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Potassium phosphate glasses used as agro-fertilizers with controlled solubility

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Two series of potassium phosphate glasses have been prepared, AG2 compositions containing P_2O_5, K_2O, MgO with B_2O_3, Fe_2O_3, ZnO, MoO_3 and AG3 compositions containing P_2O_5, K_2O, MgO, CaO with B_2O_3, Fe_2O_3, ZnO, MoO_3, MnO_2. The glasses have been prepared by a conventional route: (i) preparation of raw materials; (ii) melting and refining; (iii) fritting; (iv) grinding of the glass; (v) screening of glass powder. Both for AG2 and AG3 glasses, FTIR spectra recorded in the 400-4000 cm^{-1} range, revealed optical phonons specific for the phosphate matrix. In the case of AG2.1 and AG3.1 glasses containing B_2O_3, FTIR spectra put in evidence optical phonons specific for B-O bond from BO_3 and BO_4 units. Raman spectra, recorded in the 100-4000 cm^{-1}, by 785 nm laser excitation show stretching vibration modes specific for phosphate matrix together with Mg-O vibration mode in the 320-336 cm^{-1} range. Information about vitreous fertilizers solubility was achieved by conduct-metric method. For AG2 series, minimum solubility was measured for the sample containing iron oxide and maximum solubility for base sample. From AG3 series, the sample containing iron oxide also showed minimum solubility, but the maximum solubility appeared for the sample with molybdenum oxide.

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1. Introduction

Ideas like “Sustainable agriculture” and “Ecological agriculture” are important in Romania and the European space. By comparison with intensive agriculture that utilizes synthetic fertilizers and pesticides in order to assure the necessary of nutrients and to control bad plants diseases, and damages, “the ecological technologies “ are oriented to the diminution of chemical interventions, reduction of pollutant impact of agricultural activities on environment and to obtain agricultural products with superior biological quality. Today, Agricultural Policy at the European level sustains ecological farms, processing and commercialization of ecological products. It is a process in full development in Romania and of big interest for all that are involved in a way or other in areas of production-processing-commercialization-consummation of ecological agricultural products.

Vitreous fertilizers are a new type of fertilizers, made of a vitreous matrix with low and controlled solubility in water (made of macro elements useful for plants, K, P, Mg) in which are introduced microelements (Mo, B, Mn, V, Fe, Zn and so on) necessary for growth and development of plants. The quantity of microelements as oxides is 1-5%.

The main advantages of new type of fertilizers against classical fertilizers are: increased grade of assimilation by plants, do not release insoluble compounds in soil, remain in the soil during the entire period of plant development, and do not pollute the freatic water [1-4]. At the same time, these fertilizers have special peculiarities: (i) controlled solubility in time for many vegetable cycles, (ii) possibility to incorporate in the vitreous matrix of many useful microelements [5,6] and (iii) do not contain toxic compounds and do not release insoluble residues.

The aim of this paper is to study the obtaining and characterization of potassium phosphate glasses for utilization as agricultural fertilizers. These new type of fertilizers are characterized by a controlled solubility in water that results in a slow releasing of nutrients in the soil and in small loses of macro- and micro-elements.

2. Experimental

2.1 Raw materials and oxide compositions

They were established two series of compositions, one for spring and autumn crops, the other for wine-grape. The AG 2 code glass sample contains the major compounds necessary for spring and autumn crops and the next samples contain the same base oxides together with oxides of micro-elements also necesarry for plants growth, one oxide for each sample, corresponding to 7 wt % over 100 % for every element. Table 1 presents the oxide composition of these glasses.

The AG 3 code sample contains major compounds necessary for wine-grape and next samples contain the same base oxides together with micro-elements oxides necessary for wine-grape, one for each sample, 5 wt % for iron, 3 wt % for boron and 2 wt % for zinc, molibdenum and manganese, respectively, over 100%. Table 2 presents the oxide composition of AG3 series samples.

Table 1. Oxide composition of glasses for spring and autumn crops, in weight %.

