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PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

30th International Conference Ecological Truth & Environmental Research
20–23 June 2023, Serbia

CRYSTALLIZATION CHARACTERISTICS OF BIOACTIVE POLYPHOSPHATE GLASSES

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Abstract

The essence of this paper is to present the effect of adding TiO_2 and SrO to the crystallization characteristics of polyphosphate glasses. The crystallization of glasses has been studied by using DTA, HSM and XRD methods. Sintered phosphate glass-ceramics containing bioactive β-CaP_2O_6, and β-$Ca_3(PO_4)_2$ phases were successfully prepared. The increasing presence of Sr (1-5%), as well as Ti at the expense of phosphate mole fraction in polyphosphate bioactive glass increases the density of these glasses, transformation temperature and resistance to crystallization.

Keywords: polyphosphate glass, bioactive glass-ceramic, sinter-crystallization.

INTRODUCTION

Because of their promising application in biology, medicine, pharmacy and agriculture, different types of polyphosphate glasses are being widely studied [1,2]. The polyphosphate glasses have recently been examined as drug carriers and also their effect on bone regeneration was documented [3]. The addition of strontium is considered to have a therapeutic effect [4,5].

Furthermore, β-tricalcium phosphate (β-$Ca_3(PO_4)_2$ doped with lanthanum using a precipitation technique was developed. The anti-bacterial efficacy of the modified β-$Ca_3(PO_4)_2$ was confirmed by its effect on Staphylococcus aureus and Escherichia coli [6]. The parent multicomponent phosphate glasses were derived from the basic CaO-P_2O_5-Na_2O system. With the addition of Sr, and Ti as a nucleator [7], new glasses were obtained by standard melt-quenching method: $46P_2O_5 \cdot 40CaO \cdot SrO \cdot 10Na_2O \cdot 3TiO_2$ (mol%) (GSSr1) and $42P_2O_5 \cdot 40CaO \cdot 5SrO \cdot 10Na_2 \cdot 3TiO_2$ (GSSr5). The analysis of the crystallization process was carried out by DTA, HSM and XRD methods. Sintered phosphate glass-ceramics containing bioactive β-CaP_2O_6, α-$Ca_2P_2O_7$ and β-$Ca_3(PO_4)_2$ phases were successfully prepared.

MATERIALS AND METHODS

The starting materials used for glass synthesis were high purity reagents $(NH_4)_2HPO_4$, Na_2CO_3, $CaCO_3$, $SrCO_3$ and TiO_2. These reagents were homogenized and prepared in an

agate mortar. To avoid foaming of the melts, the samples were thermally treated at 190 °C during 3 h. The appropriate compositions of the prepared mixtures were melted at 1250 °C in Carbolite BLF 17/3 furnace for 0.5 h in a Pt crucible, after which the melts were poured onto a steel plate and cooled in air.

The chemical analysis was performed using spectrophotometer AAS PERKIN ELMER Analyst 703. The method of atomic absorption spectrophotometry (AAS) was used to determine the content of oxides, CaO, Na_2O, TiO_2, P_2O_5, SrO in glass, after destruction of the sample by NaOH, the composition was determined by analyzing the content of their cations in the solution. The measurement uncertainly is 0.86%.

The DTA-SDT Q600 TGA/DSC/TA Instruments, USA, with Al_2O_3 powder as the reference material, was used to test the non-isothermal crystallization of the glass samples. Powder samples (10 mg) were prepared by crushing and grinding pieces of cast glasses in an agate mortar with a pestle and sieving the prepared samples to the appropriate granulation (<0.048 mm). The glasses were observed in a temperature range of T=20-800 °C at a heating rate of v=10 °C min^{-1}. Before the DTA experiment, the device was calibrated with quartz standard purity of 99.995% of known crystallization temperature. The characteristic temperatures of the tested glasses were determined from the DTA curve.

