Structural features of phosphate glasses for the production of agrotechnical materials

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Abstract. The paper presents the study of the structure and properties of phosphate glasses. The analysis of parameters of their properties to select the optimum structures of glasses, suitable for use as fertilizers, ameliorants and petroleum biosorbents, is carried out. The study of macroscopic, physical and chemical characteristics of glass samples showed the presence of characteristic kinks in certain areas of compositions, which is associated with structural changes occurring in the glass.

1. Introduction

In the conditions of increased challenges regarding the growing volume of agricultural production and intensive environmental pollution with traditional fertilizers it is critical to create new types of environmentally safe fertilizers and ameliorants.

The majority of fertilizers used these days are polycrystalline substances. They are freely soluble in water, and their use, especially at the stage of transportation and inclusion into soil, leads to contamination of soil, surrounding reservoirs and ground waters with soluble toxic phosphates and nitrates.

Numerous studies showed that glasses and glassy materials can be used in various industries. They include both traditional optical fields [1, 2, 3] and such advanced areas as agricultural engineering [4], biocatalysis [5, 6] microelectronics [7], and nanotechnology [8].

At the same time phosphate glassy materials in various compositions differ in terms of their high biological activity and moderate solubility under the influence of ground waters. Compositions of phosphate glassy fertilizers can be modified and alloyed by trace elements necessary for certain types of crops and according to the region of their application.

2. Materials and methods

The model system of fluorophosphate glasses (P_2O_5—ALF_3, MG, CAF_2) and phosphate glasses (P_2O_5—K_2O, MG, CAO) with a wide range of P_2O_5 concentration were chosed as objects of the study.

Glass synthesis was carried out in glassy carbon crucibles under Ar and O_2 atmosphere within 1 hour at 850-950 °C without mixing.

The infrared spectroscopy (IRS) and the Raman spectroscopy (RS) were used to study the glass structure, correlation between changes of physical and chemical properties and the structure of glasses within the studied system. The Raman spectra were obtained via 1 W argon laser excitation.

3. Results and Discussion

The dependence of the index of refraction, density, thermal linear expansion coefficient (TLEC) and viscosity on the structure in the studied fluorophosphate glass system shows the existence of characteristic kinks at $Ba(PO_3)_2$ 60 mol%, which most likely indicates structural changes within the concentration of barium metaphosphate (Fig. 1, a-f).

This assumption was confirmed by the spectroscopic study. It turned out that the infrared and the Raman spectra significantly change with the dilution of metaphosphate in glass.

The Raman spectra of the studied glasses according to their frequency position and correlation of band intensities are typical for phosphate groups (Fig. 2). The initial $Ba(PO_3)_2$ are characterized by bands at 1155 cm^{-1} and a shoulder at 1252 cm^{-1} typical for PO_2-groups oscillations, a band in the field of 680 cm^{-1} which refers to P–O–P cross-link oscillations, and a wide band around 350 cm^{-1} typical for bending oscillations of phosphate tetrahedrons [9].

