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KINETIC STUDY OF THE CRYSTALLIZATION PROCESSES OF SOME GLASS CERAMICS BASED ON BASALT, VIA THERMAL ANALYSIS

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Abstract

The paper presents the kinetic study of the crystallization processes which take place at the obtaining of some glass ceramics, starting from two basalt glasses with different oxide composition. The activation energies have been calculated using Kissinger's equation and verified with the Ozawa's equation. In this order, the DTA curves have been registered with different heating rates, between 4 and 20°C min^{-1}. By X-ray diffraction it was established that the crystalline phase formed in the crystallization process represent a pyroxenic solid solution, $\mathrm{Ca(Mg,Fe)SiO_3}$.

Keywords: glass ceramics, kinetic study of crystallization processes, nucleation agents

Introduction

Glass ceramics are polycrystalline solids obtained by controlled crystallization of shaped vitreous products. Obtaining the glass ceramic materials involve a first stage, in which the product is shaped starting from the glass melting and a second crystallization stage, during an adequate thermal treatment [1]. Glass ceramics based on basalt (natural rock easy accessible) develop a high mechanical and abrasion resistance as well as a good chemical stability; they are used for the component parts of some agricultural equipment [2, 3].

Reaching the physico-mechanical and chemical high performances is conditioned by the nature and the texture of the crystalline phases; that's why two principles are to be followed [2–5]:

- the realization of optimum ratio, crystalline phase/vitreous phase (over 85% crystalline phase);
- the obtainment of microcrystals having dimensions up to 1 μm, spread as uniform as possible in the volume of the product.

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The main crystalline phase in the glass ceramic based on basalt is represented by the pyroxene solid solution: $Ca(Mg,Fe)SiO_3$ [2–6].

The correlation between the chemical composition of the basalt glasses, the nature and the proportion of the used nucleating agents, the thermal treatment conditions and the physico-mechanical properties of the obtained glass ceramics made the object of our preoccupations [5–10].

The aim of this work is to present some kinetic studies of the crystallization processes which take place at the obtainment of basalt based glass ceramics. The activation energies have been calculated using Kissinger's equation and verified with the Ozawa's equation. In this purpose, we used the information obtained based on the differential thermal analysis (DTA).

Experimental

First, there have been elaborated the basalt based glasses using as main raw material the Şanoviţa basalt (Timiş) having the chemical composition presented in Table 1 (sample SB).

The previous studies [5–10] led to the conclusion that the best results concerning the crystalline phase content in the basalt based glass ceramic products are obtained for compositions characterized by a molar ratio SiO_2/MO, close to one (*MO*=CaO, MgO, FeO).

For the correction of the oxide composition of the studied glasses, at the natural basalt there have been added $MgCO_3$ and $CaCO_3$. Two more glasses (samples BD and BVM) were obtained. Their composition is also presented in Table 1.

Table 1 Oxide composition (% mass) of the studied mixtures

Sample symbol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O+K_2O	TiO_2	Molar ratio SiO_2/MO
SB	52.21	12.33	9.55	14.29	10.29	1.18	0.15	1.378
BD	46.39	10.98	8.45	21.00	11.42	1.65	0.11	1.009
BVM	50.82	12.05	9.28	15.48	11.08	1.14	0.15	1.266

Based on our experience and on the literature data [2–10] concerning the obtainment of pyroxene glass ceramic products, there have been also elaborated basalt glasses having in their composition nucleating agents, 10% TiO_2 (sample BVM-T10) respective TiO_2-5% and ZrO_2-2% (sample BD-T5+Z2) and TiO_2-10%, ZrO_2-2% (sample BD-T10+Z2).

After homogenization, the mixtures have been charged in sintered alumina crucibles and melted in an electrical oven having SiC bars, for two hours, at 1350ºC. The obtained melts have been then fritted by pouring in cold water and the resulted glasses have been milled up to a 3% rest on the sieve having the side of the mesh 100 μm.

The obtained samples have been thermally analyzed (DTA) using a C MOM Hungary derivatograph. In all the cases the mass of the sample was the same (m=800 mg) and the heating rate varied between 4 and 20°C min^{-1}. For each heating rate there have been determined the temperature at which the crystallisation process devolves at the maximum speed.

In Figs 1–3 there are represented the DTA curves for samples BD, BVM-T10 and BD-T10+Z2, for different heating rates.