The sintering behavior of the glass powders was observed by Hot Stage Microscopy (HSM) (Misura – HSML 1400 Expert System Solutions). The glass powder samples (<0.048 mm) were pressed into cylinders and heated in HSML at a heating rate of 10°C min changes in the shape of cylindric samples during heating are monitored and the changes in the area of the samples at the different temperatures were calculated. The shrinkage of the samples was calculated as a ratio A/A_o, where A_o is the initial area and A is the area at temperature T.

The XRD method was used to identify the phase composition of crystallized glass samples. The samples were crystallized at the appropriate temperature according to DTA analysis. XRD diagrams were obtained using an automated diffractometer Philips PW-1710 (PANalytical, The Netherlands) which uses a Cu tube operating at a voltage of 40 kV and a current of 32 mA. The instrument is equipped with a graphite monochromator and a xenon proportional counter. Diffraction data were collected at a 2θ Bragg angle of 5-70 °, with a scanning step of 1 s. The standard database (JCPDS database) for XRD pattern is used for phase identification.

RESULTS AND DISCUSSION

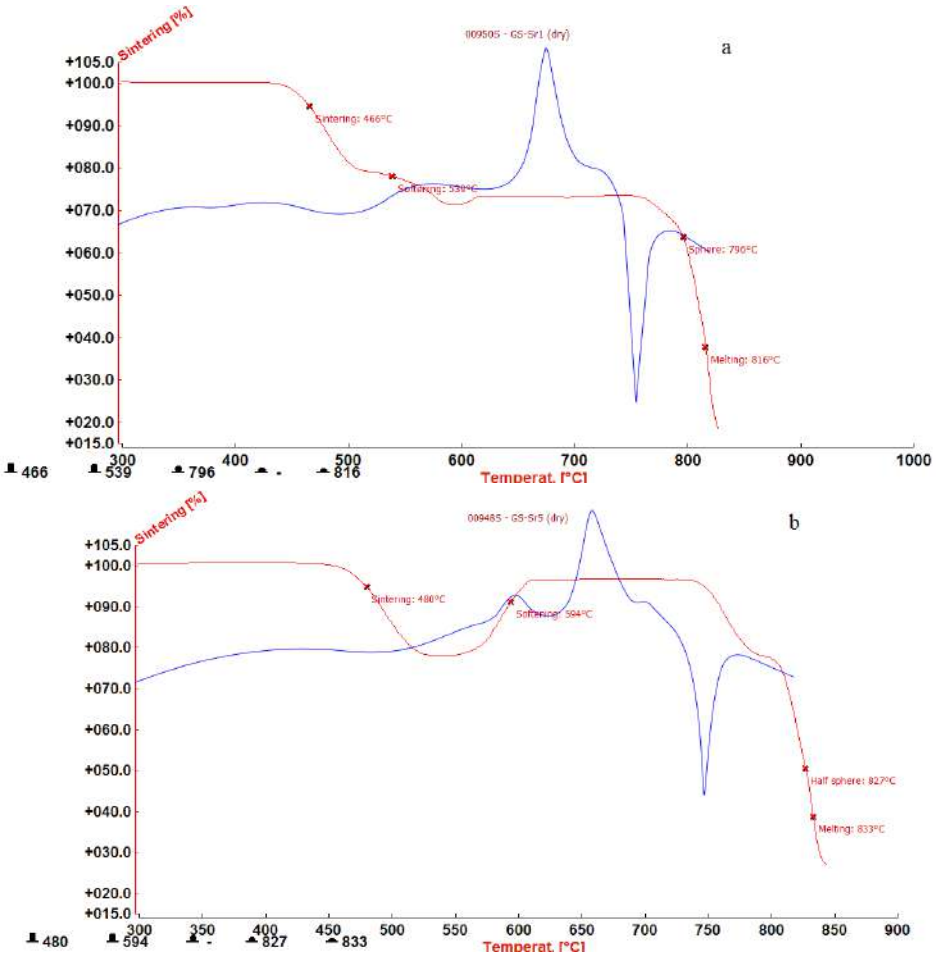
The glass mixture for obtaining the selected glass composition was melted in an electric furnace. The samples of the obtained glasses were transparent, without visible remaining gas bubbles. X-ray diffraction analysis of the powders confirmed that an amorphous structures were obtained. No peaks attributed to any crystallized compound could be identified except a broad diffraction halo (amorphism of between 20° and 35°), which is attributed to the glassy amorphous phase (figure not shown).

