EXPERIMENTAL RESEARCHES OF NA AND PB METAPHOSPHATES WITH HIGH-TEMPERATURE RAMAN SPECTROSCOPY

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The network of phosphate glasses contains a polymeric structure controlled by glass composition and conditions of synthesis [1, 2]. Existence in a melt strongly connected groupings from the atoms forming complex polyanions is examined as a basic concept of phosphate glasses structure. The structure of a melt can be transformed during of temperature alteration. It is supposed, that the fact of concurrence or difference of separate fragments structure in a melt should play a main role in processes of glass-formed and crystallization.

Works is not too much on melt phosphates research with of Raman spectroscopy (RS) at high temperatures [3, 4] while, reception of direct experimental data about their structure has a great importance for understanding of crystallization processes.

This work shows results of study with method RS the structure of Na and Pb metaphosphates in different aggregate conditions.

Glasses samples have been prepared 50 mol. % Na_2O – 50 mol. % P_2O_5 and 50 mol. % PbO – 50 mol. % P_2O_5 composition.

Raman spectra of glasses, melts and products of their crystallization have been by DFS-24 spectrometer. Pulse laser LTI-701 made excitation of spectra. Measurements were carried out by 180º geometry, thus the sample was in a platinum crucible at the usual heating furnace. For comparison of spectra received at various temperatures correction on thermal density of vibration levels [5] was carried out.

Differential-thermal analysis (ДТА) has been carried out using Derivatograph Q-1500 D. By DTA data the exothermal peak a connected with glass crystallization was observed in 573-673 K range in Na metaphosphate on data DTA. The crystallization peak was observed in 773-823 K range at Pb metaphosphate. Temperatures were fusion 900 K and 950 K correspondingly.

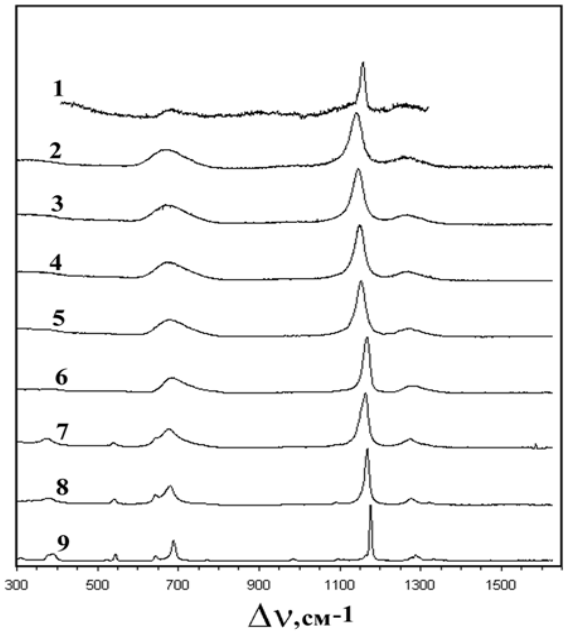

Fig.1. Raman spectra of Na metaphosphate: 1 – 20 % aqueous solution; 2 – melt, T= 1273 K; 3 – melt, T= 1113 K; 4 – melt, T= 983 K; 5 – melt, T= 893 K; 6 – glass; 7 – crystal, T= 784 K; 8 – crystal, T= 668 K; 9 – crystal, T= 293 K.

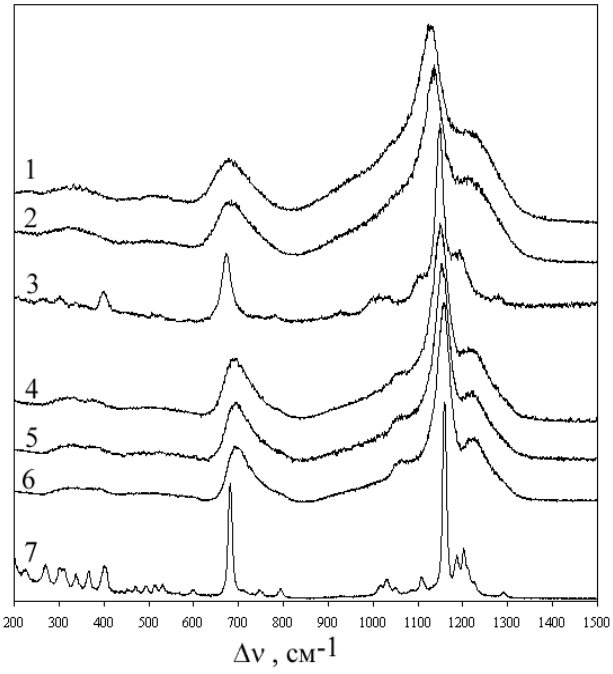

Fig.2. Raman spectra of Pb metaphosphate: 1– melt, T= 1273 K; 2 – melt, T= 1083 K; 3 – crystallization, T= 823 K; 4 – glass, T= 623 K; 5 – glass, T= 473 K; 6 – glass, T= 293 K; 7 – crystal, T= 293 K.

The Raman spectra of samples have been registered at 300–1273 K ranges. All the registered spectra (fig. 1, 2) are characterized by presence of three groups of bands: (i) vibrations of bridging oxygen $v(POP)_{sym}$ in a low-frequency range (500–800 sm^{-1}) are situated; (ii) symmetric vibrations of phosphate tetrahedrons $v(PO2)_{sym}$ are in a range of average frequencies (1100–1200 sm^{-1}); vibrations of phosphate tetrahedrons with two bridging cross-links $v(PO2)_{asym}$ are located in a high-frequency area (1200–1350 sm^{-1}). The intensive band attributed to symmetric vibrations of phosphate tetrahedrons with one non-bridging oxygen is observed at 1050–1150 sm^{-1} fields. The structure of sample glasses is constructed from "quasi-infinite" chains consisted of phosphate tetrahedrons [6] that is proves by intensive peak in the field of average frequencies.

The aggregate condition of the sample strongly changes the bands attributed to $v(POP)_{sym}$ and $v(PO2)_{asym}$. In a crystal condition these bands are split into several peaks, at temperature increase peaks become wider, and one wide band is observed in a melt. This splitting of bands appears owing to occurrence of transmitting symmetry of a crystal lattice. Crystallization does not break a tetrahedron environment of phosphorus and a condensation degree of anion motive because there is no change of the relationship metal oxides and phosphorus of mole share. The polyanion form varies during crystallization. The analysis of products of crystallization by X-ray method has shown the following: Na metaphosphate crystallized in rhombic syngony and Pb metaphosphate – in monoclinic. The discrepancy effect of anion motives structure in melt/glass and crystal is truly observed the Raman spectra.

Thus, in Na and Pb metaphosphates process of crystallization does not break tetrahedron environment of phosphorus, degree of condensation anion motive, and is also accompanied by anion motive reorganization.

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