In Table 2 there are presented the peak temperatures of crystallization for different heating rates, for samples BVM and BD-T5+Z2.

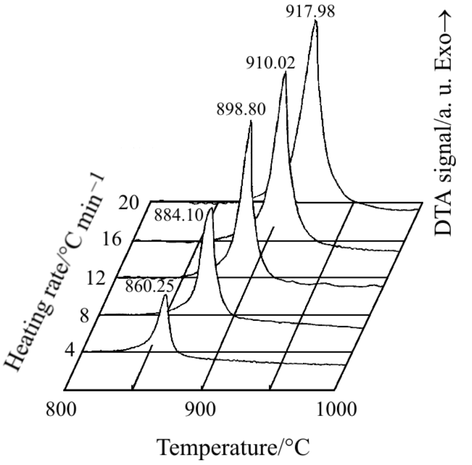

Fig. 1 The DTA curves of the BD sample, for different heating rates

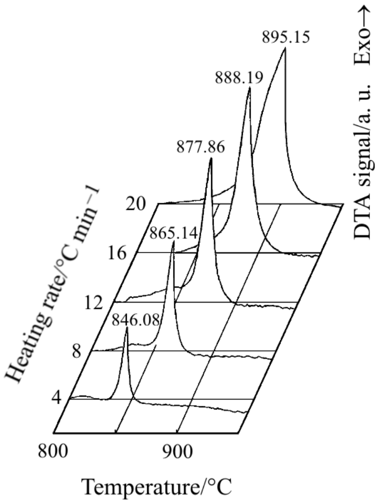

Fig. 2 The DTA curves of the BVM-T10 sample, for different heating rates

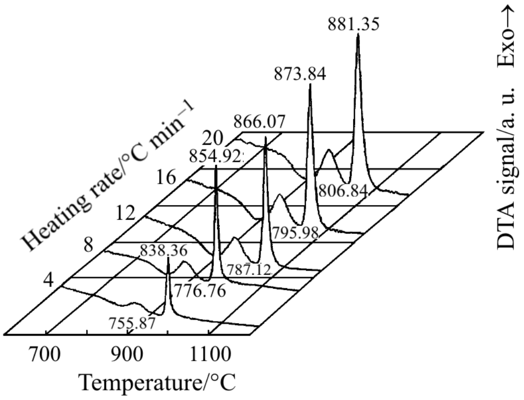

Fig. 3 The DTA curves of the BD-T10+Z2 sample, for different heating rates

Table 2 The peak temperatures of crystallization for different heating rates for the samples BVM and BD-T5+Z2

Heating rate/°C min^{-1}		4	8	12	16	20
BVM *T*/°C		906.56	923.04	932.37	943.79	951.57
BD-T5+Z2 *T*/°C	Peak 1	774.65	803.17	816.11	830.20	836.67
	Peak 2	842.26	860.86	871.67	880.36	887.37

The activation energies of the crystallization processes have been calculated using Kissinger's Eqs [11, 12] as well as Ozawa's Eqs [12, 13].

The crystalline phase formed after the thermal treatment was identified by X-ray diffraction, using a DRON 3 diffractometer (CuK$_\alpha$).

Results and discussion

Following the peak temperatures of crystallization from the Figs 1–3 and Table 2 may be noticed that in the case of each sample, these increase with the heating rate. From Fig. 1 and Table 2 may be noticed that in the case of the basic glasses (without nucleation agents) the crystallization process takes place at a lower temperature in the case of BD sample having a SiO_2/MO molar ratio closer to 1 than in the case of sample BVM with a SiO_2/MO molar ratio of 1.266.

Comparing the samples BVM (Table 2) and BVM-T10 (Fig. 2), is easily ascertained that the nucleation agent addition (10% TiO_2) leads to a significant decrease of the temperatures at which the crystallization process takes place. In the case of the samples with two nucleation agents: BD-T5+Z2 and BD-T10+Z2, the DTA curves present two exothermal maxima (Table 2, respectively Fig. 3), which proves that the two nucleation agents act successive.