Sample/ oxide	P_2O_5	MgO	K_2O	B_2O_3	Fe_2O_3	ZnO	MoO_2	Total
AG2	58.76	8.74	32.5					100
AG2.1	47.96	7.13	26.52	18.39				100
AG2.2	53.42	7.94	29.54		9.1			100
AG2.3	54.05	8.04	29.9			8.01		100
AG2.4	53.18	7.91	29.41				9.5	100

Table 2. Oxide composition of glasses for wine-grape, in weight %.

Sample/oxide	P_2O_5	MgO	K_2O	CaO	B_2O_3	Fe_2O_3	ZnO	MoO_2	MnO_2	Total
AG3	43.47	18.48	32.61	5.44						100
AG3.1	39.64	16.85	29.74	4.96	8.81					100
AG3.2	40.57	17.25	30.43	5.08		6.67				100
AG3.3	42.41	18.03	31.82	5.31			2.43			100
AG3.4	42.15	17.91	31.61	5.27					3.06	100
AG3.5	42.21	17.94	31.66	5.28				2.91		100

Phosphorus oxide, potassium phosphate, magnesium carbonate and calcium phosphate of analytical grade, have been used as raw materials for macro-elements introduction. Boron oxide, zinc oxide, ferric oxide, ammonium molibdate, and manganese dioxide, all of analytical grade, were added in order to supply the micro-elements. The raw materials corresponding to AG2 and AG3 series are presented in Tables 3 and 4, respectively.

Table 3. Raw materials composition for vitreous fertilizers oriented to spring and autumn crops.

Sample code	Raw material [g]						
	$K_3PO_4\ H_2O$	P_2O_5	$MgCO_3$	B_2O_3	Fe_2O_3	ZnO	$(NH_4)_6\ Mo_7O_{24}$
AG2	778	424.4	182.8				
AG2.1	778	424.4	182.8	225.4			
AG2.2	661.3	360.7	155.38		85.07		
AG2.3	661.3	360.7	155.38			74.06	
AG2.4	661.3	360.7	155.38				103.08

Table 4. Raw materials composition for vitreous fertilizers oriented to wine-grape.

Sample code	Raw material [g]							
	$K_3PO_4\ 7H_2O$	P_2O_5	$MgCO_3$	$3CaOP_2O_5$	B_2O_3	Fe_2O_3	ZnO	$(NH_4)_6\ Mo_7O_{24}$	MnO_2
AG3	468.42	135.1	231.96	60.18					
AG3.1	546.49	157.6	270.62	70.21	67.62				
AG3.2	546.49	157.6	270.62	70.21		50.05			
AG3.3	624.56	180.1	309.28	80.24			17.43		
AG3.4	624.56	180.1	309.28	80.24					22.12
AG3.5	624.56	180.1	309.28	80.24				27.72	

2.2 Glass obtaining

The obtaining of the vitreous fertilizers involves next steps:

- vitreous matrix obtaining (the base glass) with controlled solubility in water;
- incorporating of the micro-elements in the obtained glassy matrix.

2.3 Weighting and mixing of raw materials

The main raw materials were weighted by means of a technical balance of 2 kg. In the case of small components an analytical balance with accuracy of 10^{-5} g was used. Homogenization was performed in two stages: 1. All the raw materials, except phosphorus oxide, were mixed for 1 hour, using porcelain mortars and balls in a planetary mill; 2. Phosphorus oxide was introduced over the mixture of raw materials under continue homogenization in chemical niche, for 1 hour.

2.4 Melting the mixture of raw materials

The mixtures of raw materials, prepared by the method described above, were dried in an electric stove. The melting-refining-conditioning and cooling of the mixtures of raw materials was carried out in an electric furnace with automatic temperature control, equipped with silicon carbide heating elements, the maximum working temperature being 1400°C. The melting process was performed in refractory fireclay crucibles of 0,5 l capacity.

Table 5. The maximum melting temperatures for fertilizer glasses.

Sample code	Micro-element	Maximum melting temperature [°C]
AG 2.	Base glass for AG2 series	1150
AG 2.1.	Boron	1140
AG 2.2.	Iron	1150
AG 2.3.	Zinc	1140
AG 2.4.	Molibdenum	1050
AG 3	Base glass for AG3 series	1250
AG 3.1.	Boron	1200
AG 3.2.	Iron	1250
AG 3.3.	Zinc	1240
AG 3.4.	Manganese	1250
AG 3.5.	Molibdenum	1250

The melting duration was between four to six hours. The melting programs for the base glasses are presented in Figs. 1 and 2.

