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Infrared and Raman spectra of Ga_2O_3–P_2O_5 glasses

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Abstract

The structure of $xGa_2O_3(1-x)P_2O_5 (0.15 \leqslant x \leqslant 0.4)$ glasses is studied by infrared (IR) and Raman spectroscopy. The results of quantitative electron microprobe analysis reveal that two sets of glasses are formed with compositions corresponding to the gallium meta and pyrophosphates. Crystalline $Ga(PO_3)_3$ metaphosphate is also obtained and its IR and Raman spectra recorded in order to examine the spectral differences glass → crystal. The IR spectra of metaphosphate glasses show bands at 1250, 930, 775 and 485 cm^{-1} which, are assigned to the $\nu_{as}PO_2$, $\nu_{as}POP$, ν_sPOP and δPO_2 modes of the metaphosphate chain. In the Raman spectra are found patterns due to symmetric modes of PO_2 terminal and POP bridging bonds as well as features due to vibrations of GaO_4 tetrahedra and Ga–O–P bridges. Comparisons of the spectra of glasses with those of the crystal indicate that the interaction of Ga with the polyphosphate anions is more covalent in the glasses. The bands observed in the spectra of pyrophosphate glasses provide evidence for the involvement of ortho-, pyro- and polyphosphate groupings in the glass structure. The Raman spectra of both sets of glasses display intense low frequency bands, which we assigned to a symmetric bending of Ga–O–P bridging bonds involving four-coordinated gallium atoms. It is concluded that structure of Ga_2O_3–P_2O_5 glasses is a highly polymerized network consisting of a variety of phosphate anions cross-linked by GaO_4 tetrahedra. This account on glass structure is consistent with the great glass forming ability of the compositions studied.

1. Introduction

In a search for extending the absorption edge of oxide glasses as far as possible into the infrared (IR) Dumbaugh [1] discovered the PbO–Bi_2O_3–Ga_2O_3 glasses. Gallate glasses have a unique ability to form stable glasses while maintaining key properties such as the best IR transmission, the highest non-linear optical susceptibilities and diamagnetic Verdet constants for oxide glasses [2]. During the past decade they have been extensively studied for potential applications in the field of optoelectronics, non-linear and IR optics [3–6]. The great interest in Ga_2O_3 based glasses fostered numerous structural studies including X-ray and neutron diffraction [7–9] IR spectroscopy [10], Raman scattering [11–13], XPS

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[14] and ^{71}Ga NMR [15]. The results revealed that Ga^{3+} ions are mainly fourfold coordinated even in glasses, where the quantity of modifiers is not sufficient to compensate the negative charge on GaO_4 tetrahedra. These systems very often produce threefold oxygen atoms in order to maintain the charge balance thus violating Zachariasen's criteria for glass formation. In the Ga_2O_3–TeO_2 system Ga atoms also take tetrahedral coordination, as the compensation mechanism remains yet unknown [16]. In the systems studied so far [6–15,17,18] Ga_2O_3 is a component of glasses, which can be termed 'basic' viewed through the concept of optical basicity [19,20]. In basic glasses (consisting predominantly of TeO_2, PbO, Bi_2O_3, V_2O_5) the oxygen atoms bear significant negative charges and are able to donate electron density on Ga^{3+}. This provides an explanation of the good glass forming ability of Ga_2O_3 in basic glasses and its preference for fourfold coordination. Despite the interest gallate glasses have attracted in recent years the Ga_2O_3 systems containing classical glass formers are still little documented. Among Ga_2O_3–M_xO_y systems (M = Si, Ge, B, P) the phosphate system seems to be the most appropriate for investigation due to the large area of glass formation at slow cooling rates [21,22]. It is well-known, however, that the low chemical resistance and moisture degradation of phosphate glasses poses many restrictions on their commercial exploitation and usefulness. In this respect the addition of Ga_2O_3 into phosphate networks is expected to yield materials with improved characteristics. From a structural point of view the Ga_2O_3–P_2O_5 glasses could be attractive theme as well since the cation–polyanion interactions are expected to be highly covalent. This implies that the assignments of the bands in vibrational spectra will not be readily based on comparisons between crystal phonon modes and glass vibrations.

