INFLUENCE OF THE SILVER ON THE PHASE FORMATION IN THE SYSTEM P_2O_5 -CaO-ZnO

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Abstract The influence of the silver on the phase formation and structures was studied in the system P_2O_5 -CaO-ZnO-Ag. Homogeneous distribution of the Ag particles was realized in the materials after heat treatment at 1100-1350°C. The samples were studied by TEM, X-ray, IR spectroscopy and the microhardness was determined. It was proved that the silver stimulates the formation of polyphase materials containing mainly $Zn(PO_3)_2$ and in some cases $Ca_3(PO_4)_2$ also.

INTRODUCTION

The physical and chemical properties and structural special features of the different phosphate materials¹⁻⁷ have been a subject of many investigations. The introduction of silver in some phosphate compositions gives a possibility for production of different materials with promising applications as photosensitive glass⁸, ionic conductors⁹, radiation detectors¹⁰ and another.

Moreover a limited amount of silver is sometimes added to calcium phosphate phases in order to act as an antibacterial agent in some special composites biomaterials (Hydroxyapatite/Silver)^{11,12}. In these cases the simultaneous presence of biocompatible crystalline phases and silver, is the most desirable combination in the materials.

For this reason the study of the role of silver during the crystallization of phosphate glasses and glass-ceramics provokes our interest. The purpose of this paper is to trace the influence of the silver on the phase formation and the microstructure of phosphate glasses and glass-ceramic materials in the system P_2O_5 -CaO-ZnO-Ag. The phase formation in the experimented compositions was compared with analogous ratio of the components in the system P_2O_5 -CaO-ZnO¹³.

EXPERIMENTAL PROCEDURE

The batches were prepared for 10 g with the following high purity raw-materials: $NH_4H_2PO_4$, $Ca_3(PO_4)_2$, ZnO and $AgNO_3$. We used $Ca_3(PO_4)_2$ for introduction of all

CaO quantity and from some quantity of P_2O_5 . The remaining necessary quantity of P_2O_5 was introduced by $NH_4H_2PO_4$. ZnO was used for introduction of ZnO. The introduction of silver was used $AgNO_3$ as starting material. The samples were obtained by traditional glass melting technology. The batches were milled and homogenized in agate mortar. The mixtures were melted in corundum crucibles in electrical furnace in the temperature range 1100 to 1350°C with holding for 10 min. The melts were poured from the crucibles onto massive stainless steel plate. Table 1 presents the nominal batch compositions and the heat treatment temperatures. The analytical contents of the glasses are not determined.

TABLE 1. Nominal batch compositions and temperatures of the heat treatment

No.	Nominal batch compositions in wt%				Temperature of the heat treatment/°C
	P_2O_5	CaO	ZnO	Ag	
1	55.00	13.00	12.00	20.00	1300
2	54.00	9.00	18.00	19.00	1250
3	51.00	15.00	13.00	21.00	1100
4	45.00	18.00	15.00	22.00	1250
5	39.00	15.00	13.00	33.00	1250
6	32.00	19.00	37.00	12.00	1100
7	30.00	12.00	35.00	23.00	1100
8	30.00	7.00	41.00	22.00	1100
9	29.00	3.00	46.00	22.00	1350
10	24.00	3.00	37.00	36.00	1350

The crystalline phase formation was investigated by means of X-ray diffraction analysis with X-ray diffractometer DRON UM-1 with Cu- K_α radiation. The microstructure of the samples was observed by means of transmission electron microscopy (TEM; Philips EM-400). Infrared spectra (from 300 to 1300 cm^{-1}) of the samples were measured using apparatus SPEKORD, Carl Zeiss Jena. The investigations for microhardness (MHV₃₀) were carried out by Vickers method.

RESULTS AND DISCUSSION

The TEM observation was investigated on samples containing Ag and their analogs without silver. The samples were observed by double-stage gelatin C+Pt replicas method. Figure 1 (A) presents the microheterogeneous structure of sample with composition 57.69 P_2O_5 -23.08CaO-19.23ZnO. A combination between crystalline

formations and inhomogeneous amorphous matrix was found. The crystal size were larger than 2-3 μm . The comparison of this structure with the structure of Ag containing glass-ceramic with analogous proportion of the components (composition No. 4: $45\text{P}_2\text{O}_5\text{-}18\text{CaO-}15\text{ZnO-}22\text{Ag}$) shows the presence of extracted homogeneous distributed silver particles. Their sizes were found to be lower than 0.1 μm (Figure 1 (B)).