The results of the chemical analysis of the investigated glasses are listed in Table 1.

Table 1 *Chemical compositions of the glasses*

Sample	Composition [wt%]					
	P_2O_5	CaO	Na_2O	TiO_2	SrO	Σ
GSSr1	67.07	23.04	6.39	2.46	1.06	100
GSSr5	62.21	23.41	6.47	2.50	5.41	100

Figure 1 shows the DTA/HSM curve of the powdered glass samples (<0.048 mm) recorded at a constant heating rate of 10 °C min^{-1}.



Figures 1 *show comparative thermal analyses of the examined glass samples a) GSSr1 and b) GSSr5 on a DTA (blue line) and HSM (red line)*

The crystallization of the selected glasses is shown on the DTA curve by the exothermic peaks with the temperatures of the beginning of the crystallization processes in T_x = 625-635 °C range and the maximum crystallization temperatures in T_p = 660-675 °C range. Pronounced endothermic peaks, which represent the melting of the glass samples, were observed after the crystallization process.

The onset melting temperatures (T_{om} ~ 700-730 °C) and the maximum liquidus peak temperatures (T_m = 745-755 ºC) can be observed on the DTA curve. The bends that correspond to the temperature ranges of glasses transformation T_g = 420-425 °C can also be

seen on the curve. In this area a solid body begins to behave like a viscoelastic body when heated. Hruby proposed the use of the K_H parameter to assess the resistance of glass to the crystallization process based on DTA analysis [8].

$$K_H = \frac{T_x - T_g}{T_m - T_x} \quad (1)$$

Glasses with high K_H values should show higher resistance to crystallization, and therefore their ability to vitreously solidify the melt during cooling should be higher. The obtained glasses with the addition of strontium have a lower tendency to crystallize than the parent phosphate glass, and the value of the Hruby parameter ranges from 2.53 (GSSr1) to 2.89 (GSSr5).

Thermal properties, viscosity and sinterability of oxide glasses are strictly dependent on their composition. The almost even shift of the characteristic temperatures of transformation T_g, crystallization T_p and melting T_m, of the obtained glasses can be explained by the influence of replacing the oxide P_2O_5 in the starting glass with SrO in the derived glasses.

Namely, the density of P_2O_5 is 2.30 g cm^{-3}, and of the added SrO 4.70 g cm^{-3}. Increasing the density of these glasses by adding strontium oxide to the glass mixture also affects the increase in viscosity and the increase in transformation temperatures, softening temperatures and sinterability (Figure 1).

Temperatures corresponding to the characteristic values of the viscosity of the tested glasses were determined: first sample shrinkage (T_{fs}), maximum shrinkage (T_{ms}), softening (T_d), sphere (T_s), half-ball (T_{hb}) and viscous flux (T_f). Sample sintering occurs in the 466 °C (GSSr1) - 480 °C (GSSr5) range, softening of the samples occurs in the 539 °C (GSSr1) -594 °C (GSSr5) range, and crystallization in the 625 - 730 °C range. Based on the comparative analysis (Figure 1), we can conclude that the sintering and crystallization processes are independent in the obtained glasses. Bearing in mind the possible application, this is significant data.

Based on the value (0.60) of reduced glass transition temperature $T_{rg} = T_g/T_m > 0.58$ it can be assumed that surface crystallization takes place in these glasses [9].

Activation energies for the crystallization process were determined by the method of Kissinger (E_a) because it was determined that the samples crystallize by surface mechanism [10]. The relatively low energies for the crystallization process of the obtained glasses can be attributed to the presence of a nucleator (TiO_2) added to the composition of the starting mixture to control the crystallization process in each glass. TiO_2 is considered an intermediate oxide that affects the chemical stability of glass.