In this paper we report our results and interpretation on IR and Raman spectra of Ga_2O_3–P_2O_5 glasses. The crystalline $Ga(PO_3)_3$ metaphosphate is also obtained and its IR and Raman spectra measured in order to make comparisons of the spectra of glasses with those of the crystal. Furthermore, glass structure is discussed in terms of the results obtained and conclusions are made on the relation: glass structure → glass-forming ability.

2. Experimental

2.1. Preparation of samples

$xGa_2O_3 \cdot (1-x)P_2O_5$ glasses (with $x = 0.15/0.40$) were prepared from reagent-grade Ga_2O_3 and $NH_4H_2PO_4$ following Urusovskaja et al. [22]. After preliminary heating at 400°C the batches were melted in Pt crucibles in air for 20 min in the temperature range 1300–1550°C. The glassforming tendency of the liquids is high so that they can vitrify even at the slowest cooling rates employed. The compositions of the end product glasses were analyzed by a JEOL 733 electron probe microanalyser. The results revealed that irrespective of initial compositions, batches containing from 0.15 to 0.30 mole fractions Ga_2O_3 form glasses with very similar content close to that of gallium metaphosphate. In the rare earth phosphate systems the glass formation follows a similar trend [23,24].

The samples comprising 0.35 and 0.40 mole fractions Ga_2O_3 yield end glasses with composition corresponding to the pyrophosphate – $Ga_4(P_2O_7)_3$. These results can be understood in terms of the stability of condensed phosphates of gallium. The small Ga^{3+} cation ($r_{Ga} = 0.58$ Å) does not form ultraphosphates [25]. The tri-phosphate is stable up to 350°C as polymerizes upon increasing temperature [25]. Similarly to the majority of R^{3+} cations gallium does not interact with P_2O_5 to yield stable solid-state pyrophosphates [26]. There is a hydrated form – $Ga_4(P_2O_7)_3 \cdot 20H_2O$ which disproportionates into poly- and orthophosphates at the crystallization temperature (800°C) [26]. The stable phases are – $Ga(PO_3)_3$ which is the metaphosphate and $GaPO_4$ – the orthophosphate [25,27].

Crystalline $Ga(PO_3)_3$ was synthesized via solid-state reaction from Ga_2O_3 and $NH_4H_2PO_4$. The mixture of raw materials was heated successively at 170, 210, 350 and 450°C for 5 days [28]. The crystalline phase was identified by X-ray diffraction (XRD) (ICDD card N = 47-0509).

2.2. Measurements of IR spectra

IR absorption spectra were recorded on a Bruker (IFS 113 v) FT-IR spectrometer in the 4000–400 cm^{-1} range. Samples in powder form were pressed into disks using spectroscopically pure KBr.

2.3. Measurements of Raman spectra

Polarized (HH, HV) and depolarized Raman spectra were recorded by a Spex 1403 spectrometer in the 45° and 90° scattering geometry, respectively. The spectra were measured in the Stokes spectral range between 2000 and 50 cm^{-1}. The excitation source was the 514.5 nm line of an Argon ion laser operating at a power of 100 mW on the sample. During measurement a broad luminescence background was observed for samples with $x = 0.35$–0.40. Those spectra were examined additionally using the 488.0 nm laser line to test which bands do indeed constitute the Raman spectra. The scattered light was detected by a cooled photomultiplier with a computerized photon counting system.

3. Experimental results

3.1. IR spectra

The IR spectra of Ga_2O_3–P_2O_5 glasses along with that of crystalline $Ga(PO_3)_3$ in the 2000–400 cm^{-1} range are given in Fig. 1. As can be seen the glasses are not hygroscopic as revealed by the lack of bands at about 1600 cm^{-1} (δH_2O). Due to the similarity in the chemical composition, two sets of IR spectra are recognizable, called in what follows the 'metaphosphate' and 'pyrophosphate' set, respectively. The IR spectra of metaphosphate glasses show four distinct bands at ~1250, 930, 775 and 480 cm^{-1} and a weak feature at ~1150 cm^{-1}. In the spectra of glasses belonging to the pyrophosphate series the 1250 cm^{-1} band shifts down to 1180–1090 cm^{-1}. The absorption maximum at 930 cm^{-1} moves to 950 cm^{-1}. Simultaneously the 480 and 775 cm^{-1} bands shift to 515 and 765 cm^{-1} accordingly as both decrease in integral intensity. Finally, a new band peaking at 640 cm^{-1} appears in the spectra of pyrophosphate glasses.

