Structure and properties of phosphate glasses containing Mo, B, V and Fe

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Phosphate glasses are materials able to incorporate many different oxides such as MoO_3, B_2O_3, V_2O_5, and Fe_2O_3 in their composition, valuable for electronics, optoelectronics, agriculture, etc. The paper presents the study of vitreous materials based on phosphate glass matrix to which 1-7 mol % of MoO_3, B_2O_3, V_2O_5, and Fe_2O_3 were added. Glass was prepared by melting the raw materials in electric furnace at 1150 - 1250 ^oC for 2h using ceramic crucibles. In order to establish phosphate glasses solubility, the conductometric method was used. Glass structure was analyzed by FTIR and Raman spectroscopy. Analyzes of glasses microstructure, composition and homogeneity were made by using energy-dispersive X-ray spectroscopy microanalysis - EDAX and scanning electron microscopy - SEM.

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1. Introduction

Glasses are versatile materials which can be used in buildings, as art objects, in optics, electronics, medicine and agriculture.

Phosphate glasses are widely used in past decades in several technological applications such as: hosts for rare-earth ions used for solid state lasers or optoelectronic devices [1, 2], vitreous magneto-optical devices [3, 4], neutralization and incorporating of toxic wastes [5 - 7] and also as biomaterials [8] or for agricultural uses [9 - 11].

Spectroscopic and diffraction studies of phosphate glasses, including v-P_2O_5, binary and polinary phosphate compositions, are described in recent papers [12 - 15]. The addition of iron to phosphate glasses showed an effect on glass transition temperature, thermal expansion coefficient and chemical durability [16]. The improvement of the chemical durability is attributed to the replacement of P-O-P bonds with P-O-Fe bonds [17].

The aim of this paper is to study the structure and properties of complex potassium-magnesium-phosphate glasses containing molybdenum, boron, vanadium and iron oxides in 1-7 weight %, taking into consideration that, so far the structure of these glasses is not completely investigated. Raman, FTIR, SEM and EDAX analysis were used in order to clarify the glass structure and composition which are essential in designing the desired properties. Chemical solubility in water was dynamically measured by conductometric method.

2. Experimental

The vitreous investigated compositions were chosen in a complex phosphate system, containing phosphorus oxide as network former and potassium and magnesium oxide as modifiers. Molybdenum, boron, vanadium and iron oxide were introduced in the composition in order to improve the chemical stability of these materials and also to confer them some special magnetic and electrical properties, such as high Faraday and magneto-optic Kerr effect or electrical conductivity [18, 19].

Glasses were obtained by melting the raw materials in ceramic crucibles, in electric furnaces equipped with superkanthal heating elements. The oxide composition corresponding to the starting batch after CO_2 and H_2O removal is presented in table 1.

2.1 Glass preparation

The raw materials used to prepare these glasses were K_3PO_4 $7H_2O$, P_2O_5, $MgCO_3$, B_2O_3, Fe_2O_3, $(NH_4)_6$ Mo_7O_{24}, V_2O_5, all of analytical grade, produced by Merck.

The melting process comprises the following steps: (i) introducing the homogenized mixture of raw materials in ceramic crucibles; (ii) melting in the electrical oven, Nabertherm type, at temperatures between 1150 and 1250^oC, for 2 ÷ 4 hours; (iii) pouring the glass melt in graphite moulds and (iv) glass annealing in an electric furnace, Caloris type, at 480^oC, for 6 hours.

Table 1. Phosphate glass oxide composition (wt. %)

Sample code / oxide	K_2O	MgO	P_2O_5	MoO_3	B_2O_3	V_2O_5	Fe_2O_3
MO1	32.04	8.62	57.94	1.40	-	-	-
MO3	31.17	8.38	56.37	4.08	-	-	-
MO5	30.35	8.16	54.87	6.62	-	-	-
MO7	29.56	7.95	53.46	9.03	-	-	-
MOB3	30.47	8.19	55.09	4.21	2.04	-	-
MOV3	29.50	7.93	53.34	4.08	-	5.15	-
MOF3	29.69	7.98	53.68	4.10	-	-	4.55

