International Journal of Innovative Science and Modern Engineering (IJISME)
ISSN: 2319-6386, Volume-4 Issue-8, December 2016

Microstructural Characterization and Local Ordering of Fluorophosphate Ternary MnF_2-$NaPO_3$-ZnF_2 Glasses

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Abstract: ***The investigation of physicochemical properties of glasses in connection with their structure and potential applications is an important field of studies. In this work, the microstructural nature of ternary glasses from the MnF_2-$NaPO_3$-ZnF_2 system has been evaluated by such structure-sensitive parameters as the glass transition temperature (Tg), Vickers microhardness (HV) and their relation. These glasses possess relatively high values of Tg (240-290 oC) and HV (160-275 kg.mm-2). Based on the free-volume theory, the average volume of microvoids (Vh), their formation energy (Eh) and the module of elasticity (Em) have been determined. The relationship between them and the glass composition has been specified. The observed changes in the variation of these parameters have been discussed by the data from Raman scattering and infrared absorption of the glasses studied.***

Keywords: ***Fluorophosphate glasses; Physical properties; Local structure***

I. INTRODUCTION

Phosphate and fluorophosphate glasses have been considered as attractive materials for a wide range of possible applications due to their suitable combination of properties. They are excellent hosts for active rare earth cations because of advantageous local structure effect and consequent high solubility, which is essential for such photonic devices as high power lasers, fibre and waveguide amplifiers, etc [1]. Fluorescence properties of Tm^{3+} doped tungstate fluorophosphate glasses have been investigated by their transition probabilities, branching ratios, and radiative lifetimes, considering radiative relaxation, multiphonon processes and energy transfer among Tm^{3+} ions [2]. The origin of the observed frequency upconversion process has also been described. Numerous $NaPO_3$-BaF_2 based fluorophosphate glasses are known, either with a high content of transition metal ions [3] or rare-earth ions [4-6]. The spectral behavior (spectral intensities and calculated radiative lifetimes) is intermediate between fluoride and oxide glasses. These glasses are characterized by low values of melting temperature, refractive index and dispersion. Fluorophosphate glasses have been the subject of numerous studies because of the increased interest in various perspective technological branches such as optical materials, biomaterials, for storage of radioactive wastes, etc. [7-11].

The high UV transparency of these glasses enables the exploitation of different electronic transitions of active ions situated in the UV spectral range [10]. They usually exhibit small optical non-linearity and low viscosity [12]. In particular, fluorophosphate glasses containing manganese exhibit interesting magnetic and optical properties that could be also used for potential applications. It has been found that sodium polyphosphate ($NaPO_3$) makes an efficient stabilizer of fluoride glasses based on MnF_2.

In a general way, phosphate glasses based on $NaPO_3$ are easy to prepare and are often hygroscopic, which limits practical use. However, the incorporation of fluorides increases chemical durability as this has been observed in the $NaPO_3$-BaF_2-MF_n ternary systems (M=Mg, Mn, Zn, Fe, Cr, Ga) [3]. The addition of sodium polyphosphate in binary MnF_2-ZnF_2 glass really reduces the tendency to devitrification, which allows preparing bulk samples that are stable in ambient atmosphere. This additive keeps a low temperature of melting, which limits fluorine losses that occur with the formation of gaseous POF_3. While pure $NaPO_3$ glass is some what sensitive to water, the incorporation of insoluble fluoride increases chemical durability, especially in wet atmosphere.

Among other features, fluorophosphate glasses containing manganese have a good infrared transmission extending up to 4.5 µm and are excellent host for rare-earth cations, which predict their application as active optical devices [4-6]. More recently, glasses in the system MnF_2-$NaPO_3$-ZnF_2 have been studied in detail [13-16]. The stabilizing effect of $NaPO_3$ in fluoride glasses based on MnF_2 has been confirmed, together with the compatibility of phosphate and fluoride vitreous networks. Manganese concentration may be large, about 50 mol% in some cases, while zinc and manganese cations may be substituted almost completely. Especially, the MnF_2-$NaPO_3$-ZnF_2 system exhibits a large glass-forming region [13]. The evolution of the physical properties versus chemical composition has shown that the incorporation of MnF_2 at the expense of $NaPO_3$ leads to the increase of the basic physical parameters such as glass transition temperature, density, microhardness, Young module, thermal expansion and refractive index. The magnetic susceptibility of $(MnF_2)_x(NaPO_3)_{90-x}(ZnF_2)_{10}$ series has been determined in order to identify magnetic behavior of divalent manganese [15]. It has been found that clusters with antiferromagnetic interactions between Mn^{2+} ions are formed by increasing MnF_2 content. The electrical and dielectrical properties of these glasses have also been investigated, in order to identify the conduction mechanism and their thermal behavior [16].

