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THE EFFECT OF La_2O_3 ADDITION ON THE CRYSTALLIZATION CHARACTERISTICS OF POLYPHOSPHATE GLASSES

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Abstract

The purpose of this study is to investigate the effect of La_2O_3 addition on the crystallization characteristics of polyphosphate glasses. Differential scanning calorimetry (DSC), and X-ray diffraction (XRD) methods were used to investigate the crystallization behavior of glasses. The addition of La_2O_3 (1-5%), at the expense of phosphate mole fraction in polyphosphate glass, raises the characteristic temperature of glasses, and resistance to the crystallization. The glasses show a complex crystallization leading to the formation of several crystalline phases.

***Keywords**: polyphosphate glass, glass-ceramic, crystallization*

1 INTRODUCTION

Polyphosphate glasses of various types are being intensively studied due to their promising applications in biology and medicine. They have lately been investigated as the drug carriers [1] and their effecte on a bone regeneration has been documented [2,3].

Phosphate-based bioactive glasses are potentially useful biodegradable materials for the soft-tissue engineering, such as wound healing [4,5].

Glass composition is adjusted by addition the "dopants," or extra additives, such as Cu, Zn, In, Ba, La, Y, Fe, Cr, and Sr. Lanthanum was shown to increase the biocompatibility in modified apatite [6].

The effect of La_2O_3 addition on the crystallization properties of polyphosphate glasses was experimentally investigated in this study.

2 EXPERIMENTAL

The parent multi-component phosphate glasses were derived from the basic CaO-P_2O_5-Na_2O system. The two glasses were obtained by the standard melt-quenching method: $46P_2O_5 \bullet 40CaO \bullet La_2O_3 \bullet 10Na_2O \bullet 3TiO_2$ (L1) and $42P_2O_5 \bullet 40CaO_5 \bullet 5La_2O_3 \bullet 10Na_2O \bullet 3TiO_2$ (L5). The analysis of the crystallization process was carried out by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) methods.

2.1 Synthesis of glasses

The L1 and L5 glasses have been prepared from the high purity reagents $(NH_4)_2HPO_4$, Na_2CO_3, $CaCO_3$, La_2CO_3, and TiO_2. The well-homogenized batches were thermally treated at 1250°C for 0.5h (Carbolite, BLF 17/3, Sheffield, UK) in a Pt crucible. The melts were

poured onto a steel plate and allowed to cool in the air. The obtained bulk glasses were clear, transparent, and free of apparent bubbles. The powder samples were made by crushing and grinding the bulk glasses with a pestle in an agate mortar and sieving the resulting samples to the suitable granulation (<0.048 mm).

The chemical compositions of glasses were determined by spectroscopic methods, i.e., by AAS using a PERKIN ELMER 703 (Waltham, USA) instrument.

2.2 Glass crystallization experiments

The DSC curves recorded in the temperature range 400-820 °C at a heating rate of 10°C min^{-1} were used to determine the characteristic temperatures (*T*g – glass transition temperature; *T*x – onset temperature of crystallization; *T*p – crystallization peak temperature; Tm – onset melting temperature) of the glasses. The DTA-SDT Q600 TGA/DSC/TA Instruments, USA, with Al_2O_3 powder as the reference material, was used.

The crystallization of bulk glass samples was accomplished by heating the samples in an electric furnace with automatic regulation and temperature accuracy of ±1°C (Carbolite CWF 13/13, UK) up to the crystallization temperatures at a heating rate of 10°C min^{-1} and then maintaining them at these temperatures for 1 hour. The samples were taken from the furnace after heat treatment and used for microstructure analysis and phase identification of phases crystallized during heat treatment.

The XRD method was used to identify the crystalline phases present in the crystallized bulk glass samples. The XRD patterns were obtained using an automated diffractometer Philips PW-1710 (PANalytical, The Netherlands) which uses a Cu tube operating at voltage of 40 kV and current of 32 mA. The instrument is equipped with a graphite monochromator and xenon proportional counter. Diffraction data were collected with a scanning step of 1s at a 2θ Bragg angle of 5-70°.

3 RESULTS AND DISCUSSION

The resulting glass samples were transparent, homogenous, and with no obvious remaining gas bubbles. Table 1 shows the results of chemical analyses of studied glasses.

Table 1 *Chemical compositions of glasses*

Sample	Composition, wt%					
	P_2O_5	CaO	Na_2O	TiO_2	La_2O_3	Σ
L1	65.56	22.53	6.23	2.41	3.27	100
L5	55.74	20.98	5.79	2.24	15.23	100

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

The thermal properties such as glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_p), melting temperature (T_m), and reduced glass transition temperature (T_{rg}), obtained from the DSC studies, are summarized in Table 2.

