OPTOELECTRONICS AND ADVANCED MATERIALS RAPID COMMUNICATIONS Vol. 4, No. 9, September 2010, p. 1301 - 1303

Obtaining and characterization of calcium/magnesium/iron lithium phosphate glasses

M. ELISA[a], B. A. SAVA[b*], R. IORDANESCU[a], I. FERARU[a], C. VASILIU[a], M. CALIN[a], A. DIACONU[b], L. D. URSU[b], L. BOROICA[b], Z. PLAIASU[b], F. NASTASE[c], C. NASTASE[c], A. DUMITRU[c]
[a]*National Institute of Optoelectronics-INOE 2000, Department of Optospintronics, RO-77125, Magurele, Romania*
[b]*National Institute of Glass, Department of Optical Glass, 032258, Bucharest, Romania*
[c]*University of Bucharest, Faculty of Physics, Department of Polymers, Bucharest, Romania*

The paper reports a study on lithium phosphate glasses, containing calcium or magnesium and ferric/ferrous oxides. Iron oxides provide high chemical stability against water and enhance the glass capacity to embed different chemical compounds. The wet synthesis method provides an enhanced homogeneity of the glass batch and improves the optical quality of the glass samples. FTIR and Raman spectroscopy revealed the network former role of P_2O_5 as well as the modifier/former role of iron. The vibration mode shifted at 1250 cm^{-1} is attributed to the iron that enters into the phosphate network, forming Fe-O-P bonds instead of P-O-P bonds.

(Received August 4, 2010; accepted September 15, 2010)

Keywords: Phosphate glass, Iron oxide, FTIR, Raman

---

1. Introduction

Recently, phosphate glasses gained a real scientific interest due to their low melting temperature as well as their ability to embed high amounts of alkali oxides and transition oxides as well as aluminium, sulphides, chromates, and molybdenites. Phosphate glasses are suitable to retain the radioactive wastes enrich in sodium and sodium aluminates, wastes that contain products of uranium fission (radio nuclei of caesium, strontium, rare-earth, etc), corrosion products of the nuclear reactor (radio nuclei of iron, cobalt, nickel, manganese), compounds of the nuclear fuel (uranium and plutonium) and impurities of the nuclear process (sulphides, chlorides) [1]. Iron oxides (FeO and Fe_2O_3) used as adding compounds provide interesting phenomena revealed by the structure and the properties of phosphate glasses [2]. Small amounts (2-5 %) of Fe_2O_3 induced an increase of 10^4-fold of the chemical strength against water. Thus, the iron-doped phosphate glasses are used to embed and make inert the nuclear wastes from the atomic-electrical plants [3].

The present work intends to perform structural investigations on phosphate glasses containing iron ions, prepared by a known wet method [4]. Structural information on the phosphate glasses are obtained by FT-IR and Raman spectroscopy that aims at revealing the vibration modes specific for P-O and P-O-Fe bonds.

2. Experimental procedure

The molar composition of the phosphate glass samples, intended to be obtained as metaphosphate compounds, is presented bellow:

C1: $60LiPO_3\ 10Mg(PO_3)_2\ 30Al(PO_3)_3$

C2: $60LiPO_3\ 10Ca(PO_3)_2\ 30Al(PO_3)_3$

C3: $53{,}33LiPO_3\ 10Mg(PO_3)_2\ 26{,}66Al(PO_3)_3\ 10Fe(PO_3)_3$

C4: $53{,}33LiPO_3\ 10Ca(PO_3)_2\ 26{,}66Al(PO_3)_3\ 10Fe(PO_3)_3$

The molar oxide composition of the projected glass, calculated according to the molar formulas and taking into consideration phosphorous oxide volatility of about 25%, is presented in the Table 1.

Table 1. Molar oxide composition of Li_2O-MgO (CaO)-Al_2O_3-P_2O_5 un-doped and iron-doped glasses.

Glass sample	Oxide composition (mol. %)					
	Li_2O	MgO	CaO	Al_2O_3	Fe_2O_3	P_2O_5
C1	22,63	7,51	0	11,3	0	58,56
C2	22,60	0,00	7,52	11,29	0,00	58,59
C3	20,9	7,92	0	10,59	3,98	56,61
C4	20,9	0	7,94	10,58	4	56,58

The chemical reagents used for the glass preparation experiments were: Li_2CO_3, Al_2O_3, $MgCO_3$, $CaCO_3$, H_3PO_4, $FeSO_4\ 7H_2O$, all of analytical grade.

The glass samples C1, C2, C3 and C4 were melted at 1200 ^oC for 2 hours and subsequently, annealed according to the heat diagram resulted from the thermal expansion measurements. The drying was made in an electric stove, Caloris type and the thermal treatments in an electric Nabertherm four, equipped with superkanthal elements.

