

University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor



Technical Faculty in Bor
University of Belgrade

51st International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:

Prof. dr Srba Mladenović
Prof. dr Čedomir Maluckov

Bor Lake, Serbia,
October 16-19, 2019



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THE CRYSTALLIZATION OF GLASS SAMPLES FROM THE SYSTEM P_2O_5 -CaO-SrO-Na₂O-TiO₂

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Abstract

In this paper the crystallization of glass 42P₂O₅·40CaO·5SrO·10Na₂O·3TiO₂ (mol %) was studied. The glass was prepared by the standard melt-quenching method. The experiments were performed under non-isothermal conditions using the XRD and DTA methods. It was determined that the surface and volume crystallization mechanism act simultaneously in bulk glass samples. The sintered calcium phosphate glass-ceramic which contains bioactive β -Ca₃(PO₄)₂ and β -Ca₂P₂O₇ phases was prepared. From the experimental data an activation energy of crystal growth is calculated $E_a = 126.61 \pm 2.39$ KJ/mol.

Keywords: polyphosphate glass, crystallization, bioactive glass-ceramic, activation energy

1. INTRODUCTION

Phosphate glasses have many unique properties that make them good candidates for different applications because of their specific structure (low melting points, low glass transition temperatures, low softening temperatures and high thermal expansion coefficient) [1, 2]. In recent years, because of dissolution behavior, bioactivity and biocompatibility, an expanding interest for development and application of phosphate-based glasses as biomaterials in medicine exist [3].

Depending on [O]/[P] ratio the glasses of different structures can be made. Polyphosphate glasses contain < 50 mol % P₂O₅ and their structure consist of chains formed by Q² groups terminated with Q¹ groups [4, 5]. The phosphate-based glasses containing Ca²⁺ and Na⁺ ions show bioactivity and have potential applications in both soft-and hard-tissue engineering [6, 7]. Calcium (Ca²⁺) and strontium (Sr²⁺) behave similarly and the strontium ions can be incorporated into glass structure. It was documented that in tissue engineering the release of strontium ions from bioactive glass scaffolds has a therapeutic effect in bone healing [8]. By crystallization of these glasses the bioactive calcium phosphate glass-ceramic materials can be prepared. The phase composition and microstructure of as-prepared glass-ceramic have an effect on all its properties including bioactivity and it is essential to determine the crystallization behavior of the glass powder [9].

2. EXPERIMENTAL

2.1 Synthesis of starting glass

The raw materials used for glass synthesis were reagent grade (NH₄)₂HPO₄, Na₂CO₃, CaCO₃, SrCO₃ and TiO₂. The appropriate batch composition was melted at 1250 °C for 0.5 h in a Pt crucible, after which the melt was cast on a steel plate and cooled in air.

2.2 Glass crystallization experiments

To examine glass crystallization the non-isothermal and isothermal experiment were performed on the powdered and bulk glass samples. Non-isothermal crystallization was studied using a DTA - Netzch STA 409 EP instrument with Al_2O_3 powder as the reference material. Powder samples of the following granulations were prepared: <0.048; 0.048-0.063; 0.063-0,1; 0.1-0.2; 0.2-0.3; 0.3-0.4; 0.4-0.5; 0.5-0.65; 0.65-0.83 and 0.83-1.0 mm. Powder samples (100 mg) were prepared by crushing and grinding the bulk glass in an agate mortar and sieving it up to appropriate grain size. The glass was heated from 20 to 900 °C at a heating rate of 10 °C min⁻¹. The second group of experiments was performed for determination of kinetic parameters of crystallization and the DTA crystallization peaks were recorded at several heating rates, i.e., 5, 10, 15 and 20 °C/min. The temperature of crystallization peak (T_p) was determined.

The isothermal crystallization of bulk glass samples was performed by heating the samples in an electric furnace Carbolite CWF 13/13 with automatic regulation and temperature accuracy of ± 1 °C, up to the crystallization temperatures previously determined by DTA, at a heating rate 10 °Cmin⁻¹, and maintained at these temperatures for 1 hour. After heat treatment the samples were removed from the furnace, cooled in air and then prepared for analyses.

The XRD method was used to determine the phase composition and the XRD patterns were obtained by using a Philips PW-1710 automated diffractometer with a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 5 to 70°, counting for 1 s. The XRD measurements were performed at room temperature in a stationary sample holder.

3. RESULTS AND DISCUSSION

The obtained glass sample was transparent, without visible residual gas bubbles. Powder X-ray diffraction analysis confirmed the quenched melt to be vitreous. The results of the chemical analysis show that a glass composition of $42\text{P}_2\text{O}_5 \cdot 40\text{CaO} \cdot 5\text{SrO} \cdot 10\text{Na}_2\text{O} \cdot 3\text{TiO}_2$ (mol %) was obtained. In order to identify the formed crystal phases, the bulk samples were crystallized in a one-stage heat treatment. XRD patterns of the sample thermally treated at $T = 650$ °C for $t = 1$ h is shown in Figure 1.

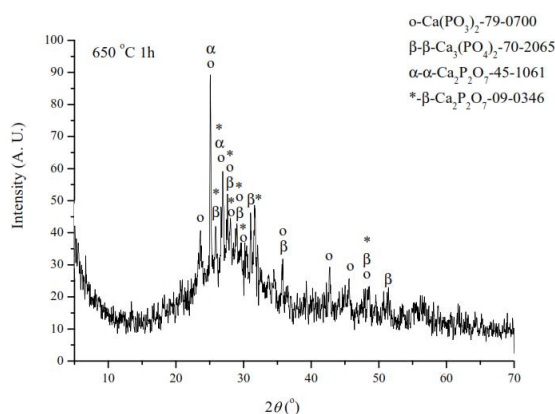


Figure 1. XRD pattern of sample annealed at $T = 650$ °C for $t = 1$ h.