Glass structure was analyzed by FTIR spectroscopy by using a Perkin Elmer- Spectrum 100 spectrometer equipped with an UATR (Universal Attenuated Total Reflectance) device, in the range 500 - 2000 cm^{-1}, 10 scans for each sample for FTIR measurements. Raman spectra were acquired by means of Raman NRS-3100 JASCO equipment, laser excitation wavelength of 785 nm, duration 1 sec, in the domain 100 - 4000 cm^{-1}, at room temperature. In order to establish the vitreous fertilizers solubility, the conductometric method was used based on a genuine experimental set-up device, at University "Politehnica" of Bucharest. Conductivity method measures the dynamic variation of electrical conductance of a glass powder suspension in water, keeping constant temperature, amount of glass powder, its specific surface and the suspension concentration from one experiment to another. The apparatus consist in a thermostated vessel in which the suspension of the glass powder in water is placed with an electrode of platinum for suspension conductance measurement.

The analyzes of glasses microstructure, composition and homogeneity were made by energy-dispersive X-ray spectroscopy microanalysis – EDX, using an EDAX 9 Panalytical X' PERT MPD spectrometer, and by scanning electronic microscopy – SEM, using a QUANTA INSPECT F scanning electron microscope.

3. Results

The EDX spectra for MO1, MO3, MO5, MO7 series are presented in the Fig. 1a-1d, respectively.