The activation energies of the crystallization processes have been calculated based on Kissinger's equation [11, 12]:

$$\ln\left(\frac{a}{T^2}\right)=-\frac{E}{RT}+\text{const.} \tag{1}$$

where a – heating rate (K min^{-1}); T – temperature at the peak maximum (K); E – activation energy (J mol^{-1}); R – general constant of gases (J mol^{-1} K^{-1});

In Figs 4–6 there are presented the $\ln(a/T^2)=f(1/T)$ dependences for the BD, BVM and BVM-T10 samples.

The calculated values for the activation energies for all the studied samples, as well as the correlation coefficients (ρ), are presented in Table 3.

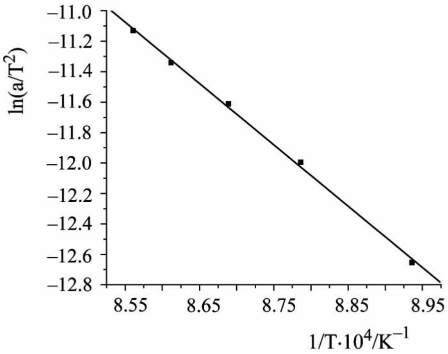

Fig. 4 The $\ln(a/T^2)=f(1/T)$ dependence for the BD sample

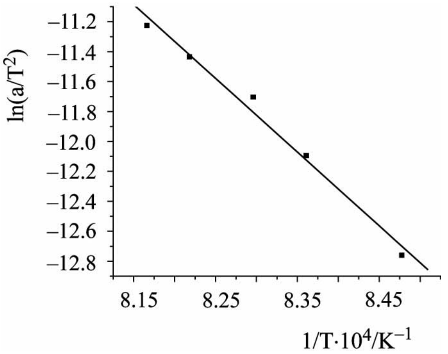

Fig. 5 The $\ln(a/T^2)=f(1/T)$ dependence for the BVM sample

The activation energies of the crystallization processes have also been calculated based on the Ozawa's equation [12–14]:

$$\ln a=-1.052\frac{E}{RT}+\text{const.} \tag{2}$$

Table 3 The values of the activation energies and the correlation coefficients obtained with the Kissinger's and Ozawa's equations

<table>
<tr><th rowspan="2">Sample</th><th colspan="4">Kissinger method</th><th colspan="4">Ozawa method</th></tr>
<tr><th colspan="2">ρ</th><th colspan="2">E/kJ mol^{-1}</th><th colspan="2">ρ</th><th colspan="2">E/kJ mol^{-1}</th></tr>
<tr><td>BD</td><td colspan="2">0.99993</td><td colspan="2">292</td><td colspan="2">0.99994</td><td colspan="2">296</td></tr>
<tr><td>BVM</td><td colspan="2">0.99367</td><td colspan="2">410</td><td colspan="2">0.99427</td><td colspan="2">408</td></tr>
<tr><td>BVM-T10</td><td colspan="2">0.99907</td><td colspan="2">335</td><td colspan="2">0.99918</td><td colspan="2">336</td></tr>
<tr><td></td><td colspan="2">Peak 1</td><td colspan="2">Peak 2</td><td colspan="2">Peak 1</td><td colspan="2">Peak 2</td></tr>
<tr><td></td><td>ρ_1</td><td>E_1/kJ mol^{-1}</td><td>ρ_2</td><td>E_2/kJ mol^{-1}</td><td>ρ_1</td><td>E_1/kJ mol^{-1}</td><td>ρ_2</td><td>E_2/kJ mol^{-1}</td></tr>
<tr><td>BD-T5-Z2</td><td>0.99808</td><td>231</td><td>0.99972</td><td>367</td><td>0.99833</td><td>236</td><td>0.99975</td><td>367</td></tr>
<tr><td>BD-T10-Z2</td><td>0.99653</td><td>283</td><td>0.99888</td><td>383</td><td>0.99694</td><td>285</td><td>0.99900</td><td>382</td></tr>
</table>

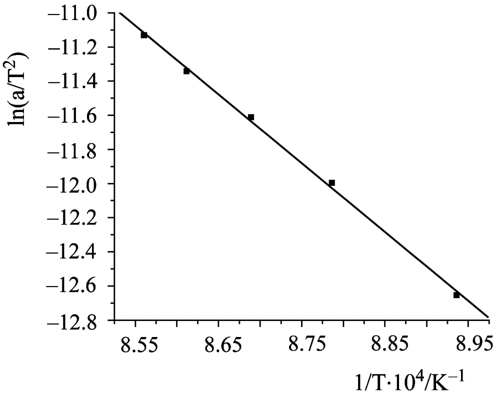

Fig. 6 The $\ln(a/T^2)=f(1/T)$ dependence for the BVM-T10 sample

where a – heating rate (K min^{-1}); T – temperature at the peak maximum (K); E – activation energy (J mol^{-1}); R – general constant of gases (J mol^{-1} K^{-1});

In Figs 7–9 there are presented the $\ln a=f(1/T)$ dependences.