After the melting-refining-conditioning cycle, fluid melts without inclusions were obtained. The glass melts were casted as a thin layer and left to cool in air.

2.5 Grinding and sieving the obtained glasses

The obtained glasses were milled in a planetary ball mill for 8 hours. The obtained glass powder was passed through 0.4 mm mash sieve.

FTIR spectra were acquired using a spectrophotometer Perkin Elmer, Spectrum 100, equipped with UATR (Universal Attenuated Total Reflectance) in the 400-4000 cm^{-1} domain, 10 scans for each determination.

Raman spectra were recorded using a Raman JASCO NRS-3100 with a wavelength of 785 nm laser.

Spectra were recorded with an exposure of 1 second and 100 accumulations. It used a diffraction grating having 600 lines/mm and 0.5 x 6 mm aperture. Laser power during spectra collection was between 13.6 and 19.9 mW. Spectra were recorded between 100 and 4000 cm^{-1} at room temperature. The objective of the microscope used was x 20.

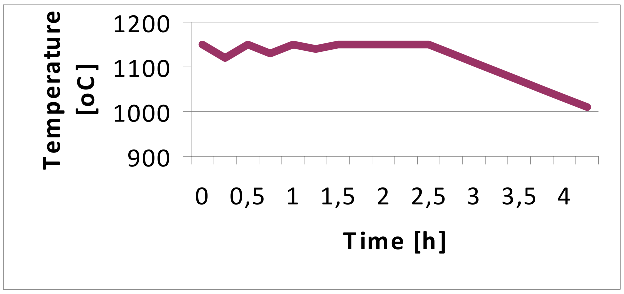

Fig. 1. The melting-refining-conditioning program for AG2 code samples.

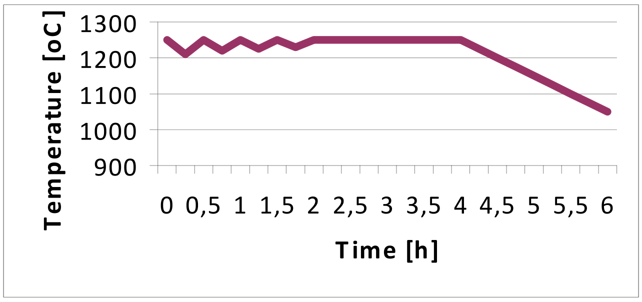

Fig. 2. The melting-refining-conditioning program for AG3 code samples.

The solubility of the vitreous fertilizers was measured by conductometric method. The conductometric method implies the conductance measuring in time of an aqueous solution in which the sample glass is introduced, which is directly proportional to the leaching of glass in water. The method shows in evidence the kinetics of the process of attacking the glass by water.

The glass to be analyzed is grinded in a porcelain mortar, then screened through two sieves with different mesh size. The fraction to be used is the one between the two sieves. The sieve mesh sizes are closer to each other, so the size fraction between them will be less dispersed and average size fraction (ie its specific surface) will be constant from sample to sample. The procedure is repeated for all the glasses examined.

The equipment consists of: • measuring cell consisting of double-walled vessel thermostat made of chemically resistant glass, in which is introduced the glass powder suspension in water • platinum electrode for measuring the conductance of the suspension; • an accurate thermometer for temperature reading.

Glass powder of about ~ 63-100 µm is used which appearance is that of very fine salt.

3. Results

Fig. 3 presents FTIR spectra of potassium-magnesium-phosphate glass samples in the 500-1800 cm^{-1} domain.

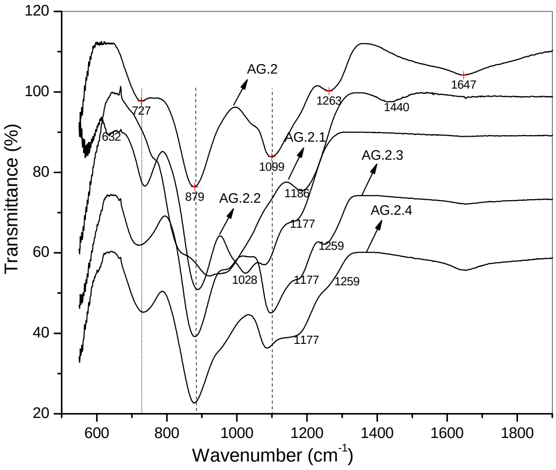

Fig. 3. Transmission FTIR spectra for potassium-magnesium-phosphate glass samples, AG2 type.