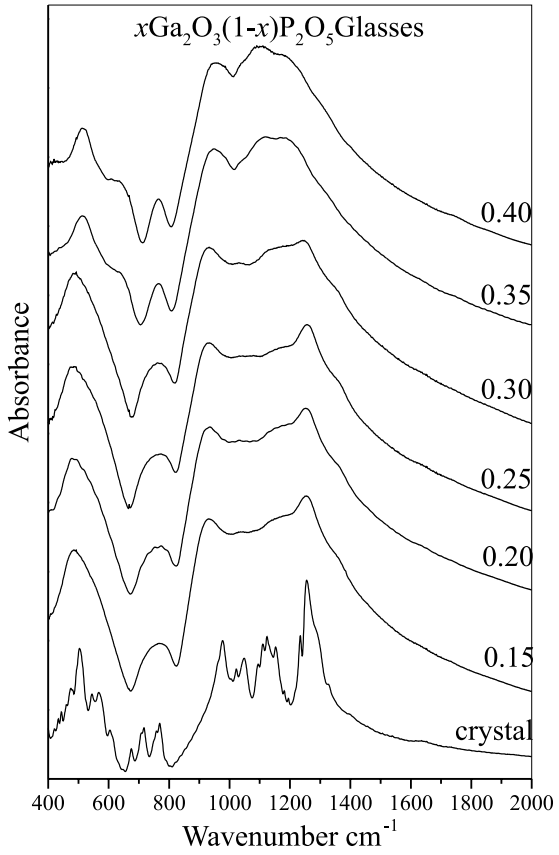

Fig. 1. IR absorption spectra of crystalline $Ga(PO_3)_3$ and $xGa_2O_3 \cdot (1-x)P_2O_5$ glasses (x = mole fraction by synthesis).

IR reflectance spectra of Ga_2O_3–P_2O_5 glasses have been reported by Urusovskaja et al. [22]. Their spectra show the same trend and similarly can be divided in two sets. Following the numerous spectral studies on phosphate crystals and glasses [29–36] the bands observed can be assigned as follows. The principal band at 1250 cm^{-1} in the IR spectra of metaphosphate glasses is due to the asymmetric stretching of PO_2 terminal groups. The bands at 775 and 930 cm^{-1} can be associated with symmetric and asymmetric motions of the bridging oxygen in POP bonds. The intense band at 480 cm^{-1} is attributed to deformation modes of PO_2 fragment. Symmetric stretching of PO_2

groups gives rise to the 1150 cm^{-1} bands. In pyrophosphate glasses the high-frequency bands shift to lower energies where bands due to vibrations of gallium tripoly-, pyro- and orthophosphates are placed [26,27,37]. The band at ~1190 cm^{-1} can be assigned to stretching vibrations of PO_3 terminal groups from poly- and pyrophosphate groups. The bands in the 1090–1100 cm^{-1} range can be associated with an overlap of several modes namely: stretching of the PO_3 terminal and PO_2 middle groups. It is worth mentioning, however, that the vibrational dynamics of the short polyphosphate chains is such that it is difficult to expect characteristic modes in the entire spectrum [38]. In addition, $v_3(F_2)$ mode of the ortho anion can also contribute to the absorption at 1100 cm^{-1}. The 765 and 950 cm^{-1} bands can be assigned to stretching vibrations of POP bridges while the 510 cm^{-1} band is due to deformation modes of PO_2 and PO_3 groups. The 640 cm^{-1} peak can be assigned to vibrations localized on GaO_4 tetrahedra [10].