The values of the activation energies obtained and the corresponding correlation coefficients are also presented in Table 3.

It may be noticed that in the case of both used methods the correlation coefficients may be appreciated as very good. Regarding the activation energies of the crystallization processes, the values obtained by the two methods are in reasonable agreement.

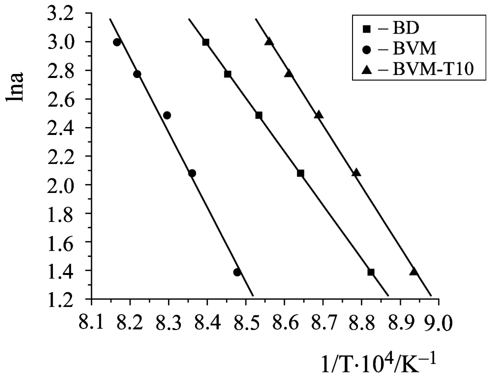

Fig. 7 The $\ln a=f(1/T)$ dependences for the BD, BVM and BVM-T10 samples

We specify that, the activation energies in the case of the Ozawa method were computed only at the peak maximum, corresponding to a given conversion degree ($\alpha = 50\%$)

It may be said that the activation energies of the crystallization processes are relatively high, which is specific for the crystallization processes of some silicatic glasses, where the nucleation processes take place rather difficult. Comparing samples BD and BVM, is ascertained a significant smaller activation energy in the case of

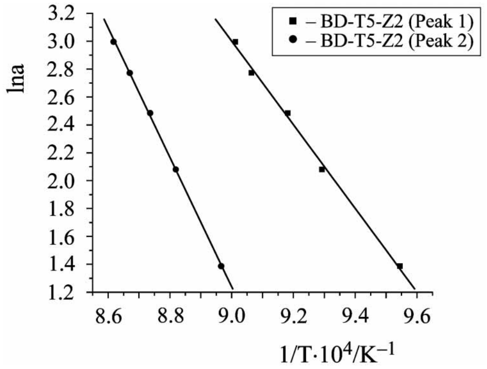

Fig. 8 The ln$a$=f(1/T) dependences for the BD-T5+Z2 sample

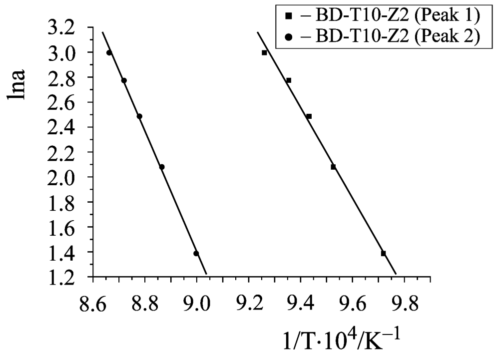

Fig. 9 The ln$a$=f(1/T) dependences for the BD-T10+Z2 sample

sample BD, which may be explained by the oxide composition of this glass, closer to the composition of the pyroxene phase (molar ratio SiO_2/MO≅1).

On the other hand, comparing samples BVM and BVM-T10, it may be easily noticed the influence of the nucleation agent, which lowers the activation energy of the crystallization process; this may be explained by a heterogeneous nucleation due to the presence of TiO_2. The nature of the crystalline phase formed during the studied crystallization processes has been established by X-ray diffraction.

In samples BD and BVM, the only crystalline phase is the pyroxene one, while in the samples with 10% TiO_2 content, pyroxene and brookite phases are both present. Concerning the composition of the pyroxene phase, this is a solid solution described by the formula Ca(Mg,Fe)SiO_3 or even more complex. The identification of the pyroxene phase has been made based on the 41-1370 [15] and 41-1372 [16] JCPDS files.

For example, in Fig. 10 there are presented the XRD spectra of samples BD, BVM and BD-T10+Z2.