Fig. 4 presents FTIR spectrum of potassium-magnesium-phosphate glass sample containing boron as micro-element, spectrum deconvoluted in the 650-1300 cm^{-1} domain. Fig. 5 presents the transmission spectra of potassium-calcium-magnesium-phosphate glasses, AG3 series, in the 500-1800 cm^{-1} domain.

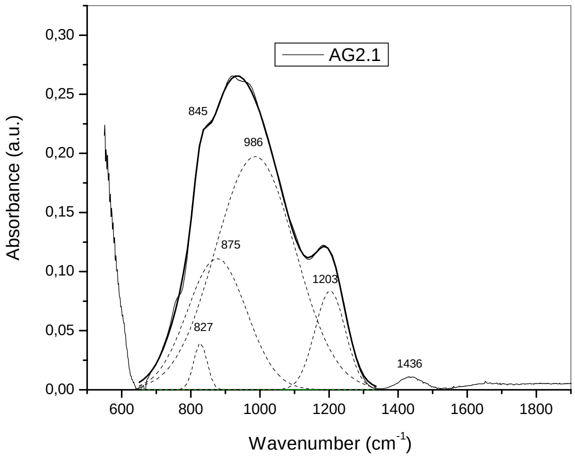

Fig. 4. Transmission FTIR spectra for potassium-magnesium-phosphate glass sample containing boron oxide, deconvoluted in the 650-1300 cm^{-1} domain.

Raman spectra of the samples from AG2 and AG3 series are presented in Figs. 6 and 7, respectively. Figs. 8 and 9 present the results of solubility measurements made by conductmetric method for the samples from the two potassium-phosphate series.

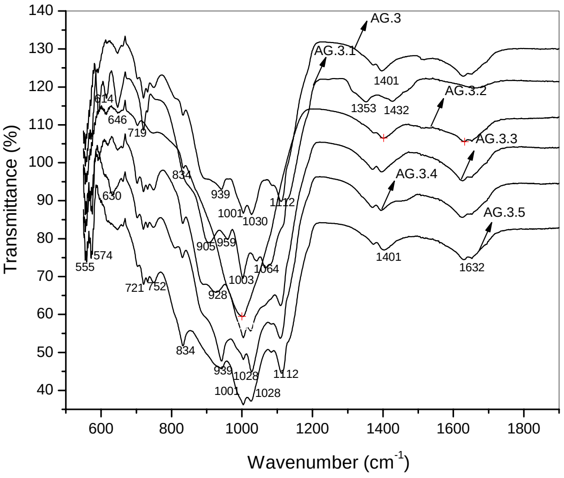

Fig. 5. Transmission spectra of AG3 series, in the 500-1800 cm^{-1} domain.

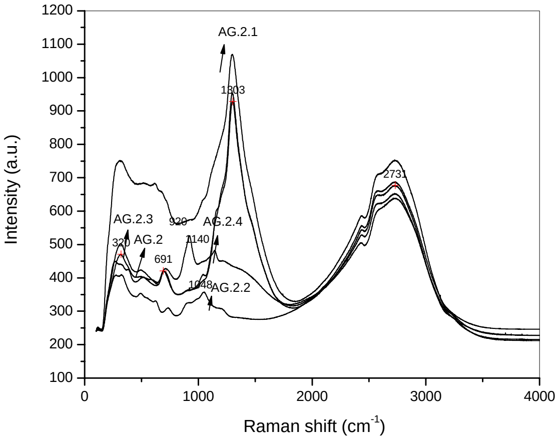

Fig. 6. Raman spectra of the glass samples from AG2 series, recorded in the 100-4000 cm^{-1} domain.