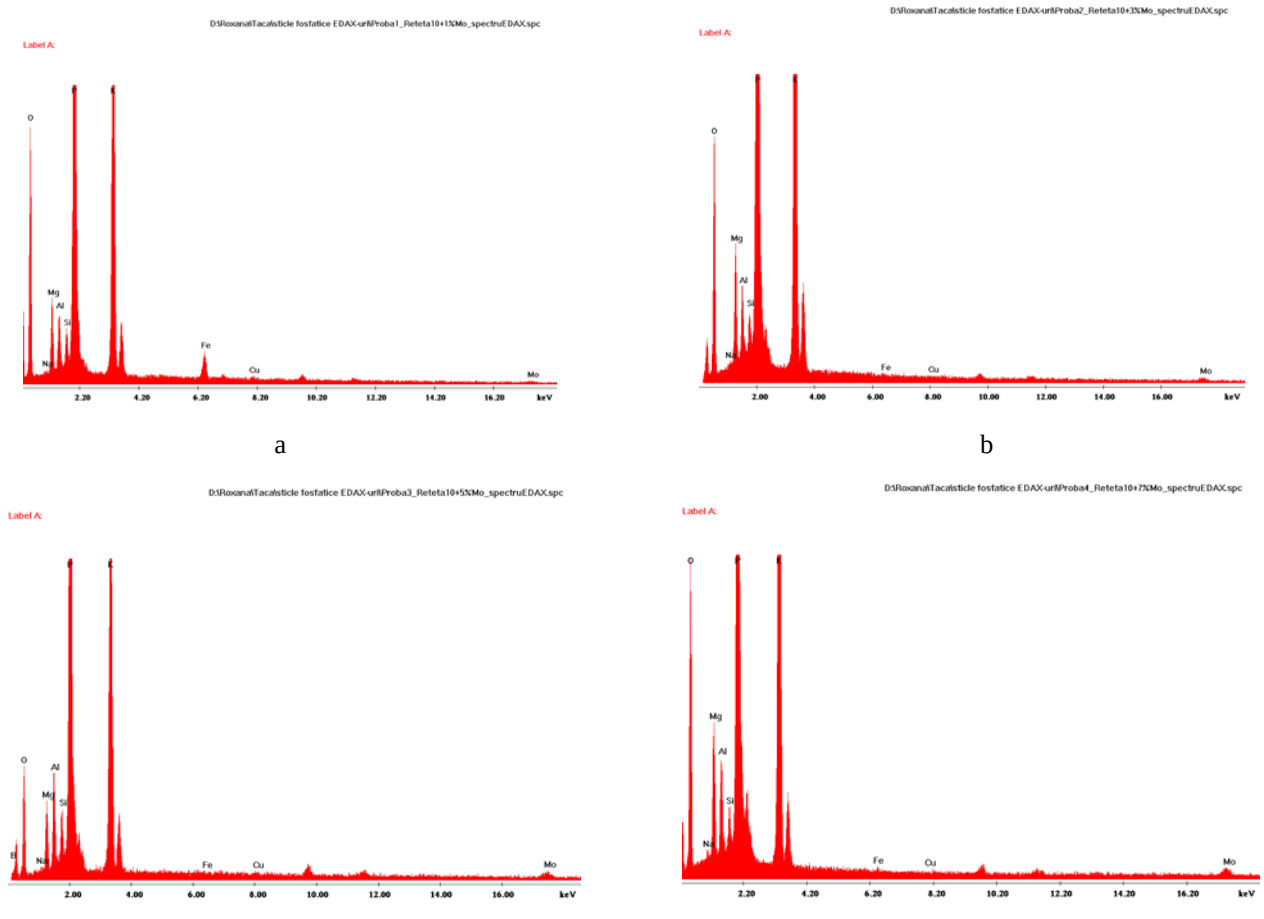

Fig. 1. Results of EDAX analyze for: a. Glass sample MO1; b. Glass sample MO3; c. Glass sample MO5; d. Glass sample MO7

SEM photos for MO series are presented in the Fig. 2a-2d.

FTIR spectra of glass samples MO1, MO3, MO5 and MO7 are presented in Fig. 3.

Raman spectra of MO1, MO3, MO5 and MO7 glasses are presented in Fig. 4.