3.2. Raman spectra

Fig. 2 shows the depolarized Raman spectra of $xGa_2O_3 \cdot (1-x)P_2O_5$ $(x = 0.15/0.40)$ glasses together with the spectrum of crystalline $Ga(PO_3)_3$ obtained from excitation at 514.5 nm. These spectra also fall into two distinct categories. In the spectra of the metaphosphate glasses there are two intense bands at 1210 and 715 cm^{-1} due to symmetric modes of PO_2 terminal and POP bridging bonds. The weak satellite line at ~1320 cm^{-1} is attributed to $v_{as}PO_2$. The low-frequency part of Raman spectra differs, however, from the corresponding spectra of alkali, alkali-earth and rare-earth metaphosphate glasses [33,39]. First, there is a new feature at 610 cm^{-1} distinct in both depolarized and HH Raman spectra (see Figs. 2 and 3). The detailed investigation of vibrational spectra of gallate glasses performed by Sakka et al. [10,11] showed that the Raman bands at ~600–650 cm^{-1} are due to stretching modes of GaO_4 tetrahedra. Second, the 350 cm^{-1} band is more intense compared to weak features in glassy $NaPO_3$ and $Mg(PO)_3$ [33]. The 350 cm^{-1} bands in glassy and crystalline metaphosphates were assigned to PO_2 and in chain O–P–O bending vibrations [29,33].

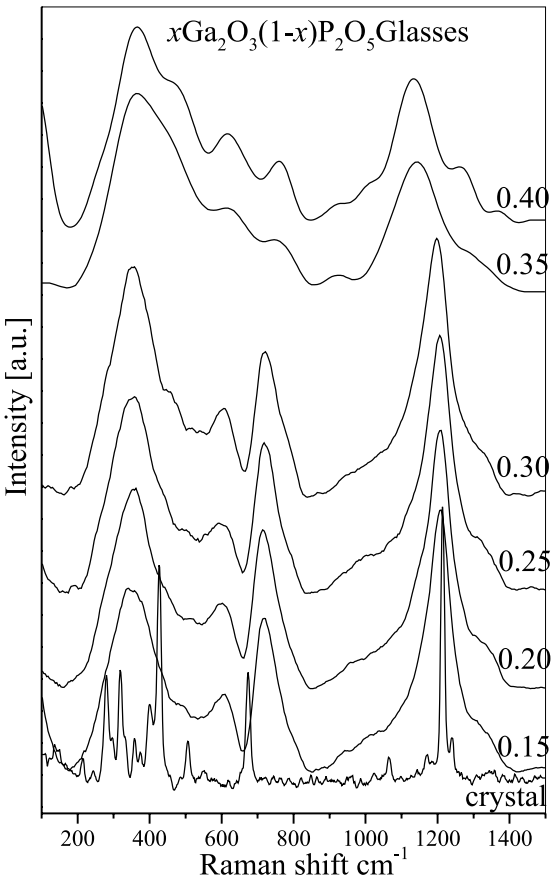

Fig. 2. Depolarized Raman spectra of crystalline $Ga(PO_3)_3$ and $xGa_2O_3 \cdot (1-x)P_2O_5$ glasses (x = mole fraction by synthesis, 514.5 nm).

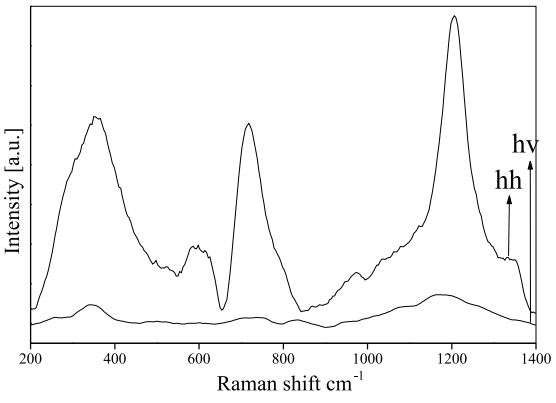

Fig. 3. HH and HV Raman spectra for $0.20Ga_2O_3 \cdot 80P_2O_5$ glass.

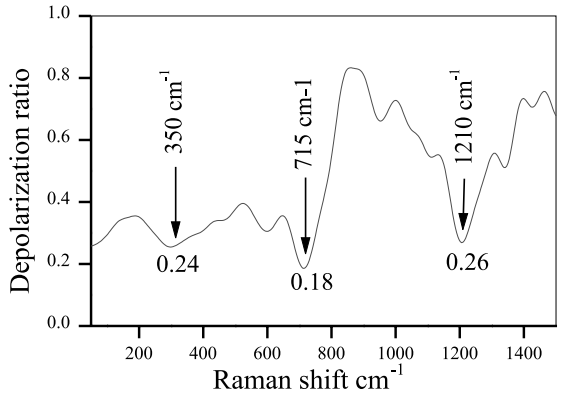

Fig. 4. Depolarization ratio vs frequency shift for $0.20Ga_2O_3 \cdot 0.80P_2O_5$ glass.