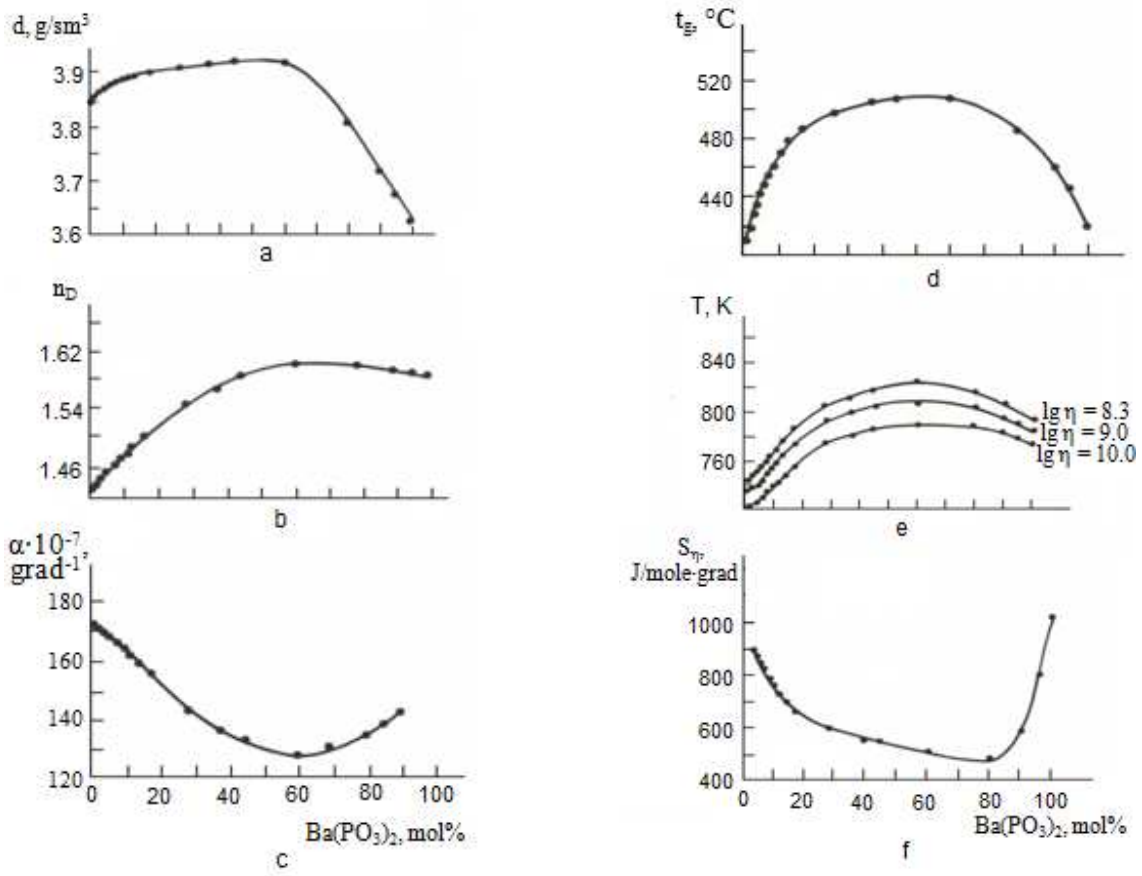

Figure 1. Dependencies of density (a), index of refraction (b), TLEC (c), glass transition temperature (d), viscosity isokoms (e), activation entropy of viscous flow (f) on $Ba(PO_3)_2$ content in glasses