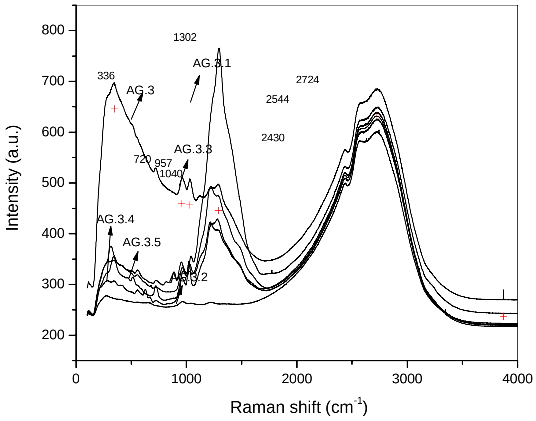

Fig. 7. Raman spectra of the glass samples from AG3 series, recorded in the 100-4000 cm^{-1} domain.

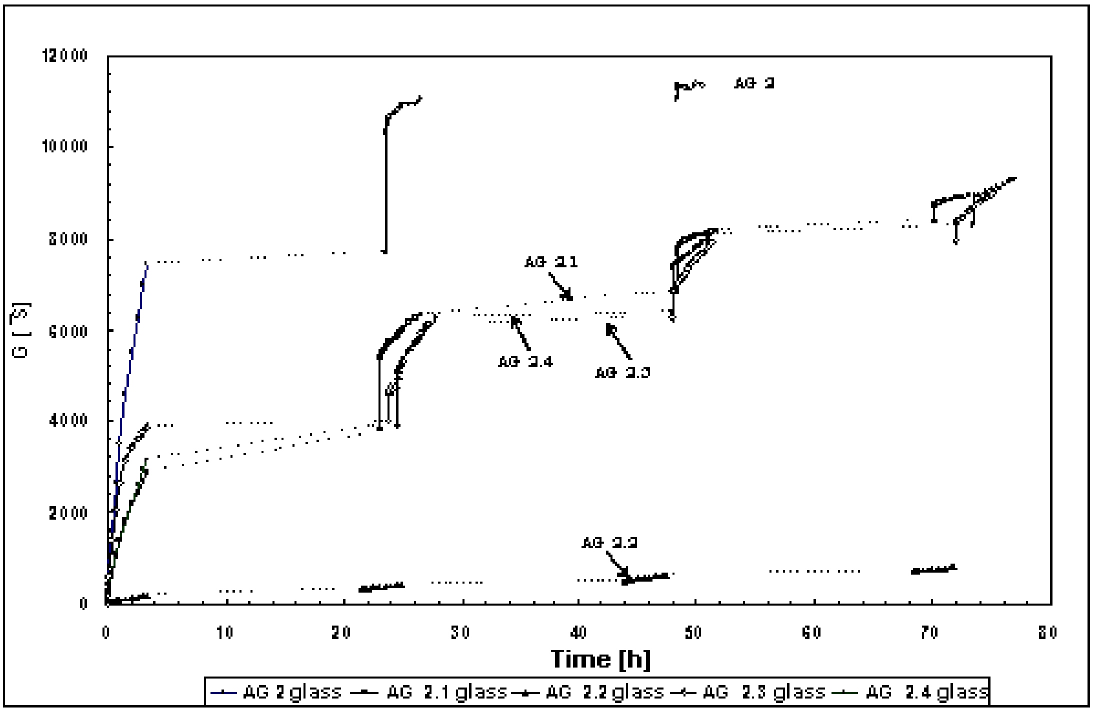

Fig. 8. Electrical conductivity evolution in time, comparatively, for the glasses from AG 2 series

