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Thermal and structural interactions in transition elements containing silicate–phosphate glasses

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ABSTRACT

The DSC, XRD and ^{31}P MAS NMR methods were applied to study the interactions between the transition elements (Zn, Cu, Mn, Mo) and structural components of glasses from the —P_2O_5—K_2O—CaO—MgO—TE (Zn/Cu/Mn/Mo) system. In order to determine the structure of domains being the result of interactions in transition elements containing silicate–phosphate glasses, the course of thermally induced crystallization of glasses was considered. To explain the different local chemical affinity of the studied transition elements to the P—O—TE bridging bonds formation, the crystallochemical analysis based on the ionicity of the chemical bonds was used.

1. Introduction

The structure of silicate–phosphate glasses is mainly formed by silicon and phosphorous oxides which is only possible due to its vitreous state. Chemical compounds with the crystal structure of silicon and phosphorous are not numerous and not very stable due to significant differences in the nature of bonds which both of these elements form. As opposed to silicate glasses, glasses containing phosphorous oxide as a glass former may receive into their structure more modifying elements, creating some specific, often unconventional properties.

Structural studies of silicate–phosphate glasses indicated, that they are characterized by domain structure and the dimensions of domains exceed dimensions of a single tetrahedra [1,2]. Thus in such glasses a middle range ordering can be distinguished. This type of order extends up to larger interatomic distances than those corresponding to short range order [3,4] defined by the interatomic correlations in the first coordination spheres of a arbitrary atom. The middle range ordering is characterized by the presence of a complex of polyhedra in the form of domains (clusters) and is determined by the chemical affinity of the components forming the glass structure [5]. The domains can differ in chemical composition and they are also crystal nucleus, which decide about the kind of phase which crystallizes during thermal heating of glass [6]. Therefore, determination of the crystalline products of the glass precursors enables to conclude about the domains structure.

The subject of the present studies were the silicate–phosphate glasses form the SiO_2—P_2O_5—K_2O—CaO—MgO system which can act in soil environment as ecological fertilizers providing controlled release rate of the nutrients for plants in the form of macroelements (P, Ca, K, Mg) [7,8]. This type of glasses show also the capability of receiving their composition, a series of transition elements (TE), acting as microelements, which play an active role in many life processes of plants [9]. The aim of the studies was to determine the interactions between the transition elements (Zn, Cu, Mn, Mo) and the phospho-oxygen structural elements of silicate–phosphate glasses from the SiO_2—P_2O_5—K_2O—CaO—MgO—TE (Zn/Cu/Mn/Mo) system. For this purpose the earlier results of thermally induced crystallization of glasses containing Cu [10], Mn [11] and Mo [12] addition were used. In the presented study, using DSC and XRD methods the influence of Zn ions on the crystallization of SiO_2—P_2O_5—K_2O—CaO—MgO glass was evaluated. Additionally the structure of glasses was characterized by ^{31}P MAS NMR method. As a measure of local atomic interactions in the structure of glasses the crystallochemical analysis based on the ionicity of the chemical bonds was used. The scientific novelty in the paper was to present the possibilities of the domains formation in the structure of analysed silicate–phosphate glasses which are responsible for the existence middle range ordering in the amorphous structure.