FIGURE 1. Electron micrographs of glass-ceramics with compositions: (A): $57.69\text{P}_2\text{O}_5\text{-}23.08\text{CaO-}19.23\text{ZnO}$; (B): $45\text{P}_2\text{O}_5\text{-}18\text{CaO-}15\text{ZnO-}22\text{Ag}$.

According to the X-ray diffraction data the obtained glass-ceramic samples indicated mainly polyphase materials. The predominant phases in the silver containing samples were found to be $\text{Zn}(\text{PO}_3)_2$ and Ag. In some cases they were combined with crystallization of phase $\beta\text{-Ca}_3(\text{PO}_4)_2$. Not so often the phases $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$, $\beta\text{-Ca}(\text{PO}_3)_2$ and Ag_3PO_4 were also identified. In the analogous compositions without Ag the main crystalline phase was $\text{CaZn}_2(\text{PO}_4)_2$ in one or several polymorphous forms (α , β , δ or γ). This phase was found together with one or a few of follows phases $\alpha\text{-Zn}_3(\text{PO}_4)_2$, $\beta\text{-Zn}_3(\text{PO}_4)_2$, $\gamma\text{-Ca}_2\text{P}_2\text{O}_7$, $\text{Zn}_2\text{P}_2\text{O}_7$, $\beta\text{-Ca}(\text{PO}_3)_2$ and ZnO.

It was established that glasses were obtained at the condition of highly P_2O_5 content over 51wt% in the system $\text{P}_2\text{O}_5\text{-CaO-ZnO-Ag}$.

The IR spectral data (Figure 2. (A), (B) and (C)) from the silver containing vitreous samples (with compositions No. 1: 55P₂O₅-13CaO-12ZnO-20Ag, No. 2: 54P₂O₅-9CaO-18ZnO-19Ag and No. 3: 51P₂O₅-15CaO-13ZnO-21Ag) show the presence of bands in the ranges 1262-1249, 1122-1106, 939-921, 815-719 and 535-514 cm⁻¹. These bands can be assigned to the following vibrations $\nu_{as}OPO$, ν_sOPO , $\nu_{as}POP$, ν_sPOP and δPO related with the $[PO_3]_n^{n-}$ groups¹⁴. The spectra of the vitreous samples without silver (analogs of the specimens with compositions No. 1, No. 2 and No. 3) indicated bands in different ranges. The bands in the ranges 1010-993 and 947-932 cm⁻¹, probably due to the vibrations $\nu_{as}PO_4$ and ν_sPO_4 , typical for the $[PO_4]^{3-}$ groups¹⁴.

FIGURE 2. IR spectra. (A), (B) and (C): Silver containing vitreous samples with compositions No. 1: 55P₂O₅-13CaO-12ZnO-20Ag, No. 2: 54P₂O₅-9CaO-18ZnO-19Ag and No. 3: 51P₂O₅-15CaO-13ZnO-21Ag.

In order to investigate the formation of crystalline phase and their growth in the glasses, the obtained vitreous samples (with compositions No. 1: 55P₂O₅-13CaO-

12ZnO-20Ag, No. 2: 54P₂O₅-9CaO-18ZnO-19Ag and No. 3: 51P₂O₅-15CaO-13ZnO-21Ag) and their analogs without Ag were heat treated at 900°C with holding for 10 min. The obtained glass-ceramic materials were opaque with light yellow colour (for the specimens with silver) and white colour (for the specimens without silver). According to the X-ray diffraction data the main crystalline phases were found to be β -Ca(PO₃)₂, Zn(PO₃)₂ and Ag for samples with silver and γ -CaZn₂(PO₄)₂ from samples without silver.

The microhardness values of the samples containing Ag (from 345 to 434 kg/mm²) were compared with those of their analogs without silver (from 409 to 604 kg/mm²) that the silver containing materials indicated lower values. The microhardness of the silver containing glasses and their analogs without Ag were lower than the corresponding values of the glass-ceramic materials obtained by heat treatment (at 900°C).

SUMMARY

As a result of this investigation the melting transparent light yellow glasses were obtained in the system P₂O₅-CaO-ZnO-Ag. During the cooling of the melts polyphase materials with bulk crystallization were synthesized in compositions containing below 51wt%P₂O₅. It was established that the silver was homogeneously distributed in the sample volume with particle sizes about 0.1 μ m. Its presence led to changes of the phase composition of the oxide samples. The presence of silver induced a decrease of the microhardness in the glasses and glass-ceramics.

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