Revised Version Manuscript Received on January 20, 2017

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The purpose of this study is evaluation of microstructural features of glasses from the series $(MnF_2)_x(NaPO_3)_{80-x}(ZnF_2)_{20}$ $(0 \le x < 50)$ on the base of such physicochemical and structure-sensitive parameters as the glass transition temperature and the microhardness has been performed. These glasses possess relatively high values of the glass transition temperature (T_g varies from 240 to 290 ^oC) and the microhardness (H_V=160-275 kg mm^{-2}) [13]. On the base of T_g, H_V data and their relation, the average volume of microvoids (V_h), their formation energy (E_h) and the module of elasticity (E_m) have been calculated. The relationship between them and the glass composition has been specified. In order to collect information about the local ordering in this glassy system, structural studies have been implemented by Raman scattering in combination with infrared spectroscopy. These results should help currently to understand the way how the respective vitreous networks of phosphates and fluorides have been combined.

II. EXPERIMENTAL

A series of glass samples has been prepared according to the general composition rule $(MnF_2)_x(NaPO_3)_{80-x}(ZnF_2)_{20}$ $(0 \le x < 50)$. This corresponds to the substitution of sodium polyphosphate by manganese difluoride. Starting materials are commercial products: anhydrous fluoride ZnF_2 (99.9 % from Aldrich), ammonium hydrogenofluoride NH_4F, HF (99.9 % from Riedel-de Haën) and sodium polyphosphate $NaPO_3$ (97 % Rectapur from WWR Prolabo). Manganese difluoride MnF_2 is prepared in the laboratory, using MnO and NH_4F, HF as a fluorinating reagent in a platinum crucible, and controlled by X-Ray diffraction. Glass synthesis includes melting in air, fining, casting and annealing (the procedures are described in Refs. [14,17]). The final annealing is carried out for 6 h at a temperature of 10 K lower than T_g in order to minimize mechanical stress resulting from thermal gradients upon cooling. The amorphous state of the samples is checked by X-ray diffraction analysis.

The glass transition temperature was measured by differential scanning calorimeter using a SEIKODSC/220 set-up. Samples with weight of 10-20 mg are set in aluminium pans under N_2 atmosphere at 10 K min^{-1} heating rate with a temperature accuracy of ± 2 ^oC [13]. The micro-hardness is measured by Vickers microindenter using a Matsuzawa MXT set-up with 50 g load for 10 seconds. A mean value is obtained after averaging several measurements.

Raman spectra were recorded in the range of 1400-100 cm^{-1} with high resolution of 1.2 cm^{-1} by an HR device 800 (from Horiba/Jobin-Yvon Company). He-Ne laser operating at 633 nm with a constant power of 10 mW was used as an excitation source. IR absorption spectra were recorded with the help of a Fourier transform infrared (FTIR) spectrophotometer Merlin Digilab FTS 3000 operating between 4000-400 cm^{-1} from powdered glasses dispersed in dehydrated KBr pellets.

III. THEORETICAL BACKGROUND

The molecular kinetic processes in glasses are defined to a large extent by the local fluctuation disorder in the structure at the expense of the deformation of the network without breaking the valence bonds. These processes can be considered as formation, migration and fluctuation at a micro-volume level on the base of the free-volume theory, which gives the correlation between the microhardness and the glass transition temperature as very structure-sensitive parameters. According to this theory [18], the microhardness can be expressed by

$$H_V = E_h/V_h, \qquad (1)$$

where E_h is the formation energy of a micro-void within a volume of V_h and is equal to

$$E_h = 3kT_g, \qquad (2)$$

in which k is the Boltzmann constant. Consequently, from equations (1) and (2) V_h can be determined:

$$V_h = 3kT_g/H_V. \qquad (3)$$

Based on the equation for the molecular interaction energy and on the microhardness definition as the pressure necessary to overcome the intermolecular forces, the following relationship is suggested:

$$H_V = (1 - 2\mu)E_m / 6(1 + \mu), \qquad (4)$$

where E_m is the module of elasticity for a single axis expansion/shrinking, and μ -Poisson coefficient, which can be expressed by

$$\Delta\alpha T_g = (1 - 2\mu)^2 / 2(1 + \mu); \qquad (5)$$

$\Delta\alpha T_g$ is the part of the free volume, which is remained below T_g and is around 0.1 [18].