The values of characteristic temperatures observed from the DSC increased with increasing La_2O_3 content. Lanthanum may strengthen the bond of oxide network in glass, resulting in ghe higher transformation, crystallization, and melting temperatures.

Based on the value of reduced glass transition temperature $T_{rg} = T_g/T_m > 0.58$, it can be assumed that the surface crystallization takes place in these glasses [7].

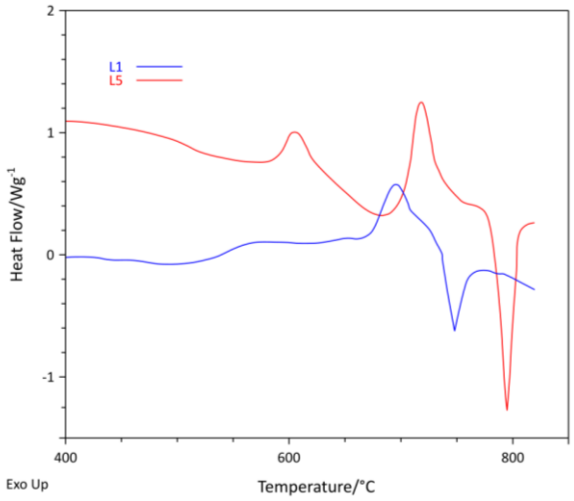

Figure 1 *DSC curves of the powdered glass samples (<0.048 mm) recorded at a constant heating rate of 10°C min^{-1}*

Table 2 *Characteristic temperatures T_g, T_x, T_p, T_m, and T_{rg} of the glass samples determined from the DSC curves*

Samples	T_g/°C	T_x/°C	T_p/°C	T_m/°C	T_{rg}
L1	430	650	695	730	0.59
L5	480	700	720	770	0.62

Several parameters, derived from the DSC curve, can be used to describe the resistance of glass to the crystallization during heating. The best known of them is the Hruby parameter [8]:

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

The values of Hruby parameters of polyphosphate glasses were 2.91 for L1, and 3.14 for L5.

According to Hruby, the higher the value of K_H for a certain glass, the higher its stability against crystallization on heating and, presumably, the higher the glass ability to vitrify on cooling.

The addition of lanthanum increases the glass stability, and relatively high values of stability parameters suggest the stronger glass stability against crystallization and, as a result, its good glass-forming capacity (GFA).

The XRD analysis was used to identify the phases present in samples following heat treatment, and the results are shown in Figure 2. All glasses show the complex crystallization, and several crystalline phases are present in samples.

The phase with the highest amount crystallizes as the primary one (CaP_2O_6 for L1, and α-$Ca_2P_2O_7$ for L5), while the others appear as the secondary phases. Tricalcium

phosphate (CaP_2O_6, TCP) is one of the most compatible materials used as a substitute for the human bones in the field of bioceramic.

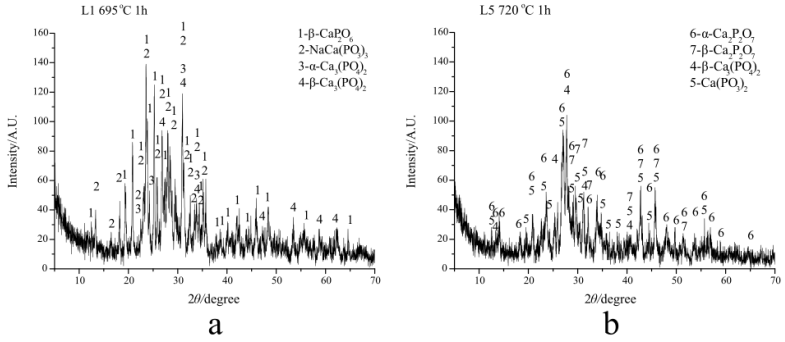

Figure 2 *DSC curves of the powdered glass samples (<0.048 mm) recorded at a constant heating rate of 10°C min^{-1}*

4 CONCLUSION

The present study investigated the effect of La_2O_3 addition (1-5 %) on the crystallization characteristics of polyphosphate glasses.

The effect of raising the La_2O_3 content on the values characteristic temperatures is pronounced and leads to an increase in these values due to the improved bonding of oxide network in the glass. Glass stability improved with the addition of lanthanum, indicating high glass stability against crystallization.

Both glasses crystallize by the complex surface crystallization, and samples contain a variety of crystalline phases. The CaP_2O_6 for L1, and α-$Ca_2P_2O_7$ for L5, were the primary phases, with the rest appearing as the secondary phases.

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