The polarization analysis performed by Bobovich [39] showed that 350 cm^{-1} band in Na, Ca, Zn, Mg, Al and Be metaphosphate glasses is depolarized. The depolarization ratio spectrum obtained for 0.20 Ga_2O_3–$0.80P_2O_5$ sample (see Fig. 4) shows that the 1210, 715 and 350 cm^{-1} bands are polarized with $DR = I_{HV}/I_{HH}$ in the range 0.18–0.26. The presence of three minima in the depolarization ratio spectrum corresponding to symmetric or nearly symmetric modes show that the amorphous solid possesses three well-defined but different bonds in the main framework of glass structure [40]. Glasses containing tetrahedrally coordinated Ga atoms give intense low-frequency IR and Raman bands assignable to bending modes of mixed Ga–O–M bridges [10,12,41]. Thus one can expect that the 350 cm^{-1} band in the Raman spectra of Ga_2O_3–P_2O_5 glasses is due to symmetric bending vibrations of P–O–Ga linkages.

As mentioned the two pyrophosphate glasses exhibit intense luminescence which leads to increased shot noise in their spectra. Raman spectra measurements performed with 514.5 and 488.0 nm laser lines show that the bands peaking at ~1150, 760, 640 and 370–400 cm^{-1} are Raman lines since they obey the requirement of Raman spectra that Δv is independent of excitation frequency. The 1270 and 1370 cm^{-1} features observable in the Raman spectrum of the $0.40Ga_2O_3 \cdot 0.60P_2O_5$ glass, are due to optical fluctuations (noise) and accordingly have no structural origin.

The broad Raman peak centered at 1150 cm^{-1} can be attributed to stretching modes of PO_3 terminal groups. Stretching vibrations of POP bonds can give rise to the 760 cm^{-1} peaks. The Raman line at 640 cm^{-1} is a feature characteristic for vitreous gallate systems with fourfold coordinated Ga atoms [10,11]. The intense bands at about 370–400 cm^{-1} can be attributed to deformation modes of the mixed Ga–O–P bridges in accordance with the assignment made for metaphosphate glasses.

3.3. IR and Raman spectra of $Ga(PO_3)_3$ crystal

The IR and Raman spectra of crystalline gallium metaphosphate are shown in Figs. 1 and 2. $Ga(PO_3)_3$ has been reported to be iso-structural to aluminum metaphosphate, which crystallizes in the monoclinic space group C_s^4 with $Z = 12$ [42,43]. The factor group analysis of $Al(PO_3)_3$ is presented in Table 1. The primitive cell comprises three slices of $[(PO_3)_6]_\infty$ chains whose onefold space groups are isomorphous with C_s and C_1. The interactions between the chains lead to a total of $101\ A' + 103\ A''$ internal chain modes active in both IR absorption and Raman scattering. The presence of six PO_4 tetrahedra in the repeatable distance of the chain are expected to produce six vibrations in each of the regions corresponding $\nu_{as}PO_2$, $\nu_s PO_2$, $\nu_{as}POP$ and $\nu_s POP$ stretching frequencies. Lazarev et al. [31,44] have proposed to use the number of the active IR ($\nu_s POP$) bands in the spectra of crystalline metaphosphates as criterion showing the configuration of the chain. In crystal of C_s^4 symmetry the POP bridges are distributed over three sets of sites of C_1 symmetry which leads to $9\ A' + 9\ A'' \nu_s POP$ stretching fre-

Table 1
Factor group analysis of $Al(PO_3)_3$ in its monoclinic form (body-centered, *non-primitive* unit cell)

C_s	E	σ^{xy}
n_o (Al)	6	0
n_o (P)	18	0
n_o (O)	54	0
n_o (AlP_3O_9)	78	0
$\pm 1 + 2\cos\varphi$	3	1
$\chi_T(h)$	231	−1
$\Gamma_{(opt)} = 115\ A' + 116\ A''$		