IV. RESULTS

The obtained results for the microstructural characterization are summarized in Table 1.

Table 1. Microstructural Data of $(MnF_2)_x(NaPO_3)_{80-x}(ZnF_2)_{20}$. Glasses.

MnF_2 mol%	T_g ^oC	H_V kg/mm^2	V_h $Å^3$	E_h kJ/mol	E_m GPa
0	240	156	7.8	7.14	22.9
5	239	160	7.5	7.11	23.5
10	242	168	7.3	7.20	24.7
15	247	184	6.8	7.35	27.0
20	250	198	6.4	7.44	29.1
25	251	209	6.1	7.47	30.7
30	254	217	5.9	7.56	31.9
35	262	234	5.6	7.79	34.4
40	271	246	5.5	8.06	36.1
50	291	275	5.3	8.66	40.4

The values of T_g and H_V both increase by the incorporation of manganese fluoride at the expense of $NaPO_3$ (Fig. 1). The crystallisation temperature (T_c) varies from 320 and 475 ^oC, consequently the glasses are considered as thermally stable.

The microhardness is obtained by measuring the diagonal length of the indentation produced by the penetration of square-based diamond pyramid indenter. In other words, this parameter is defined as the pressure necessary to overcome the induced intermolecular forces. When an indenter penetrates a solid, the applied load produces a stress field, resulting in compression and elastic deformation.

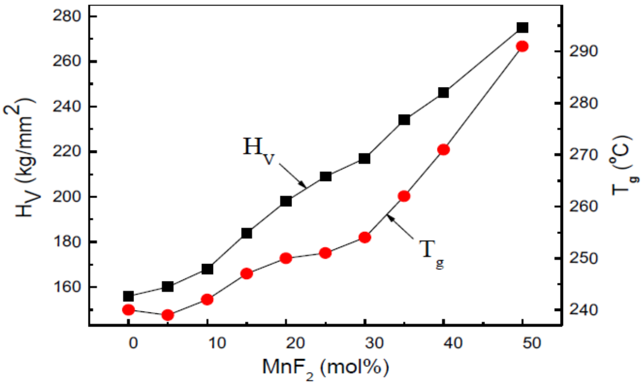

Fig.1. Dependences of Tg and HV Values on MnF2 Concentration in the Composition of the Studied Glasses.

Based on the T_g, H_V values and their relation, the average volume of microvoids (V_h), the energy of their formation (E_h) and the module of elasticity (E_m) are calculated and their compositional dependences are summarized in Figs. 2 and 3.

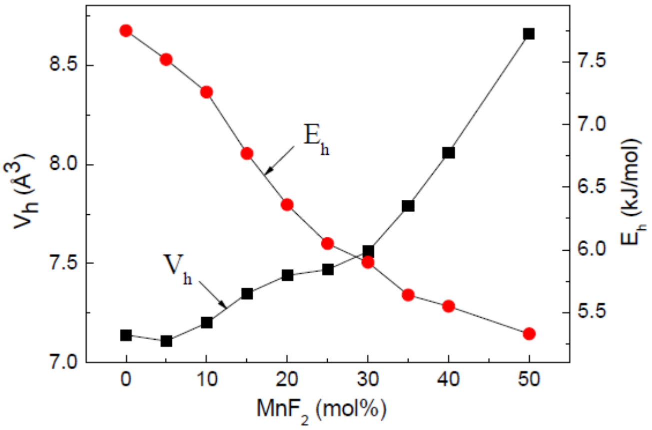

Fig.2. Average Volume of Microvoids (V_h) and Energy of their Formation (E_h) Versus MnF_2 Content in the Composition of the Studied Glasses.

With increasing MnF_2 concentration, a decrease of V_h values and a consequent increase of E_h ones are observed (Fig. 2). Besides, E_m increases at higher MnF_2 content (Fig. 3), which is in a good agreement with the variation of previously measured by an ultrasonic pulse-echo method Young module (E) of the glasses studied [13].