Between samples BD and BVM appear some differences consisting in the diffraction maximum corresponding to the ($\bar{1}$30) reticular planes – in the case of sample BVM (the maximum is noted in the JCPDS files, but it has a low intensity).

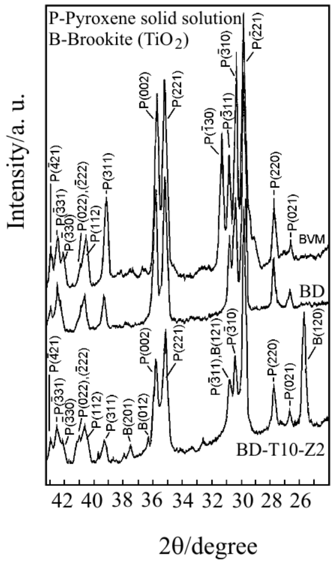

Fig. 10 XRD spectra of samples BVM, BD and BD-T10+Z2

This reflects a different development of the crystals in the two samples having different composition, but with the maintaining of the pyroxene structure.

It has to be mentioned that the physico-mechanical properties of the obtained glass ceramics are determined not only by the amount and nature of the crystalline phase, but also by the texture of the obtained product and especially by the dimension and the distribution of the crystals in the vitreous phase. In the case of some basalt glass ceramics containing pyroxene crystals to much developed, these generate internal tensions which harm the physico-mechanical properties. In order to obtain superior characteristics for glass ceramics the recommended dimension of the microcrystals is smaller than 1 μm and their distribution should be as uniform as possible in the volume of the product. This explains why for the studied samples the microhardness (Vickers HV 0.2) varies from 8248 N mm^{-2} for BVM, 8646 N mm^{-2} for BD, 16840 N mm^{-2} for BVM-T10 until 17120 N mm^{-2} for BD-T5+Z2 [10].

The attempts to correlate the activation energies of the crystallization processes with the physico-mechanical properties of the studied different composition glass ceramics proved to be very difficult. This may be explained by the large number of factors that influence upon reaching some optimum performances. But it has been proved (by electronic microscopy images) [7] that the samples developing superior physico-mechanical characteristics (BVM-T10 and BD-T5+Z2) present microcrystals smaller than 1 μm and uniformly distributed within the volume of the sample.

Comparing the samples BVM and BVM-T10, the improvement of the physico-mechanical properties may be associated to a decrease of the activation energy of the crystallization process. Concomitantly, the mechanism of the crystallization process changes because the presence of the TiO_2 in the BVM-T10 determines the heterogeneous nucleation. This leads to the simultaneous apparition of a great number of nucleation sites and, finally, to a product containing many and small crystals.

In the case of BD sample, the relatively small activation energy and still poor physico-mechanical properties of this glass ceramic may be explained by a homogeneous, easy nucleation, associated to the molar ratio $SiO_2/MO\cong 1$, specific for the metasilicatic phase formation. The formation of a small number of crystals and their unequal development (up to dimensions of 10 μm) has been proved by SEM images [7].

It may be noticed that the nucleation agents addition in samples BD-T5+Z2 and BD-T10+Z2 leads to an increase of the activation energy of the crystallization process in comparison with sample BD, if we refer to the second exothermal maximum; but these samples present a first exothermal maximum corresponding to the crystallization process having the activation energy smaller than for sample BD. The fact that these samples lead to glass ceramics having superior characteristics in comparison with sample BD may be explained by a heterogeneous nucleation which leads to a large number of nucleation sites and finally, to a product with uniformly distributed microcrystals.

Conclusions

- The utilization of the thermal analysis (DTA) allows the calculus with a good precision of the activation energies of the crystallization processes which lead to the obtainment of glass ceramic products.
- The values of the activation energies obtained by the two methods (Kissinger and Ozawa) are in reasonable agreement; in both cases the values of the correlation coefficients are very good ($\rho>0.99$).
- It is very difficult to directly correlate the activation energy of the crystallization process with the physico-mechanical properties of the obtained glass ceramics. Still, it may be said that a decrease of the activation energy associated with the formation of a large number of nucleation sites by heterogeneous nucleation leads to a texture characterized by microcrystals smaller than 1 μm, uniformly distributed, which ensure superior characteristics for the obtained product.

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