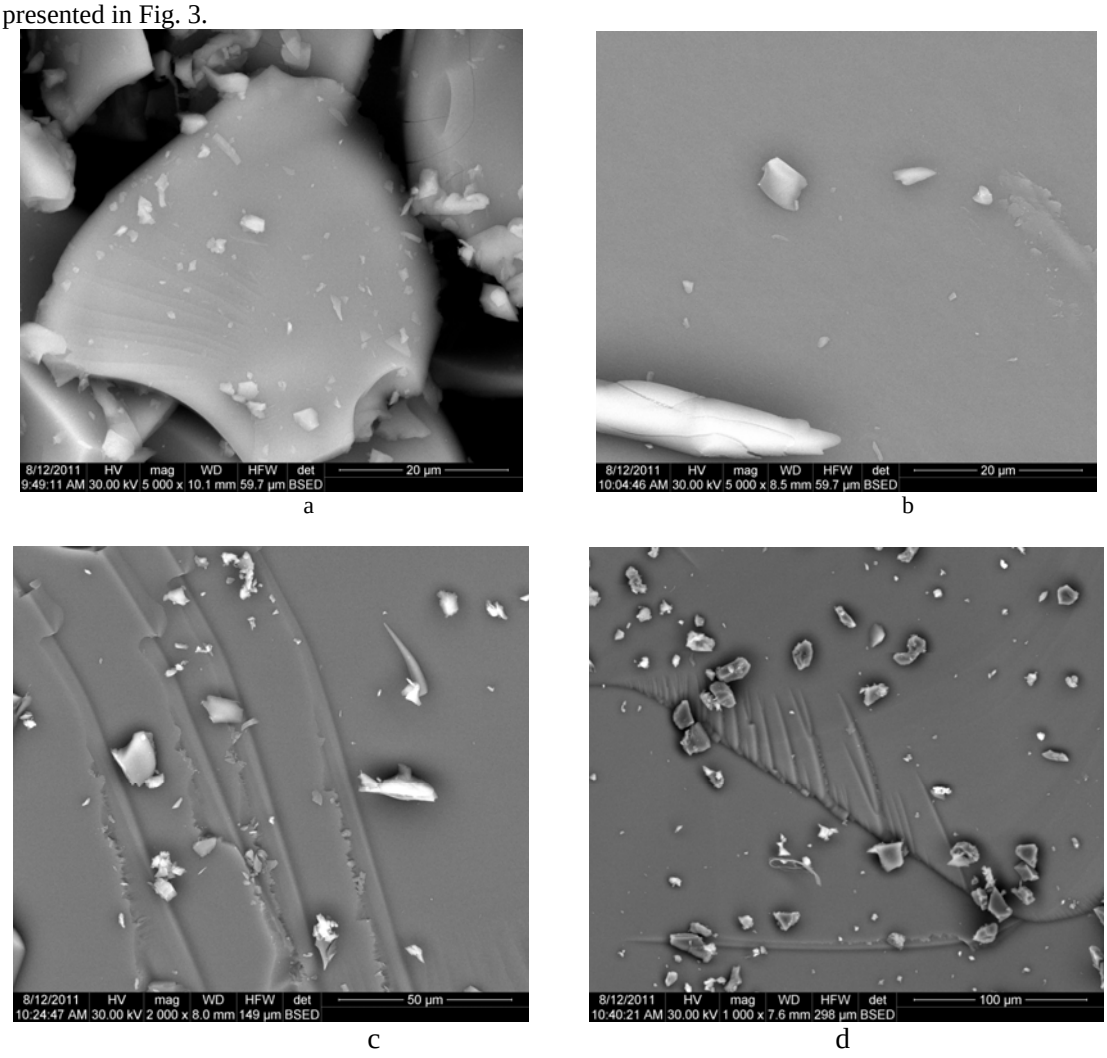

Fig. 2. SEM photos for the glass samples: a. MO1, b. MO3, c. MO5 and d. MO7

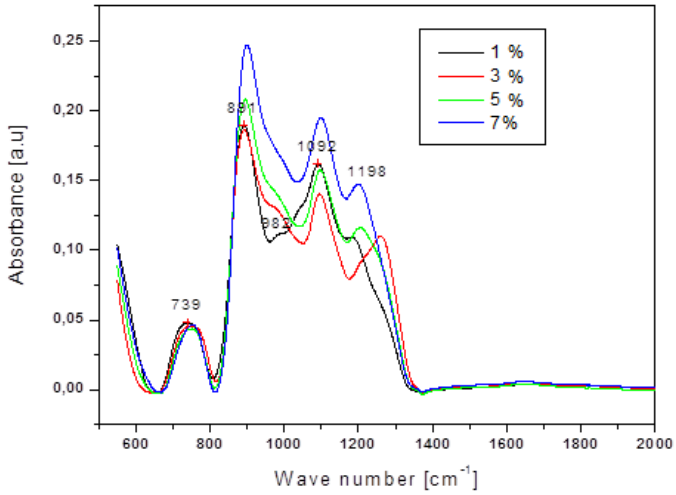

Fig. 3. FTIR spectra of glass samples MO1, MO3, MO5 and MO7

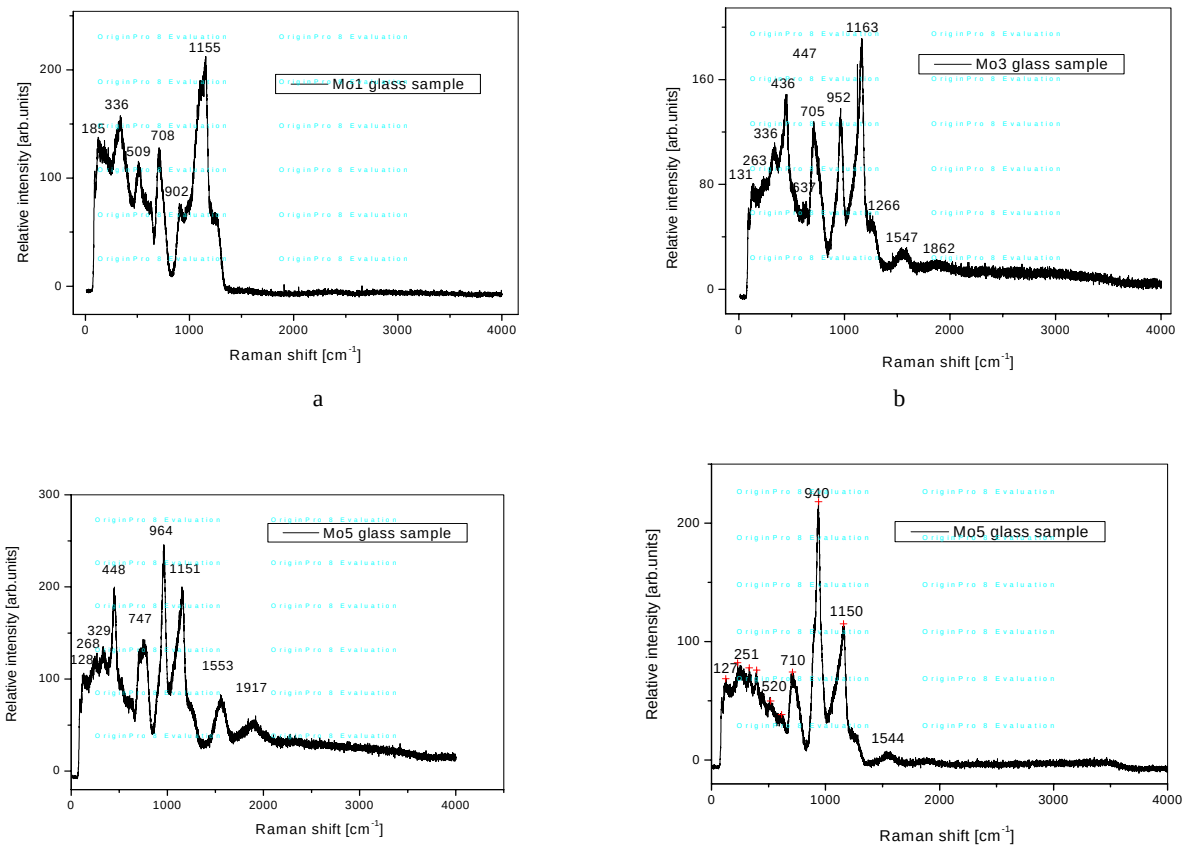

Fig. 4. Raman spectra of: a. MO1, b. MO3, c. MO5 and d. MO7 glasses

4. Discussion

EDAX results for MO samples, presented in fig. 1, a-d, identified all elements which are included in samples composition, namely Mg, P, K, Mo and O. In all cases there are also identified small amounts of Al, Si and Fe which appears in glass from crucible. Elements as Na and B, which seem to be identified also in very small quantity, are unlikely to exist in samples other than as impurities in raw materials. The EDAX spectra pointed out the increasing of Mo peaks with the increasing proportion of this oxide in glass composition. They also showed out the decrease of phosphorus peaks due to the increase of Mo ones.

SEM photos showed that the obtained phosphate glasses were homogeneous. Some crystalline inclusions, due to the crucible material disengaged by the glass melt attack are evidenced in SEM photos. Their dimensions are ranged between units to tens microns. All four MO samples show such inclusions, as revealed by SEM photos from Fig. 2, a-d.

The IR absorption maxima for MO glass series, compared to literature data for pure P_2O_5-based glass are presented in table 2.

The vibration modes of P-O-P are evidenced at 740 and 890 cm $^{-1}$, respectively.