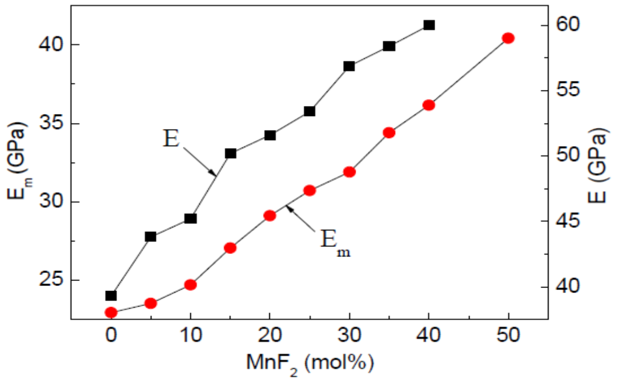

Fig.3. Compositional Dependencies of E_m and E Values on MnF_2 Content of the Studied Glasses.

The incorporation of MnF_2 into the glass matrix leads to significant changes in the Raman spectrum, as shown in Fig. 4. It is dominated by a large peak around 1050 cm^{-1} while new bands emerge at high MnF_2 concentration. Note the doublets below and above 1000 cm^{-1} for the sample with 40 mol% MnF_2 and the bands at lower frequency (390 cm^{-1} and 550 cm^{-1}) in MnF_2-rich glasses.

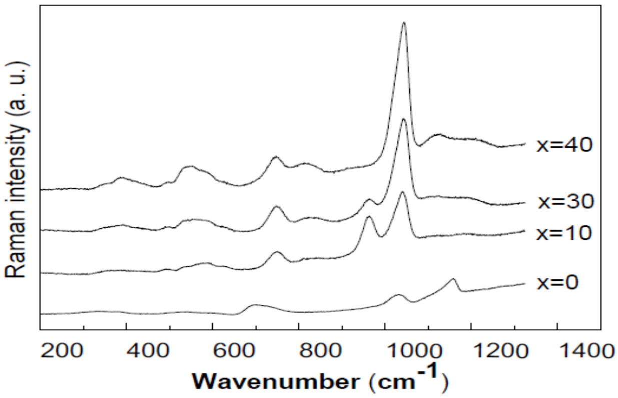

Fig.4. Raman Spectra of $(MnF_2)_x(NaPO_3)_{80-x}(ZnF_2)_{20}$ (x=0, 10, 30, 40) Glasses.

As shown in Fig. 5, the substitution of $NaPO_3$ by MnF_2 induces changes in IR absorption spectra. Six absorption bands are identified in the range of 435-445 cm^{-1}, 540-570 cm^{-1}, 745-817 cm^{-1}, 920-935 cm^{-1}, 1018-1027 cm^{-1} and 1128-1150 cm^{-1}. The corresponding attributions to vibration modes are given in Table 2. By comparison to the absorption spectrum of pure $NaPO_3$, these values are shifted to higher frequency [19].

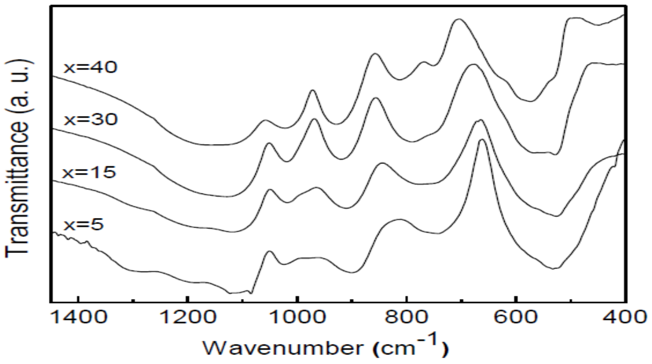

Fig.5. Infrared Spectra of MnF2)x(NaPO3)80-x(ZnF2)20 (x=5, 15, 30, 40) Glasses.

Table 2. Assignment of Vibration Modes in IR Spectra for the Studied Glasses.

(cm^{-1})	Attribution
435-445	Stretching mode of M-F bonds (in MnF_6 octahedra)
540-570	Deformation mode in Q^2 tetrahedra (δO-P-O and δP-O-P)
745-817	Symmetric stretching mode connections of P-O bridging groups in intermediate PO_2^-tetrahedra Q^2.
920-935	Elongation of asymmetric links (P-O-P) between Q^2 tetrahedra.
1018-1027	Elongation of symmetric connections P-O terminal (Q^1).
1128-1150	Elongation of symmetric connections P-O terminal (Q^1 of PO_3^{2-} group)

V. DISCUSSION

The structure of polyphosphate glasses $M(PO_3)_n$ is currently described on the basis of PO_4 chains or rings surrounding M^{n+} cations. Thus tetrahedra share only two corners, which correspond to Q^2 tetrahedra. As a consequence, IR spectrum shows absorption bands typical of P-O bonds between phosphorous and bridging oxygen and non-bridging oxygen. As reported in Table 2, IR spectrum also shows deformation of P-O-P chains, and also the stretching of the M-F bonds (M=Zn and Mn).