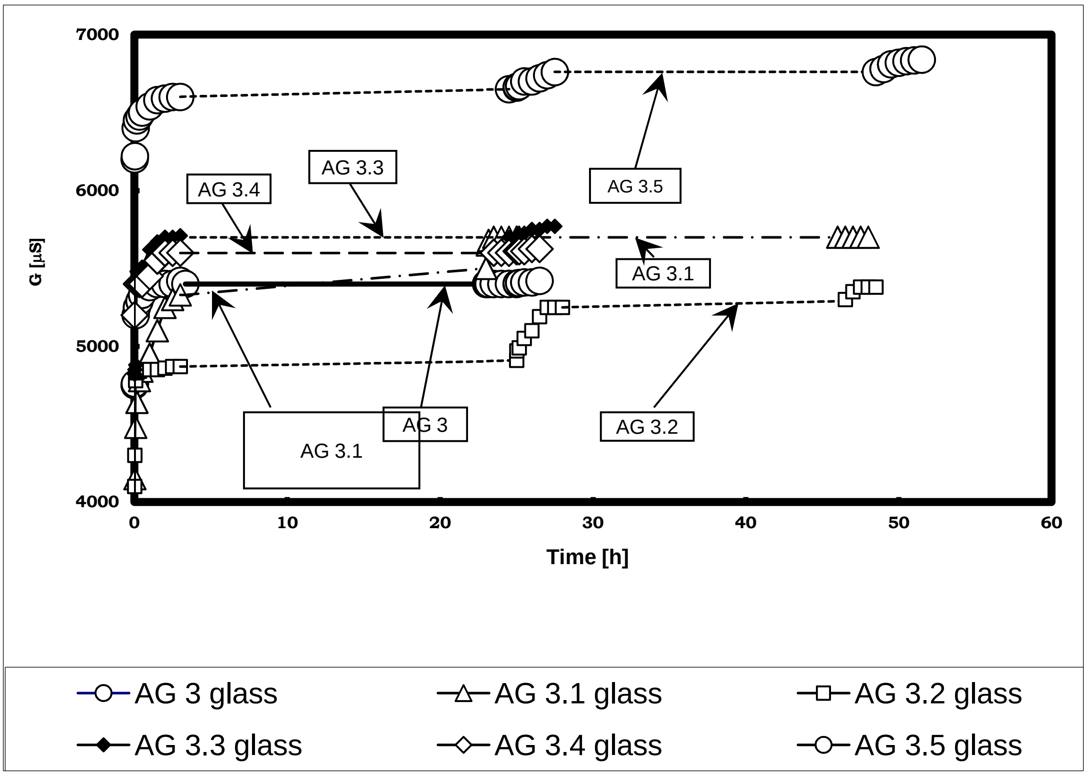

Fig. 9. Electrical conductivity evolution in time, comparatively, for the glasses from AG 3 series

4. Discussion

Optical phonons specific in IR domain of the samples from AG.2 series compared to those of pure P_2O_5 glass are presented in Table 6 and optical phonons of the samples from AG.3 series compared with those of P_2O_5 pure glass are presented in Table 7.

Table 6. Absorption bands in IR domain (cm^{-1}) of pure P_2O_5 glass and those of AG2 series glasses.

Structural groups	Pure P_2O_5 glass [7, 8]/Borate glass [9]	AG2	AG2.1	AG2.2	AG2.3	AG2.4
P-O-H water absorption	1380	-	1440	-	-	-
B-O$^-$ stretching from BO_3	1386, 1415	-	1440	-	-	-
P=O stretching, long phosphate chains	1240-1270	1263	1203	-	1259	1259
B-O stretching of BO_3 from boroxol rings	1263	-	1203	-	-	-
$[P_2O_7]^{4-}$ pyro-phosphate units	1027 1179	-	986	1028	-	-
PO_4 stretching	1030	-	986	1028	-	-
PO_2 symmetrical stretch	1100-1170	-	986 1186	1177	1177	1177
PO_4^{3-} symmetrical	1015	-	986	1028	-	-
P-O-P asymmetrical stretch ing	840-950	879	875	879	879	879
B-O stretching from BO_4	800-1200	-	827 845 875 986 1203	-	-	-
P-O-P symmetrical stretching	670-800	727	827	727	727	727
P-O-P bending	420-620	-	-	632	-	-
PO_2 asymmetrical stretching	1200-1300	1263	-	-	1259	-
PO_3^{2-} symmetrical	980-1050	-	986	1028	-	-
PO_3^{2-} asymmetrical	1110-1190	1099	-	1099	1099	1099

Table 7. Absorption bands in IR domain (cm^{-1}) of pure P_2O_5 glass and those of AG3 series glasses.