Raman analysis shown in figure 4a-4d put in evidence the symmetric stretching mode of bridging P-O-P vibration modes at about 710 cm^{-1}. The peaks at about 640 cm^{-1} and 1260 cm^{-1} can be associated to bonding (BO) and not bonding oxygen (NBO) symmetric stretching modes in metaphosphate chains of $(PO_3)^-$ units. The increase of MoO_3 amount leads to the decrease of the band at 710 cm^{-1} assigned to pyrophosphate units and to the strong increase of the maximum at about 950 cm^{-1} attributed to monomeric orthophosphate $(PO_4)^{3-}$ and also to MoO_6 units. The increasing of the MoO_3 content causes a degradation of the phosphate network which results in apparition of monomeric phosphate and molybdate units [22].

Table 2. FTIR peaks for Mo glass series compared to literature data

Structural units	Pure P_2O_5-based glass [20, 21]	MO1	MO3	MO5	MO7
PO_2 asymmetrical stretching	1200-1300	1280	1270	-	-
P=O stretching Long phosphate chains	1240-1270	1280	1270	-	-
$[P_2O_7]^{4-}$ Pyrophosphate units	1179	-	1199	1199	1198
PO_3^{2-} asymmetrical	1110-1190	-	1199	1199	1198
PO_2 symmetrical stretching	1100-1170	1170	-	-	-
PO_3^{2-} symmetrical	980-1050	1040	-	-	-
PO_4 stretching	1030	1040	-	-	-
PO_4^{3-} symmetrical	1015	982	980	978	975
P-O-P asymmetrical stretching	840-950	891	891	893	898
P-O-P symmetrical stretching	670-800	739	745	745	745

The most important property of the potassium-phosphate glass that can be designed by changing the composition is the chemical durability. By increasing the amount of MoO_3 up to 7% the glass solubility decreases as presented in the Fig. 5.

