The structural role of manganese ions in soil active silicate–phosphate glasses ☆

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HIGHLIGHTS

- Glasses from the SiO_2—P_2O_5—K_2O—CaO—MgO—MnO_2 system were prepared and analyzed.
- Glasses were characterized by spectroscopic methods.
- The relation between the structure and chemical activity of glasses was found.

GRAPHICAL ABSTRACT
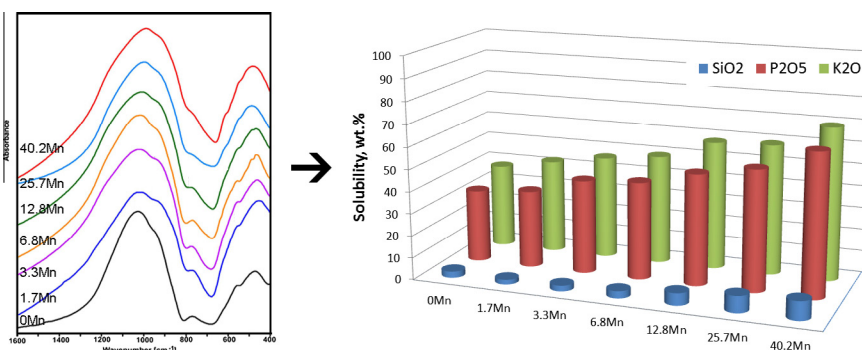
ABSTRACT

Silicate–phosphate glasses of SiO_2—P_2O_5—K_2O—MgO—CaO system containing manganese ions were synthesized by the melt-quenching technique and were investigated to obtain information about the influence of Mn-cations on the glass structure and their chemical activity. Structural properties were studied using X-ray method, FTIR and Raman spectroscopies. The chemical activity of analyzed glasses in the 2 wt.% citric acid solution was measured by chemical analysis (ICP-AES, EDS) and SEM observations.

It has been found that increasing amount of MnO_2 in the structure of investigated glasses causes their gradual depolymerization. This process is more apparent in the case of the silico-oxygen subnetwork than phospho-oxygen one. This is related to increasing amounts of SiO_4 tetrahedra containing two non-bridging oxygen atoms in silico-oxygen subnetwork. It has been also found that the presence of "weaker" chemical bonds of Si—O—Mn type in comparison to Si—O—Ca and Si—O—Mg bonds is responsible for the increase in solubility of the analyzed silicate–phosphate glasses in conditions simulating natural soil environment.

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Introduction

It is known that oxide glasses, mainly those of polymeric structure, like silicate, borate and phosphate, and mixed network glasses, like alumino-silicate, boro-silicate and phospho-silicate glasses or other three or more network-formers containing glasses have a unique ability to include into their structure a wide range of chemical compounds which can coexist together in an oxide glass structure [1]. The development of inorganic silicate and phosphate glasses has attracted both academic and industrial interest in recent years [2]. In literature, several authors [2–5] have shown that technologically interesting products can be obtained by multicomponent network formation and also by doping transition metal ions in these competitive networks [2,6]. One of the interesting glass structure modifier is manganese ion. It is known that the

introduction of manganese ions in a glass composition leads to changes in their structure and confers interesting properties, e.g. electrical, optical and magnetic [7–10]. It is also known that both Mn^{2+} and Mn^{3+} ions are well-known paramagnetic ions. Mn^{3+} ion has a large magnetic anisotropy due to its strong spin–orbit interaction of the 3d orbital whereas such anisotropy energy of Mn^{2+} ion is small because its orbital angular momentum is zero [11]. Because of its paramagnetic properties it is often referred to as a luminescent activator [12]. Manganese ions exist in different valence states with different coordination in glass matrices. Mn^{3+} ions exist in borate glasses with octahedral coordination, whereas in silicate and germinate glasses as Mn^{2+} with both tetrahedral and octahedral environment [11,13].

Introduction of the MnO into the structure of silicate glasses when its concentration is around 1.0 mol% [14] and up to 20 mol% in phosphate glasses [7], indicates that manganese ions mostly exist in Mn^{2+} state, occupy network forming positions with MnO_4 structural units or play the role of vitreous network modifier in the phosphate glasses, but when its concentration, in both silicate and phosphate glasses, is higher these ions seem to exist mostly in the Mn^{3+} state and occupy only modifying position.