It can be seen in Fig. 1, that during the crystallization of this glass four phases were formed: $\text{Ca}(\text{PO}_3)_2$ as primary phase and $\beta\text{-Ca}_3(\text{PO}_4)_2$, $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ as secondary phases. The content of secondary phases is relatively small compared to the primary phase. The XRD pattern show that for this glass the primary crystallization occurred.

The results of DTA experiments with different glass particle size show that the crystallization behavior of this glass depends on the particle size. In the range of the smallest granulations the surface mechanism of crystallization is dominant. With increasing particle size the surface mechanism of crystallization is replaced by the volume one (>0.4 mm). The height of the exothermal DTA peak (h_p) is proportional to total number of nuclei (volume and surface) contained in the glass particle (Figure 2).

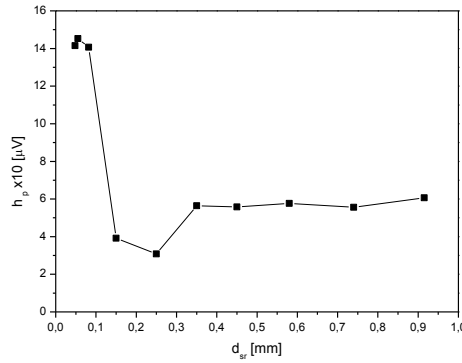


Figure 2. The effect of particle size on height of the exothermal DTA peak.

For determination of the kinetic parameters of crystallization the glass sample granulation <0.048 mm was chosen and the DTA crystallization peaks were recorded at several heating rates, i.e., 5, 10, 15 and 20°C/min (Fig. 3). For this case, the equation for the analysis of nonisothermal crystallization was derived by Matusita and Saka [10]:

$$\ln \frac{\beta^n}{T_p^2} = -\frac{m \cdot E_a}{R \cdot T_p} + const. \quad (1)$$

where R is the gas constant. The values of the parameters n and m depend on the rate controlling mechanism of the crystallization kinetics, while the value of E_a is obtained from the ratio $\ln(\beta^n/T_p^2)$ versus $1/T_p$ using the corresponding values for n and m .

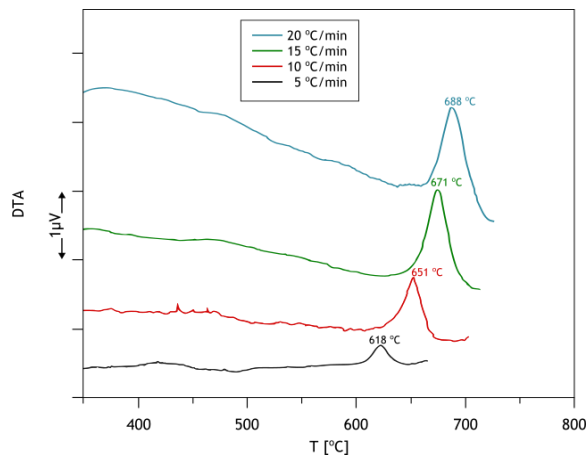


Figure 3. DTA curves for powder samples of particle size <0.048mm, recorded with different heating rates 5-20 °C/min.

Since the crystal growth in these DTA experiments occurred on a constant number of nuclei, $n = m = 1$ (surface crystallization), equation (1) becomes the same as the well-known Kissinger equation [11].

In Fig. 4, the Kissinger plot $\ln(\beta/T_p^2)$ versus $1/T_p$ is presented and an activation energy of crystal growth was calculated from the slope of the line to be $E_a = 126.61 \pm 2.39$ kJ/mol.

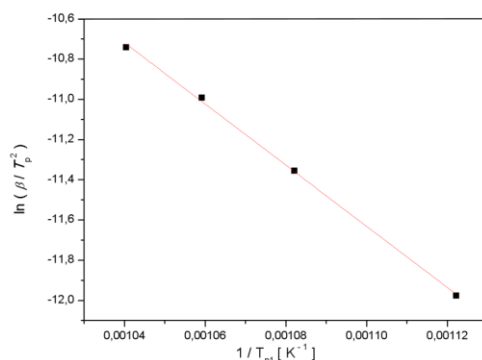


Figure 4. The Kissinger plot $\ln(\beta/T_p^2)$ vs. $1/T_p$ of glass sample < 0.048 mm.

In this case, Ozawa method [12] can also be applied for E_a calculation using the relationship:

$$\ln(\beta) = -\frac{E_a}{R \cdot T_p} + const. \quad (2)$$

The activation energy $E_a = 151.14 \pm 5.68$ kJ/mol, calculated for crystal growth, is in a good agreement with the Kissinger one.

4. CONCLUSION

The results of isothermal crystallization of the glass $42P_2O_5 \cdot 40CaO \cdot 5SrO \cdot 10Na_2O \cdot 3TiO_2$ (mol %) showed that a non-transparent white in color glass-ceramics was obtained. The dominant surface crystallization mechanism was observed. During the crystallization of this glass four phases were formed: $Ca(PO_3)_2$ as primary phase and $\beta-Ca_3(PO_4)_2$, $\alpha-Ca_2P_2O_7$ and $\beta-Ca_2P_2O_7$ as secondary phases. The values of activation energy for crystal growth calculated using the Kissinger ($E_a = 126.61 \pm 2.39$ kJ/mol) and Ozawa ($E_a = 151.20 \pm 5.71$ kJ/mol) equations are in a good agreement.

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