The prepared glass samples for X-ray analysis were isothermally heated in a Carbolite 13/13 furnace with a heating rate regulator and a temperature accuracy of ± 1 ˚C, at crystallization temperatures previously determined on DSC, 665-695 °C for 3 h. The phase composition of the sample was determined by XRD analysis and the results are shown in Figure 2.

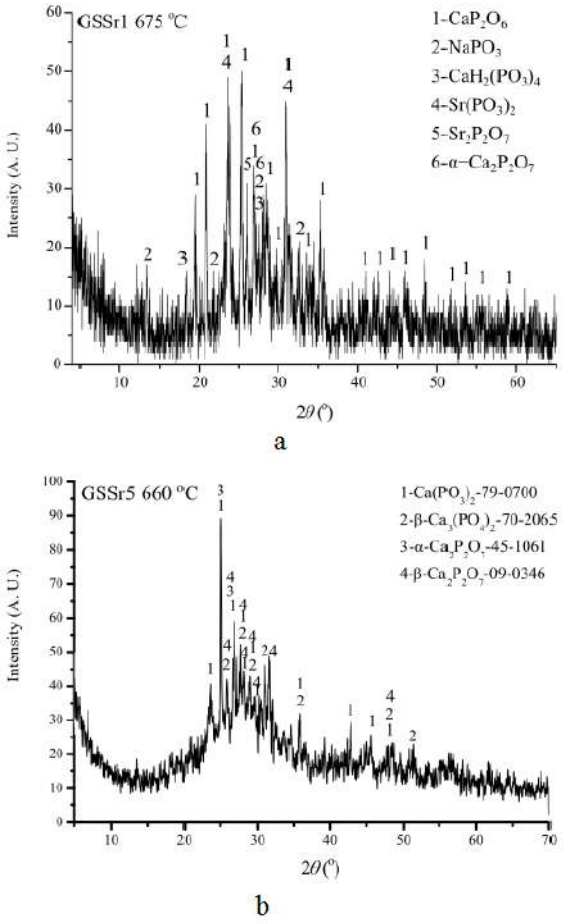


Figure 2 *XRD analyses of the crystalized samples: a) GSSr1 and b) GSSr5*

XRD analyses of the powder samples showed that during thermal treatment glass particles crystallized as opaque glass-ceramics white in color and the presence of crystalline phases was determined, among others: β-CaP_2O_6, α-$Ca_3(PO_4)_2$, β-$Ca_3(PO_4)_2$, $Ca_2P_2O_7$, and $NaPO_3$.

Tricalcium phosphate ($Ca_3(PO_4)_2$, TCP) and β-calcium phosphate (β-CaP_2O_6) found in the analyzed glass-ceramic samples are one of the most compatible materials used as a substitute for human bones in the field of bioceramics. Also, TCP can be used as a replacement for tissues in the bone defects regeneration.

We can conclude that the increasing presence of doped elements Sr (1-5%), as well as Ti at the expense of phosphate mole fraction in polyphosphate bioactive glass increases the density of these glasses (viscosity), transformation temperature and resistance to crystallization.

CONCLUSION

The obtained glasses with the addition of strontium have a lower tendency to crystallize than the parent phosphate glass. The even shift of the characteristic temperatures of transformation T_g, crystallization T_p and melting T_m, of the obtained glasses can be explained by the influence of replacing the oxide P_2O_5 in the starting glass with SrO in the derived glasses. Increasing the density of these glasses by adding strontium oxides to the glass mixture also affects the increase in viscosity and the increase in transformation temperatures,

softening temperatures and sinterability. The relatively low energies for the crystallization process of the obtained glasses can be attributed to the presence of a nucleator (TiO_2). XRD analyses of the powder samples showed the presence of β-CaP_2O_6, β-$Ca_3(PO_4)_2$, $Ca_2P_2O_7$ and $NaPO_3$ crystalline phases, among others. Based on the comparative DTA and HSM analysis, we can conclude that the sintering and crystallization processes are independent in the obtained glasses.

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