Structural groups	Pure P_2O_5 glass [7,8]/Borate glass [9]	AG3	AG3.1	AG3.2	AG3.3	AG3.4	AG3.5
P-O-H water absorption	1380	1401	1432	1401	1401	1401	1401
B-O$^-$ stretching from BO_3	1386, 1415	-	1353	-	-	-	-
P=O stretching, long phosphate chains	1240-1270	-	-	-	-	-	-
B-O stretching of BO_3 from boroxol rings	1263	-	-	-	-	-	-
$[P_2O_7]^{4-}$ pyro-phosphate units	1027 1179	1001	1064	1000	1026	1028	1028
PO_4 stretching	1030	1030	-	1000	-	1028	1028
PO_2 symmetrical stretch	1100-1170	1112	-	-	1112	1112	1112
PO_4^{3-} symmetrical	1015	1001	1001	1001	1001	1001	1001

Structural groups	Pure P_2O_5 glass [7,8]/Borate glass [9]	AG3	AG3.1	AG3.2	AG3.3	AG3.4	AG3.5
P-O-P asymmetrical stretch ing	840-950	834	834	834	834 928	834 939	834 939
B-O stretching from BO_4	670-800	719	719	719	719	719	721 752
P-O-P symmetrical stretching	800-1200	-	905 959	-	-	-	-
P-O-P bending	420-620	646	614 646	614	614 646	630	555 574 646
PO_2 asymmetrical stretching	1200-1300	-	-	-	-	-	-
PO_3^{2-} symmetrical	980-1050	1001	1064	-	1001	1001	1001
PO_3^{2-} asymmetrical	1110-1190	1110	-	-	1112	1112	1112

All the glass samples from the AG2 series exhibit a Raman maximum at about 320 cm^{-1} corresponding to Mg-O vibration mode. AG2, AG2.3 and AG2.4 glass samples present a Raman maximum at 691 cm^{-1}, specific to P-O-P symmetrical vibration mode. For AG2.2 sample a maximum appears at 1048 cm^{-1} and for AG2.4 sample at 1140 cm^{-1} assigned to PO_4 stretching mode. The samples AG2, AG2.2 and AG2.3 show a Raman peak at 1303 cm^{-1} ascribed to PO_2 symmetrical vibration mode. All the samples from AG2 series show a Raman band placed at 2731 cm^{-1} attributed to of OH bonds vibration.

All the glass samples from AG3 series show a Raman maximum at about 336 cm^{-1}, which can be assigned to Mg-O vibration mode. The samples AG3, AG3.2, AG3.3, AG3.4 and AG3.5 show a Raman maximum at about 1210 cm^{-1} and AG3.1 at 1302 cm^{-1} due to PO_2 symmetrical vibration mode. Other vibration maxima located at 2430 cm^{-1}, 2544 cm^{-1} and 2724 cm^{-1} are assigned to OH groups vibration [10,11].

The greater solving rate in time was determined for the AG2.1 sample, after 70 h**.**

In the case of AG2 glass series, the following solubility increasing order is revealed: AG2.2 – one order less soluble; AG2.3 – close to 2.4 and 2.1; AG2.4; AG2.1; AG2 about 50% more soluble than 2.1, 2.3, 2.4.

In the case of AG3 glass series, the following solubility increasing order is seen: AG3.2 – about 15% less soluble than the next one; AG3.1 – close to 3, 3.4 and 3.3 (the difference between them is of 10% maximum); AG3; AG3.4; AG3.3; AG3.5 much more soluble than the above five samples (about 15-20% more soluble than the most soluble from them, namely AG 3.3).

The most stable and less solving sample is AG3.2 sample. The difference between the solubility of those two glass sample series is about 30 %.

5. Conclusions

The FTIR absorption and Raman spectra put in evidence vibration modes specific to P-O bonds from the phosphate network as P-O-P, PO_2, PO_4, PO_3 that emphasizes the network forming role of phosphorus oxide. In the case of glass sample containing boron oxide, specific vibration modes for B-O bond are found. Raman spectra put in evidence vibration modes specific to Mg-O bond as vitreous network modifier ion.

The highest values of conductance were obtained for AG 2.1 sample, containing boron oxide and the lowest values for AG 2.2, containing iron oxide, indicating the same behavior of the samples as regards their solubility in the soil.

It can be concluded that the glass composition and structure can be designed in order to control the solubility in water and to obtain valuable vitreous fertilizer with special application in plant production.

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