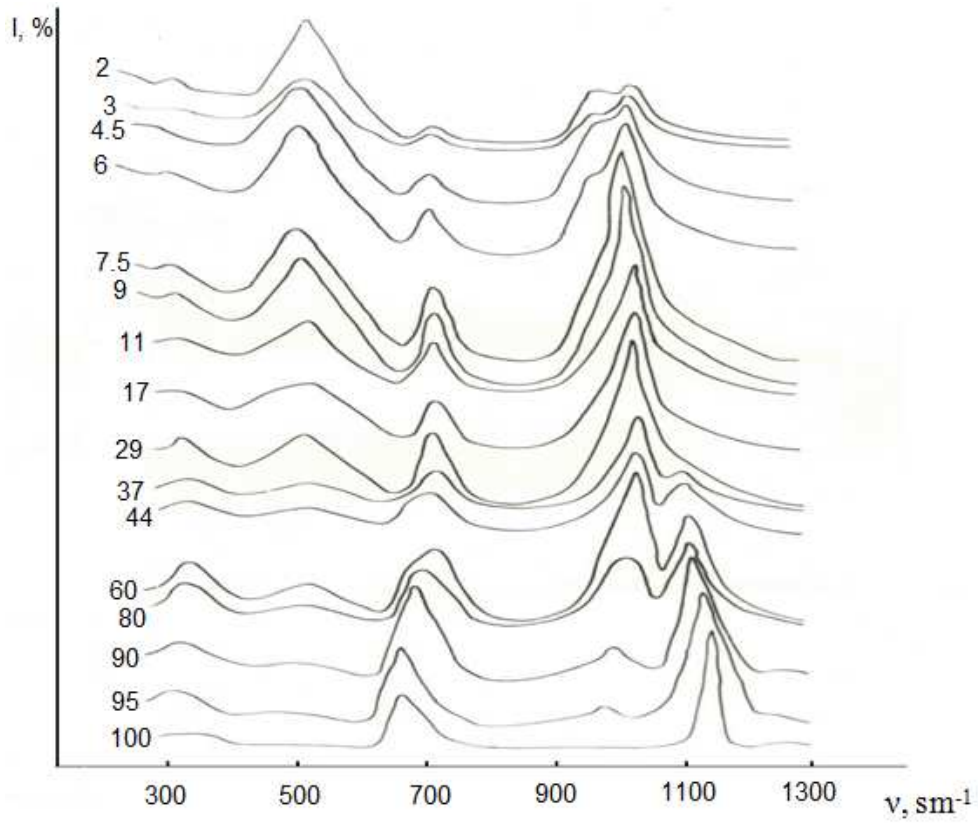

Figure 2. Raman spectra of fluorophosphate glasses with various $Ba(PO_3)_2$ content

The introduction of fluorides into glass composition results in the gradual shift of a band at 1155 cm^{-1} towards low-frequency area of up to 1115 cm^{-1} and thus to the reduction of its intensity. At the same time, there is a band at 1058 cm^{-1} corresponding to oscillations of PO_3 end-groups. The shortening of metaphosphate chains in a glass grid usually causes these spectrum changes. At fluorides concentration above 75 mol% the oscillation bands of PO_2 groups disappear. The band around 1050 cm^{-1} typical for oscillations of PO_3 end-groups and a band at 740 cm^{-1} typical for oscillations of bridge P–O–P groups hold the dominant position within the spectra of these glasses, which makes it possible to assume the presence of pyrophosphate structural groups.

A band in the field of 980 cm^{-1}, apparently belonging to oscillations of isolated PO_4-tetrahedron of orthophosphate structure, appears within the spectra of glasses containing over 85 mol% of fluorides. The wide band at 540-590 cm^{-1} belongs to AlF_4 and AlF_6 fluorine aluminate groups. The gradual frequency shift from band 537 cm^{-1} to 594 cm^{-1} throughout the increase in fluorine aluminate concentration may be explained by the transition of four-coordinate aluminum towards six-coordinate aluminum with the increase in fluoride content in glass.

The detailed study of the Raman spectra of fluorophosphate glasses showed that the decrease in P_2O_5 content in glasses leads to the change of oscillation bands typical for methaphosphate structure into diphosphate and then into orthophosphate ones. The shortening of metaphosphate chains in a glass grid and the appearance of diphosphate groups usually cause such spectrum changes.

The spectra changes correlate with changes of physical and chemical properties of glasses, which confirms the general hypothesis for the replacement of one structural polyhedron with others with the reduction of phosphorus concentration in glass [10].

Thus, it was possible to establish types and boundaries of various structures within glass and to suggest the testing method (Raman spectroscopy), which clearly shows what structural units prevail in phosphate glasses.

The obtained results allowed choosing the optimal composition of phosphate glasses – meta- and diphosphate ones as the most suitable for the production of complex slow-release glassy fertilizers. Phosphate glasses within the given compositions have characteristic, sharp temperature dependence of dissolution kinetics, which makes it possible to use them as fertilizers, ameliorants and oil biosorbents based on a glass foam. The comprehensive use of the specified materials allows solving numerous tasks related to contaminated soil remediation and water treatment from petrochemical pollution.

The analysis of the Raman spectra of phosphate glasses with 52 %wt. P_2O_5 content showed the presence of a characteristic peak around 1150–1200 cm^{-1}, which is responsible for the presence of glass meta- and diphosphate groups in glass structure, which, in turn, leads to active dissolution of such glasses in soil solutions.

4. Conclusions

The paper presents the study of the structure and properties of phosphate glasses. The analysis of parameters of their properties to select the optimum structures of glasses, suitable for use as fertilizers, ameliorants and petroleum biosorbents, is carried out.

The study of macroscopic, physical and chemical characteristics of glass samples showed the presence of characteristic kinks in certain areas of compositions, which is associated with structural changes occurring in the glass.

The study suggests the algorithm for phosphate glasses selection based on the structural survey to be further applied as glassy fertilizers.

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