quencies. An inspection of the IR spectrum of polycrystalline $Ga(PO_3)_3$ shows, however, only six bands at 768, 757, 716, 707, 675 and 667 cm^{-1} due to v_sPOP. More detailed analysis on the crystal normal modes of a variety of R(III) metaphosphates structures can be found in [45]. The comparison of the spectra of crystalline gallium metaphosphate with those of glasses reveals several differences. The 675 cm^{-1} bands seen in the IR spectrum of the crystal fall aside the frequency range covered by v_sPOP bands in glasses. Moreover, the v_{as}POP band moves from 975 cm^{-1} in the IR spectrum of the crystal to 930cm^{-1} in the spectra of glasses whereas the highest frequency v_sPOP band shifts from 765 to 775 cm^{-1}. The Raman spectrum of polycrystalline $Ga(PO_3)_3$ shows one band at 675 cm^{-1} due to v_sPOP. In the spectra of glasses, however, the corresponding band is shifted to 720 cm^{-1}. The most significant differences in the Raman spectra concern the intensity of scattering at 610 and 350 cm^{-1}. In the Raman spectrum of crystalline $Ga(PO_3)_3$ there is no band at ~610 cm^{-1} and the profile of low-frequency region is substantially different from those in glasses.

4. Discussion

4.1. Structure of metaphosphate glasses

The presence of IR and Raman bands corresponding to the stretching modes of PO_2 terminal and POP bridging bonds indicates that the $xGa_2O_3 \cdot (1-x)P_2O_5$ ($x = 0.15/0.30$) glasses consist of metaphosphate chains. The comparison of the spectra of glasses with those of crystalline $Ga(PO_3)_3$ suggests however, differences in their structures. Lazarev [31,44] in studies of the nature of POP bonds in metaphosphates notes that the v_sPOP are very sensitive to the changes in the structural motif determined by the configuration of the oxygen polyhedra surrounding cations. The lack of 675 cm^{-1} band (v_sPOP) in the IR and Raman spectra of glasses can be related to changes in the spatial arrangement of the chains in the vitreous and crystalline metaphosphates. In crystalline metaphosphates (metasilicates) decreasing the number of v_sPOP bands corresponds either to smaller number of PO_4 tetrahedra constituting the repeatable unit or to an increase in chain symmetry [31,44]. The IR spectra of glassy Li and Na metasilicates show two v_sSiOSi bands in correspondence with the spectra of crystalline counterparts which implies similarity in chain conformations [31]. As mentioned above the v_{as}POP and v_sPOP IR bands in glasses are shifted from their locations in the crystal. The ratio $= [v_{as}\text{POP} - v_s\text{POP}]/[v_{as}\text{POP} + v_s\text{POP}]$ can be used to evaluate the changes in the POP angle upon crystal $\rightarrow$ glass transition. In crystalline $Al(PO_3)_3$ the POP angles span 139°–148° which implies substantial overlap of valence orbitals of P and BO (bridging oxygen). When the frequencies of v_{as}POP and v_sPOP bands introduced in this relation an average POP angle of 109° is obtained. In [46] the vibrational frequencies (ω) of an infinitive metaphosphate chain of C_{2v} symmetry were calculated as a function of chain geometry. The variation in the POP bond angles leads to an increase in the frequency of v_sPOP mode (A_1 Raman active) of ~100 cm^{-1} upon changing the angle from 180° to the 109°. The decrease in POP bond angles is consistent with the reduction of π bond character of the bridging bonds and accordingly consistent with their elongation. Review articles dealing with the crystal chemistry of phosphates [42,47] indicate that as covalent the interaction between the cation and polyphosphate anion as longer the P–O bonds. An internal standard to measure the degree of interaction between the terminal PO_2 groups and neighboring cations is the ratio of the intensity of $v_s PO_2$ against v_sPOP bands in the Raman spectra [33]. Cations with great field strength withdraw electronic density in the direction of the M $\leftarrow$ O(P) bonds, leading to their polarization and subsequently to depolarization of POP bonds. In the Raman spectra this effect brings about redistribution of $v_s PO_2$ and v_sPOP bands intensities. Thus the ratio decreases from 5.9 in $CsPO_3$ to 1.8 in $Al(PO_3)_3$ glass [33]. In vitreous $Ga(PO_3)_3$ the ratio falls to 1.37. This effect is well manifested through comparison of relative intensities of $v_s PO_2$ and v_sPOP bands in the Raman spectra of the crystalline and vitreous gallium metaphosphates. All these facts indicate a highly covalent interac-

