To evaluate the thermal stability of studied glasses various criteria have been used. Not only the characteristic temperatures of a crystallization exotherm (T_p – the maximum peak temperature, T_f – the inflection peak temperature), but also the values of activation energy.

All these temperatures increase with the increasing content both oxides, and with increasing heating rates. Since the greater these temperatures, the more stable the glass should be, the system containing 0,2 mol TiO $_2$ and ZrO $_2$ (last system) are more stable vs. crystallization than any investigated system in this work.

For determining the activation energy the Kissinger plot (Eq. 1) and Ozawa plot (Eq. 2) have been used:

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

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

where $o = p$ or f , β is heating rate, R is gas constant, E is activation energy and A is frequency factor.

All values activation energy are listed in Table 1. From the values shown it follows that glass with 0,075 mole of both oxides is more stable vs. crystallization than the glasses without and also with 0,015; 0,031; 0,050 mole of TiO $_2$ and ZrO $_2$ oxides. Thus, on the basis of values of activation energy (in comparison with characteristic temperatures) different order of thermal stability of studied systems has been found. The result obtained can be affected by different nucleation mechanisms [10] and the formation of many a crystalline phases (Li $_2$ SiO $_3$, Li $_2$ Si $_2$ O $_5$,...) is also important.

The XRD patterns demonstrated the typical amorphous state of an as – quenched Li $_2$ O . 2 SiO $_2$. x ZrO $_2$. x TiO $_2$ systems. When the temperature of treatment has been increased to 595 °C (3 h) the crystalline phases are formed. The lithium metasilicate Li $_2$ SiO $_3$ was the primary crystalline phase. Diffraction peaks at $2\theta = 18,9^\circ$ and $27,5^\circ$ are especially characteristic for Li $_2$ SiO $_3$. The addition of 0,075 mole of ZrO $_2$ to Li $_2$ O . 2 SiO $_2$ system heated at 595 °C results in a successive transformation of Li $_2$ Si $_2$ O $_5$ to Li $_2$ SiO $_3$: diffraction peaks of Li $_2$ Si $_2$ O $_5$ ($2\theta = 23,78^\circ$ and $24,29^\circ$) disappear. When content of oxides are increased the lithium disilicate leaves to exist giving place to the lithium metasilicate (the kinetically favored crystalline phase) since the activation energy its crystallization is much less then for crystallization of lithium disilicate [9]. The interactions occurring in the Li $_2$ O . 2 SiO $_2$. x ZrO $_2$. x TiO $_2$ systems (during heating at 595 °C have been studied by means of infrared spectra. It is evident that the addition of both oxides to Li $_2$ O . 2 SiO $_2$ system causes several different effects. There are:

the down shifts of the some fundamental modes (by name ν Si-OH, ν Si-O-M, ν_{sym} Si-O-Si and ν_{as} Si-O-Si) and up shift of the ν_{as} Si-O-Si (ν_1' mode) the disappearance of some absorption when TiO₂ and ZrO₂ content increase. Thus, the addition of TiO₂ and ZrO₂ to Li₂O . 2 SiO₂ cause a significant down shift of the ν Si-O-M and ν_2 modes. These modes due to the higher charge and the greater mass of Ti^{IV} and Zr^{IV} with respect to the Li^I atoms are definitely down shifted with respect to the Si-O stretching mode of terminal Si-O-Li bonds. If we suppose that all Ti^{IV} and Zr^{IV} and Li^I atoms go to break the silicate chains [4] we must conclude that the intensity of the Si-O stretching modes of terminal Si-O-Zr bonds is stronger than that of Si-O stretching mode of terminal Si-O-Li bonds.

Tab. 1: Values of activation energies for studied systems

Sample	E(T _f) kJ/mol	E(T _p) kJ/mol	E(β) kJ/mol	E(sc) kJ/mol
LSZT - 0,000	118,3	125,8	141,2	406,9
LSZT - 0,015	116,6	119,6	135,3	471,0
LSZT - 0,031	125,5	123,0	139,2	448,7
LSZT - 0,050	137,0	132,3	148,7	504,6
LSZT - 0,075	172,0	157,6	174,4	495,1
LSZT - 0,100	175,0	159,2	176,1	520,9
LSZT - 0,150	178,5	168,6	186,0	506,5
LSZT - 0,200	180,0	170,9	188,7	519,9

5. CONCLUSIONS

The relation between kinetic parameters of thermal stability vs. crystallization (characteristic temperatures, values of activation energy) and composition of the Li₂O . 2 SiO₂ . x ZrO₂ . x TiO₂ systems (where x = 0; 0,015; 0,031; 0,05; 0,075; 0,1; 0,15; 0,2) has been studied by means of thermal analysis, diffraction and spectral analysis.

It has been found that characteristic temperatures (T_p , T_f) increase with the increasing content of ZrO₂ and with increasing heating rates. However, on the basis of values of activation energy different order of thermal stability of studied systems has been found. The diffraction patterns proved that with the increasing content of oxides TiO₂ and ZrO₂ (especially with 0,075 mole of TiO₂ and ZrO₂ and higher) lithium disilicate changed to lithium metasilicate as primary crystalline phase which requires lower value of activation energy. This structural change causes in infrared spectra down shift and disappearance of some fundamental modes.

6. REFERENCES

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