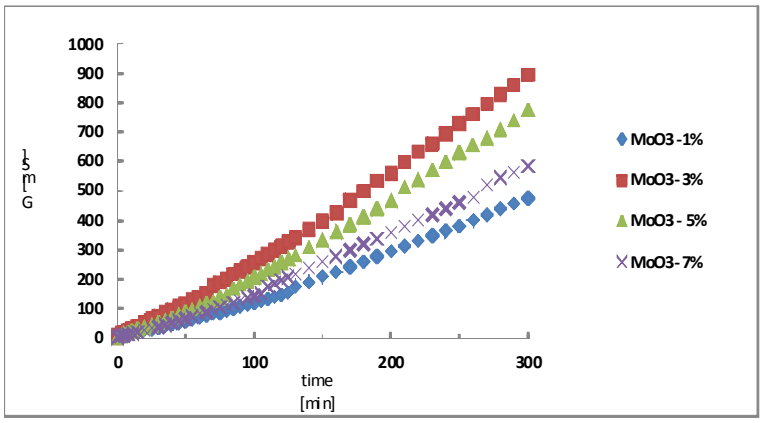

Fig. 5. Evolution of conductance of MO glass series, in time

It was established that P-O-P bonds are replaced by P-O-Fe, which are more stable against water attack [17]. Unlike the P-O-P bonds, the Fe-O-P bonds are reported to be resistant to hydrolysis [23].

It can be concluded that the chemical resistance decreases by adding MoO_3 up to 5 wt %. From 7% the chemical resistance increased due to the (MoO_6) units that are formed in the network.

In the case of mixed oxides, when keeping constant 3 wt. % of MoO_3 and adding in the first sample 3 wt. % of Fe_2O_3, in the second sample 3 wt. % of B_2O_3 and in the third one 3 wt. % of V_2O_5 the evolution of conductance, as seen in the figure 6, increases in the series Fe, B, V, which is in agreement to literature data and to our work results, that emphasizes that the addition of iron oxide increases the chemical stability of the phosphate glasses.

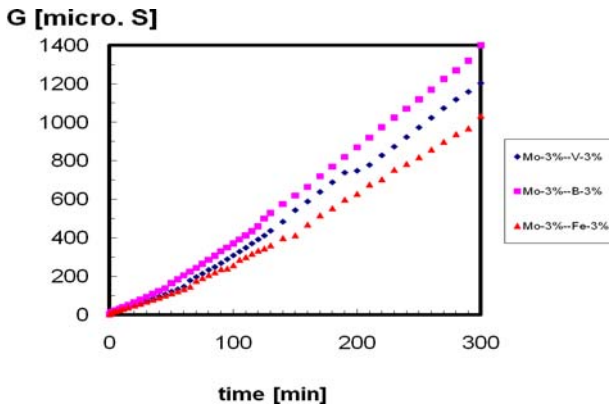

Fig. 6. Evolution of conductance of MOB3, MOV3 and MOF3 glasses, in time

5. Conclusions

Phosphate glass compositions, containing P_2O_5 as glass network formers, MgO and K_2O as network modifiers and Mo, B, V, Fe as additional components were studied for their specific properties.

The glasses were obtained by melting the raw materials in electric furnace at 1150 – 1250^o C, for 2 - 4 h. The resulted vitreous materials were milled in ball mills, till bellow 125 μm grain size particles were obtained.

The FTIR absorption spectra and Raman spectra put in evidence vibration modes specific to P-O bonds from the phosphate network as P-O-P, $(PO_3)^-$ and $(PO_4)^{3-}$ which emphasizes the network forming role of metaphosphate chains. The Raman spectra reveal that when MoO_3 content is increasing, the length of metaphosphate chains diminishes simultaneously with the formation of orthophosphate units.

The influence of maximum 1-3 wt. % of Mo, B, V, Fe oxides on the conductivity of glass powder suspension in distilled water was evidenced. This allows designing appropriate glass compositions for desired properties. According to chemical resistance and composition, the investigated phosphate glasses can be used as: (i) water soluble phosphate glass with applications in medicine as biomaterials and drugs carrier and in agriculture as vitreous fertilizers; (ii) water resistant phosphate glass obtained by a thorough control of Fe_2O_3 addition as magneto-optical and optoelectronic devices and (iii) water resistant phosphate glass for toxic waste embedding and neutralization.