tion between Ga and P–O bonds and can be connected with the change in the coordination state of Ga (from octahedral in the crystal to tetrahedral in glasses). In phosphate systems, a mutual neutralization of the charges on GaO_4 and PO_4 tetrahedra is possible similarly to the crystalline $GaPO_4$. The electronic configuration of the set of two tetrahedra is equivalent to one SiO_4 tetrahedron. It would be of particular significance to compare results on gallium phosphate glasses with data dealing with glassy $Al(PO_3)_3$ [48–50]. Most results are in favor of a mixture of tetrahedral and octahedral sites of Al^{3+} in the phosphate network. Hoppe et al. [51] reported, however, a coordination number of six for Al^{3+} in the vitreous metaphosphate. In Ga_2O_3–P_2O_5 glasses along with the 610 cm^{-1} Raman band (νGaO_4) very convincing indication for the involvement of tetrahedrally coordinated gallium atoms in the phosphate network is the change in the polarization properties of these glasses. If multiplicity of local environments ($GaO_4 + GaO_6$ polyhedra) were present in the network then the Raman spectrum would display weakly polarized and broader low-frequency bands as observed in the Raman spectrum of $Al(PO_3)_3$. It is worth mentioning that in the K_2O–Ga_2O_3–GeO_2 glasses the low-frequency bands reflecting the motion of bridging oxygen in the Ga–O–Ge linkage decrease in intensity with increasing the fraction of GaO_6 octahedra (changing the ratio Ga_2O_3/K_2O) [41].

4.2. Structure of glasses of pyrophosphate composition

As mentioned the high-frequency features presented in the spectra of pyrophosphate glasses cannot be related to the vibrations of a single species. Sales et al. [52] determined the exact distribution of anionic species in a $Ga_4(P_2O_7)_3$ glass by high-performance liquid chromatography. They found that the glass is composed of three major fractions namely: pyro, tri and tetra anions. Ortho groups and polyphosphates containing five and six PO_4 tetrahedra are present as well. No cyclic anions were found in contrast to other trivalent phosphate glasses. The high-frequency bands in the Raman spectra of gallium phosphate glasses reminds the spectra of other glasses which disproportionate near the pyrophosphate composition. Typical examples in this respect are Zn pyrophosphate glasses as reported by Brow et al. [34]. The structural differences between the two sets of glasses are best reflected by the changes in ν_sPOP and ν_{as}POP bands indicative for phosphate network connectivity. The mutual frequency shift of symmetric (775 → 765 cm^{-1}) and asymmetric (930 → 950 cm^{-1}) POP bands in the IR spectra of pyrophosphate glasses is consistent with the transition from the metaphosphate structure (small POP angles) into a network dominated by discrete phosphate anions with greater POP angles as found in the crystalline poly- and pyrophosphates [31,44,53]. Regardless similarity to the spectra of other pyrophosphate glasses the low-frequency Raman spectra of Ga_2O_3–P_2O_5 glasses have no analog among the phosphate systems. They remind the Raman spectra of vitreous silica and other tetrahedrally bonded glasses [40]. The dominant highly polarized Raman line occurring at low-frequencies corresponds to a symmetric vibration of bridging oxygen atom from T–O–T bonds (where T is a tetrahedrally coordinated cation) [40]. The bands due to GaO_4 tetrahedra are present in both IR and Raman spectra. It is expected that these GaO_4 units cross-link the discrete phosphate anions into a three-dimensional network resembling the framework of the silicate and germanate glasses. These results can explain the high glassforming tendency of the melts near the pyrophosphate composition.

5. Conclusions

Stable phosphate glasses containing up to 40 mol% Ga_2O_3 can be obtained by ordinary melt quenching.

The compositions of end product glasses can be divided in two sets corresponding to the $Ga(PO_3)_3$ metaphosphate and $Ga_4(P_2O_7)_3$ pyrophosphate.

The structure of metaphosphate glasses consists of chains interconnected by GaO_4 tetrahedra.

Pyro-, ortho- and polyphosphate groups as well as GaO_4 tetrahedra make up the framework of glasses with the pyrophosphate composition.

The intense low-frequency Raman bands in the spectra of both sets glasses suggest that the network of Ga_2O_3–P_2O_5 glasses is a highly polymerized matrix.

The observed diversity of phosphate anions as well as Ga atoms in glass forming positions can explain the high vitrification ability of glasses under study.

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