The FTIR studies conducted by Pascuta and others [7] show that the controlled addition of MnO in the $MnO—P_2O_5—ZnO$ system generates several rearrangements in the network structure at the short-range order level. The authors suggested that it may be due to the formation of the P—O—Mn bonds at the expense of the rest of the P—O—P linkages. The formation of bridging oxygen (P—O—Mn) would increase the cross-link density of the glass network improving the chemical durability of the glass. The authors concluded that with increasing content of MnO in the phosphate, glass structure increases, confirming the role of manganese ions as glass modifiers. These results are also confirmed by other scientists [2,15–17]. Simultaneously, Soliman et al. [14], Mohan et al. [18] and Durga and Veeraiah [13] maintain that in the case of silicate glasses the number of silicon ions associate with one or more nonbridging oxygens increases, because of the excess of manganese ions which are able to associate with silicon. This leads to a decrease in the polymerization of the silicate network and expands the structure of the glass structure and in turn, leads to an increase in the molar volume. Also a decrease in density beyond 0.4 mol% MnO_2 supported that the network weakened as manganese oxide is accommodated in the glass including a rearrangement of the network.

Until now, extensive studies are conducted mostly on the structure of Mn-doped silicate or phosphate glasses, but not silicate–phosphate glasses. Therefore, the author has undertaken detailed studies using XRD, FTIR and Raman techniques as analytical methods in order to examine the effect of MnO_2 addition into the structure of model silicate–phosphate glasses from $SiO_2—P_2O_5—K_2O—CaO—MgO$ system acting as ecological fertilizers providing a controlled release rate of the nutrients for plants. In these glasses manganese plays a role of a micronutrient necessary for the proper development of plants [19]. Manganese influences plants' growth

process by regulation of ox-redox reactions and activation of some enzymes in the metabolic processes of plants. Additionally, the author has determined the relation between the structure of analyzed MnO_2-doped silicate–phosphate glasses and their chemical activity under conditions simulating the biological soil environment.

Experimental procedure

Preparation of the glasses

Silicate–phosphate glasses from $SiO_2—P_2O_5—K_2O—CaO—MgO$ system modified by MnO_2 addition were prepared. In all glasses, constant quantities of P_2O_5, K_2O, and SiO_2 were kept, and the increasing amount of MnO_2 was introduced at the cost of the decreasing amount of MgO and CaO, with the constant MgO/CaO ratio. The silicate–phosphate glasses were produced by traditional melting of raw materials mixture, i.e., SiO_2, H_3PO_4, K_2CO_3, MgO, $CaCO_3$, and MnO_2 in platinum crucibles at 1300–1450 °C. Then the obtained amorphous material was fritted in water. All glasses were ground to grain size of 0.1–0.3 mm.

X-ray fluorescence spectroscopy

The chemical composition of glasses was controlled by X-ray fluorescence spectroscopy using ARL Advant 'XP spectrometer. Chemical composition of the examined glasses was presented in Table 1. Amorphous state of the analyzed silicate–phosphate glasses was confirmed by X-ray diffraction method.

FTIR spectroscopy

Middle infrared (MIR) spectroscopic measurements of the glasses were made with a Bruker Vertex 70v spectrometer. Transmission technique, samples as KBr pellets. Spectra were collected after 124 scans at 4 cm^{-1} resolution. The position of bands on the MIR spectra was defined automatically in Win-IR. Spectra decomposition has been carried out according to the mathematical self-deconvolution method using the minimization of the number of the bands rule, proposed by Handke et al. [20].

Raman spectroscopy

Raman studies were caried out using Horriba Yvon Jobin Lab-RAM HR micro-Raman spectrometer equipped with a CCD detector. Excitation wavelength of 532 nm was used and beam intensity was about 10 mW. Acquisition time was set to 30 s. The position of bands on the Raman spectra was defined automatically in Win-IR. Due to the high level of noise, for better legibility of the spectra, it was necessary to conduct Fourier smoothing of the Raman spectra.

Table 1
The chemical composition of silicate–phosphate glasses studied in the present work.

No	Chemical composition of silicate–phosphate glasses/mol%					
	SiO_2	P_2O_5	K_2O	MgO	CaO	MnO_2
0 Mn	42.59	6.47	6.74	21.22	22.98	0.00
1.7 Mn	43.60	6.17	7.06	19.82	21.65	1.71
3.3 Mn	44.17	6.71	7.06	18.44	20.35	3.26
6.8 Mn	43.39	6.68	7.00	16.97	19.20	6.77
12.8 Mn	43.78	6.52	7.05	14.05	15.76	12.84
25.7 Mn	43.79	6.83	7.11	7.79	8.79	25.7
40.2 Mn	43.82	6.88	7.06	0.95	1.08	40.21