The synthesis stages of the phosphate glasses were: (i) homogenization and evaporation of the reagents up to 100-120 ^oC, in quartz crucible, (ii) drying process at 180-

200 ^{o}C, (iii) preliminary heat treatment at 200-800 ^{o}C, (iv) glass melting and refining at 1200 ^{o}C, (v) casting and (vi) annealing stage [4-7]. In the stages (ii), (iii) and (iv) the batch was processed in an alumina crucible and then, after melting and refining, the glass was poured into a preheated graphite mould that aimed at casting and annealing. The wet synthesis method provides a higher homogeneity of the glass batch in comparison with the conventional "dry method" and improves the optical quality of the final samples. At the same time, the stages (iii) and (iv) of the wet synthesis method enable the release of the residual OH^- groups from the glass network. Thus, FTIR absorption spectra did not show any OH^- absorption peak in the 2500-3500 cm^{-1} range.

FT-IR spectra were acquired by means of a Perkin Elmer Spectrophotometer-Spectrum 100, provided with UATR accessory (Universal Attenuated Total Reflectance) in the range 550-4500 cm^{-1} and 32 scans. The measurement error is ± 0.1%.

Raman spectra were collected with a Jobin- Yvonne LabRam microscope provided with 633 nm laser excitation, 250-5500 cm^{-1} range; laser power on the sample 10.23 mW; exposure time 5s; accumulation number 5. The measurement error is ± 0.1%.

3. Results and discussion

FT-IR absorption spectra of glass samples C1, C2, C3 and C4 are presented in the Fig. 1. The peak at about 1280 cm^{-1} (sample C1) was attributed to $(PO_2)^-$ asymmetrical stretch and/or to P=O stretch [8, 9]. Glass sample C3 exhibits the same vibration mode as sample C1, but shifted to 1250 cm^{-1}. The shift is supposed to be due to the iron ions that enter the phosphate network, forming Fe-O-P bonds instead of P-O-P bonds, modifying the energy of the vibration modes. The replacement of magnesium by calcium, for samples C1 and C2 leads to a similar shift of this absorption maximum towards lower wavenumber.

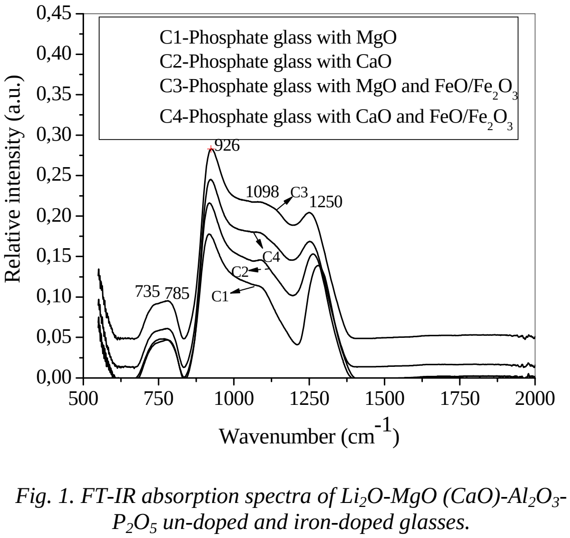

Fig. 1. FT-IR absorption spectra of Li_2O-MgO (CaO)-Al_2O_3-P_2O_5 un-doped and iron-doped glasses.

The shoulders at 1074-1098 cm^{-1} are ascribed to $(PO_3)^{2-}$ symmetrical vibration mode and/or to $(PO_2)^-$ symmetrical stretch mode. The shoulder is less pronounced in the case of iron-containing samples, C3 and C4. The peaks at 919 cm^{-1}, 926 cm^{-1} and 923 cm^{-1} are assigned to $(PO_3)^{2-}$ symmetrical vibration mode and/or to P-O-P asymmetrical stretch vibration mode, corresponding to C1-C2, C3 and C4 respectively. It is observed a shift towards higher wavenumber in the case of iron-doped samples. The peaks ranged between 735 cm^{-1} and 785 cm^{-1} are ascribed to P-O-P symmetrical stretch.

Raman spectra of ecological glasses C1, C2, C3 and C4 are presented in Fig. 2.

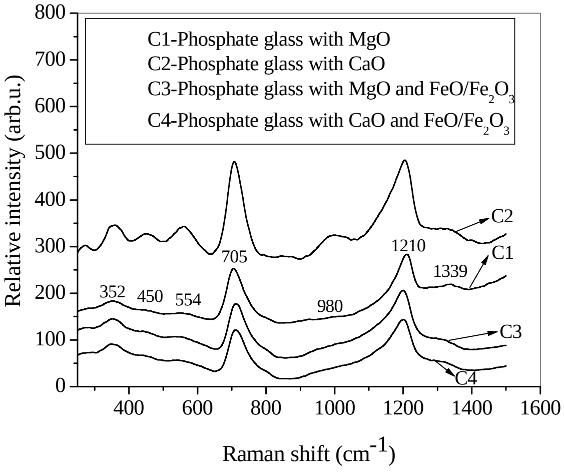

Fig. 2. Raman spectra of *Li_2O-MgO (CaO)-Al_2O_3-P_2O_5 un-doped and iron-doped glasses, obtained by 633 nm laser excitation.*

Strong signal from the glass matrix at about 1210 cm^{-1}, is assigned to $(PO_2)^-$ symmetrical stretching mode [10] from the phosphate network, with some Fe^{2+} ions included. This confirms FTIR results, which indicate the apparition of Fe-O-P bonds and a partially mixed iron-phosphate network. XPS analysis made on glasses with similar chemical composition [11] indicated the presence of pair Fe^{2+}/Fe^{3+} species in different ratios depending on the presence of MgO or CaO. It was found that magnesium oxide increases Fe^{2+} amount at the expense of Fe^{3+} amount as compared to calcium oxide that had an opposite effect. These results, correlated with FTIR and Raman analyses made on our glasses indicate the possible influence of the phosphate matrix on Fe^{2+}/Fe^{3+} ratio. Iron ions contribute to form, together with phosphorous, partially mixed oxide networks.