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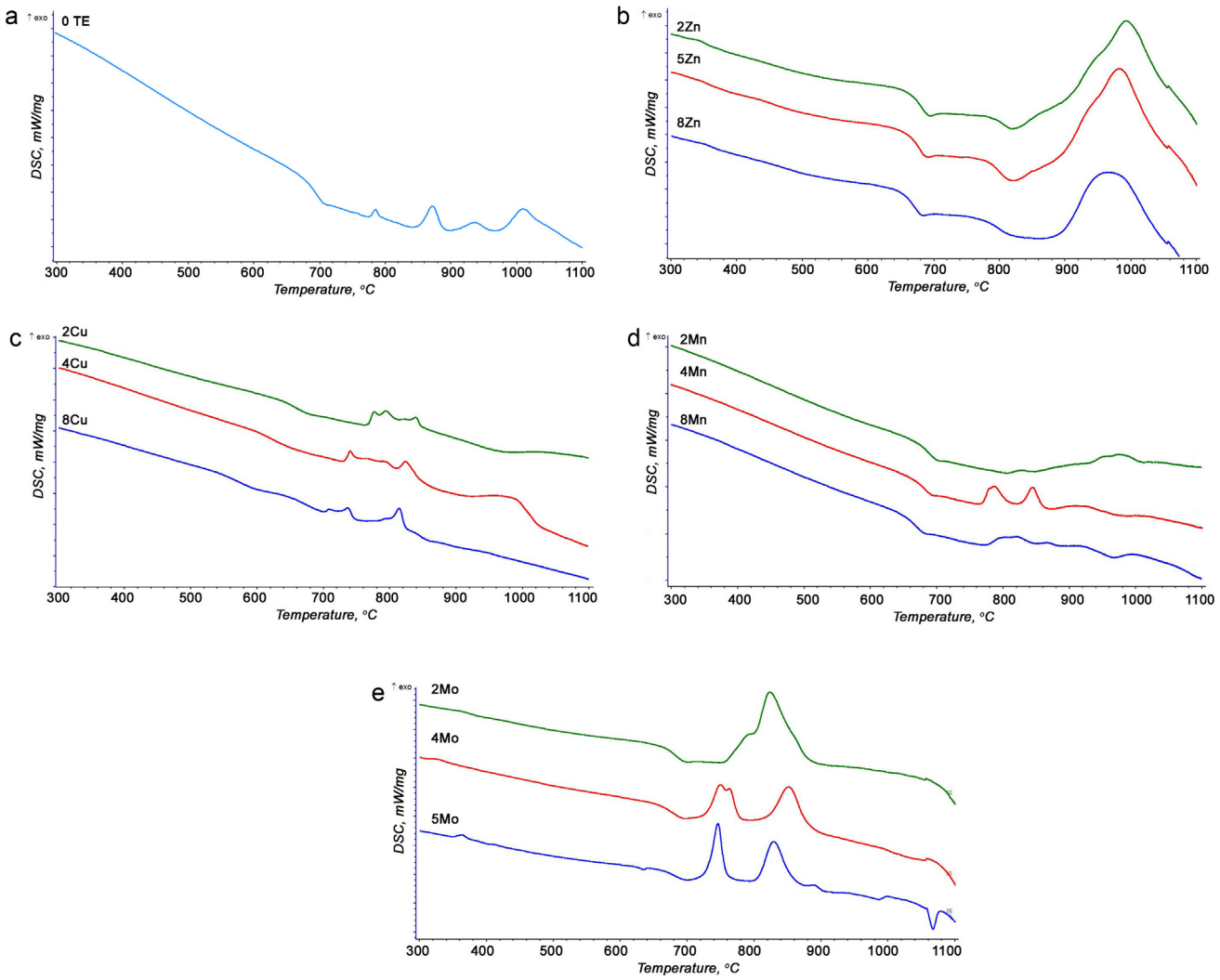

Fig. 1. DSC curves of (a) 0 TE, (b) Zn-containing glass, (c) Cu-containing glass, (d) Mn-containing glass, and (e) Mo-containing glass.

2. Experimental

A series of silicate–phosphate glasses from the SiO_2—P_2O_5—K_2O—MgO—CaO system with variable contents of ZnO, CuO, MnO_2 and MoO_3 was prepared. Keeping the K_2O, P_2O_5 and SiO_2 constant, an increasing amount of transition element (TE) oxides was introduced at the cost of MgO and CaO, with the constant MgO/CaO ratio (Table 1). The samples were produced by melting the mixture of raw materials, i.e., SiO_2, H_3PO_4, MgO, K_2CO_3, $CaCO_3$ and ZnO, CuO, MnO_2 and MoO_3 at the temperature of 1450 °C. Then the batch-free glasses were fritted in water and grinded to the particle size of 0.1–0.3 mm. The X-ray diffraction (XRD) method using the X'Pert PRO Diffractometer (Philips) was applied to confirm the amorphous state of the synthesized glasses, and the results are also shown in the Table 1.

Table 1
The chemical composition of the glass studied.

Glass name	SiO_2 (mol. %)	P_2O_5 (mol. %)	K_2O (mol. %)	CaO (mol. %)	MgO (mol. %)	ZnO (mol. %)	CuO (mol. %)	MnO_2 (mol. %)	MoO_3 (mol. %)
0TE	41	6	6	19	28				
2Zn	41	6	6	18	27	2			
4Zn	41	6	6	17	26	4			
8Zn	41	6	6	16	23	8			
2Cu	41	6	6	18	27		2		
4Cu	41	6	6	17	26		4		
8Cu	41	6	6	16	23		8		
2Mn	41	6	6	18	27			2	
4Mn	41	6	6	17	26			4	
8Mn	41	6	6	16	23			8	
2Mo	41	6	6	18	27				2
4Mo	41	6	6	17	26				4
5Mo[a]	41	6	6	16.5	25.5				5

[a] In glasses with higher content of MoO_3 the crystallization process during cooling of the melt took place.