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References

[1] M. Elisa, B. A. Sava, I. C. Vasiliu, F. Nastase, C. Nastase, A. Volceanov, S. Stoleriu, Materials Chemistry and Physics. **131**, 647 (2012).
[2] M. Elisa, I. C. Vasiliu, B. A. Sava, F. Nastase, C. Nastase, A. Volceanov, V. Dima, S. Stoleriu, M. Eftimie, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B. **51**(6), 309 (2010).
[3] M. A. Ghauri, S. A. Siddiqi,, W. A. Shah, M. G. B. Ashiq, M. Iqbal, J. Non-Cryst. Solids, **355**, 2466 (2009).
[4] M. Elisa, R. Iordanescu, B. A. Sava, G. Aldica, V. Kuncser, C. Valsangiacom, G. Schinteie, F. Nastase, C. Nastase, V. Bercu, A. Volceanov, S. Peretz, J. Mater. Sci. **46**, 1563 (2011).
[5] B. Samuneva, P. Tzvetkova, I. Gugov, V. Dimitrov J. Mater. Sci. Letters. **15,** 2180 (1996).
[6] D. E. Day, Z. Wu, C. S. Ray, P.Hrma, J. Non-Cryst. Solids. **241**, 1 (1998).
[7] Xiangyu Fang, Chandra S. Ray, Gaya K. Marasinghe, Delbert E. Day, J. Non-Cryst. Solids, **263&264,** 293 (2000).
[8] M. Taca, E. Vasile, L. Boroica, M. Udrea, R. Medianu, M. C. Munteanu, International Symposium on Gas Flow, Chemical Lasers, and High-Power Lasers. Proceedings of the SPIE. **7131**, 71311Q1 (2008).
[9] B. A. Sava, L. Boroica, M. Sava, M. Elisa, C. I. Vasiliu, F. Nastase, C. Nastase, R. Medianu, J. Optoelectron. Adv. Mater. **13**(11-12), 1534 (2011).
[10] I. Waclawska, M. Szumera, J. Alloys and Compounds, **468**(1–2), 246 (2009).
[11] B. A. Sava, L. Boroica, M. Sava, M. Elisa, Romanian Journal of Materials. **41**(4), 371 (2011).
[12] R. K. Brow, J. Non-Cryst. Solids, **263–264**, 1 (2000).
[13] M. Elisa, B. A. Sava, R. Iordanescu, I. Feraru, C. Vasiliu, M. Calin, A. Diaconu, l. D. Ursu, l. Boroica, Z. Plaiasu, F. Nastase, C. Nastase, A. Dumitru, Opt. Adv. Mat. Rap. Comm., **4**(9), 1301 (2010).
[14] A. Mogus-Milankovic, A. Santic, A. Gajovic, D.E. Day, J. Non-Cryst. Solids **325,** 76 (2003).
[15] A. Mogus-Milankovic, A. Gajovic, A. Santic, D. E. Day, J. Non-Cryst. Solids, **289**, 204 (2001).
[16] X. Yu, D. E. Day, G. J. Long, E. K. Brown, J. Non-Cryst. Solids. **215**, 21 (1997).
[17] R. K. Brow, C. M. Arens, X. Yu, D. E. Day Physics and Chemistry of Glasses. **35**, 132 (1994).
[18] H. Akamatsu, K. Fujita, S. Murai, K. Tanaka, Applied physics letters, **92**, 251908 (2008).
[19] A. V. Chandrasekhar, A. Radhapathy, B. J. Reddy, Y. P. Reddy, L. Ramamoorthy, R. V. S. S. N. Ravikumar, Optical Materials, **22**, 215, (2003).
[20] W. Guomei, L. Jiaheng, Submolecular Glass Chemistry and Physics, Proceedings of SPIE. **229**, 1590 (1991).
[21] S. V. Stefanofanovskii, I. A. Ivanov, Glass Phys. Chem. **20 (2),** 103 (1994).
[22] A. Magus-Milonkovic, A. Santic, A. Gajovic, D. E. Day, J. Non-Cryst. Solids. **325**, 76 (2003).
[23] X. Fang, C. S. Ray, G. K. Marasinghe, D. E. Day, J. Non-Cryst. Solids. **263&264**, 293 (2000).

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