The series of glass samples of this study have been prepared in the MnF_2-$NaPO_3$-ZnF_2 ternary system. They correspond to the incorporation of manganese difluoride at the expense of sodium metaphosphate. This results in the increase of the F/O ratio. In classical oxide glasses this leads to the depolymerization of the vitreous network. In the case of polyphosphates, vitreous network is somewhat loose as it is monodimensional and is built from chains of tetrahedra. The specific feature of this vitreous system lies in the structural part of the Zn^{2+} and Mn^{2+} cations. Both have been reported to act as weak glass formers, as demonstrated by the occurrence of binary glasses ZnF_2-SrF_2 and MnF_2-BaF_2 [14]. Then one may expect that the vitreous network shows a hybrid character, associating fluoride polyhedra and phosphate tetrahedra.

As the fluoride content increases, one bridging oxygen is replaced by two non-bridging fluorides, leading to shorter chains and the transformation of Q^2 tetrahedra into Q^1 tetrahedra [19,20]. The observed changes in IR absorption spectra resulting from fluoride incorporation are consistent with this scheme. As pointed out by Corbridge [21], the band corresponding to elongation of P-O-P bridges around 900 cm^{-1} is shifted toward lower frequencies when the length of P-O-P chain increases. This is correlated to difluoride content as seen in Fig. 5. The larger Q^1 number leads to the relative increase of the absorption bands around 1020 cm^{-1} and 1130 cm^{-1} formation of pyrosphate groups (P_2O_7).

The main feature of the Raman spectrum is the emergence of the 1050 cm^{-1} peak as manganese fluoride concentration increases (Fig. 4). This peak corresponds to the vibration mode of PO_4 tetrahedra, and its relative intensity appears proportional to the amount of Q^n groups. It is consistent with the value of the phonon energy in phosphate glasses. The low frequency peaks correspond to the vibration modes of the MnF_6 octahedra.

At high MnF_2 content, structure contains almost exclusively P_2X_7 (X = O, F) dimers. These large complex anions are linked to MF_6 (M=Zn, Mn) octahedra. Thus vitreous network is constructed from two structural units: PX_4 tetrahedra and MX_6 octahedra sharing not only corners but also edges, like in the rutile-type structure. In this respect, these glasses are rather similar to heavy metal fluoride glasses, with a vitreous network constructed from large polyhedra-octahedra in this case and P_2X_7 groups. There are two types of fluorine anions, those linked to phosphorus, and those linked to Mn and Zn in a rutile-like arrangement. The observed decrease of V_h (increase of E_h and E_m, respectively) is connected with structure strengthening and extension of the local ordering. Vibrational spectroscopy and NMR measurements reflect a change in the fluorophosphate matrix by a shortening of the chains, due both to the incorporation of fluorine and manganese [19]. While vitreous sodium polyphosphate consists ideally of $(PO_4)_n$ indefinite chains trapping isolated Na^+ cations, the incorporation of 20 mol% ZnF_2 reduces the chain length. When the MnF_2 concentration increases, the structure changes from one-dimensional in polyphosphates to a highly cross linked three-dimensional network, i.e. *1D* $\rightarrow$ *3D* transition is manifested. The structural changes, induced by introduction of manganese difluoride MnF_2 at the expense of $NaPO_3$, resulting in the distribution of the corresponding structural units, are specified by the combination of Raman and infrared spectroscopies (Figs. 4, 5).

VI. CONCLUSIONS

The microstructural peculiarities of the studied $(MnF_2)_x(NaPO_3)_{80-x}(ZnF_2)_{20}$ glasses have been determined on the base of such structure-sensitive parameters as the glass transition temperature, the microhardness and their relation. The influence of MnF_2 addition into the $(NaPO_3)_{80}(ZnF_2)_{20}$ glass at the expense of $NaPO_3$ on the local ordering has been evaluated by Raman scattering and infrared absorption. While vitreous $(NaPO_3)_n$ structure contains long chains, made from corner-sharing $(PO_4)_n$ tetrahedra trapping isolated Na^+ cations, the presence of 20 mol% ZnF_2 causes reduction of chains length. At high MnF_2 concentrations, the glassy network is constructed by combination of two structural units - PO_4 tetrahedra and MnF_6 octahedra, sharing not only corners but also edges, and consequently, three-dimensional network is formed.

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