The strong peak at about 700 cm^{-1} is attributed to P–O–P symmetrical stretching vibration mode [10]. The weak band that appears at about 350 cm^{-1} is assigned to P-O-P bend vibration mode [10]. We could not detect the presence of $(AlO_4)^{5-}$ tetrahedra in the glass network, taking into account that alumina content is below 10 mol.% [12].

In Table 4 we present Raman and FTIR bands, comparatively, for Li_2O-MgO (CaO)-Al_2O_3-P_2O_5 undoped and iron-doped glasses.

Table 4. Raman and FTIR bands for Li_2O-MgO (CaO)-Al_2O_3-P_2O_5 un-doped and iron-doped glasses.

Wavenumber (cm^{-1})								
C1		**C2**		**C3**		**C4**		**Assignment**
FTIR	**Raman**	**FTIR**	**Raman**	**FTIR**	**Raman**	**FTIR**	**Raman**	
	352		354		352		353	δ (O-P-O)
	450		450		449		452	δ (P-O-P)
	554		555		554		552	δ (P-O-P)
	705		708		704		708	ν_s (P-O-P)
746				735				ν_s (P-O-P)
760		779		785		779		ν_s (P-O-P)
919		919		926		923		ν_{as} (P-O-P)
1074	980	1091	982	1098	981	1076	981	$\nu_s (PO_3)^{2-}$
1280	1210	1263	1208	1250	1210	1253	1209	$\nu_s (PO_2)^-$
	1339		1342		1339		1339	$\nu_s (PO_2)^-$

4. Conclusions

We have obtained un-doped and iron-doped phosphate glasses, by a known wet non-conventional method. FT-IR and Raman spectra show vibration modes specific for the phosphate vitreous matrix, emphasising the vitreous network former role of phosphorous oxide and iron oxides as revealed by the vibration mode at about 1250 cm^{-1}, assigned to P-O-Fe bonds. Fe^{2+}/Fe^{3+} ratio is influenced by the glass composition, calcium oxide replacement by magnesium oxide increases the quantity of Fe^{2+} at the expense of Fe^{3+} amount, ions which can play a vitreous network former role.

References

[1] S. V. Stefanovskii, I. A. Ivanov, Glass Phys. Chem., **20**(2), 103 (1994).

[2] R. K. Brow, C. M. Arens, Phys. Chem. Glass. **35**(3), 132 (1994).

[3] B. C. Sales, L. A. Boatner, J. Non-Cryst. Solids, **79**, 83 (1986).

[4] M. Elisa, C. Vasiliu, A. Meghea, N. Iftimie, M. Giurginca, H. J. Trodahl, M. Dalley, Phys. Chem. Glass., **46**(6), 499 (2005).

[5] M. Elisa, I. C. Vasiliu, C. E. A. Grigorescu, B. Grigoras, H. Niciu, D. Niciu, A. Meghea, N. Iftimie, M. Giurginca, H. J. Trodahl, M. Dalley, J. Opt. Mat. **28**(6-7), 621 (2006).

[6] M. Elisa, C. E. A. Grigorescu, C. Vasiliu, M. Bulinski, V. Kuncser, D. Predoi, G. Filoti, A. Meghea, N. Iftimie, M. Giurginca, Rev. Adv. Mat. Sci., **10**, 34 (2005).

[7] M. Elisa, C. Vasiliu, C. Grigorescu, J. Striber, D. Radu, J. H. Trodahl, M. Dalley, J. Optoelectron. Adv. Mater. **8**(2), 810 (2006).

[8] W. Guomei, L. Jiaheng, Submol. Glass Chem. Phys., SPIE, **1590**, 229 (1991).

[9] D. Muresan, M. Dragan-Bulandra, C. Popa, L. Baia, S. Simion, Rom. Journ. Phys., **51**(1-2), 231 (2006).

[10] A. Mogus-Milankovic, A. Gojovic, A. Santic, D. E. Day, J. Non-Cryst. Solids, **289**, 204 (2001).

[11] M. Elisa, M. Elisa, B. A. Sava, A. Diaconu, L. Boroica, D. Ursu, I. Stamatin, F. Nastase, C. Nastase, Glass Physics and Chemistry, **35**(6), 596 (2009).

[12] R. K. Brows, R. J. Kirkpatrick, G. Turner, J. Am. Ceram. Soc., **73**(8) 293 (1990).

---

[*] Corresponding author: savabogdanalexandru@yahoo.com