

THERMAL BEHAVIOUR OF SILICATE-PHOSPHATE GLASSES IN RELATION TO THEIR BIOCHEMICAL ACTIVITY

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Abstract

Glasses of the K_2O – MgO – CaO – SiO_2 and K_2O – MgO – CaO – P_2O_5 – SiO_2 systems with microelements (Fe, Mo, Zn, B, Mn, Cu) were obtained by melting of apatite and serpentinite rocks, K_2CO_3 and oxides of appropriately metals mixtures. The amorphous state of glasses and the structural changes during their heating were determined by RDF and DTA/DSC methods. The solubility of the glasses in 2 mass% citric acid solution was studied by chemical analysis (ICP-AES, EDS) and SEM observations.

It has been found that the biochemical activity of silicate-phosphate glasses depends on the content of P_2O_5 and K_2O in their framework and is related to crystallisation ability of these glasses.

Keywords: glass bioactivity, glass crystallisation, silicate-phosphate glasses

Introduction

In recent applications it has often been required that the glassy material has the chemical reactivity manifested in strictly defined conditions, such as e.g. increased temperature or in the presence of solutions of specific composition. In many glass systems subjected to the action of respective solutions, the process of selective washing-out of the components of these glasses takes place. An example here is the selective removal of silicate-phosphate glass components under the influence of biological solutions, which has been applied in designing glasses acting as ecological fertilisers of controlled release rate of the nutrients for plants and farm animals [1, 2].

They may supply P, K, Ca and Mg and a wide selection of microelements in a biologically active form, without releasing Cl^- , SO_4^{2-} ions or other anions, usually hardly tolerated by the plants. The nutrients and the microelements are released from the glassy fertilisers under the influence root systems in amounts needed at the particular stage of their growth. Moreover, they are dissolved to a minimal degree and carried away by the atmosphere water, which is a great disadvantage of the traditional fertilisers as well as the enveloped fertilisers.

The subject of the investigations discussed in the present study was the thermal behaviour of silicate-phosphate glasses and physico-chemical phenomena accompanying the interaction between these glasses and acid solutions produced by biological systems. The knowledge of these processes may help in designing and producing this kind of materials used for the protection of the natural environment.

Experimental

Glasses of the $K_2O-MgO-CaO-SiO_2$ and $K_2O-MgO-CaO-P_2O_5-SiO_2$ -microelements (MnO , CuO , B_2O_3 , MoO_3 , ZnO , Fe_2O_3) systems were synthesised from apatite, serpentinite, technical potassium carbonate and oxides which introduced the appropriate microelements, by melting them at $1450^\circ C$ for about 2 h.

The amorphous state of glasses and the structural changes during their heating were followed by RDF and thermal methods. A Perkin Elmer DTA-7 system operating in heat flux DSC mode, under nitrogen atmosphere and a heating rate of $10^\circ C\ min^{-1}$ was used for glass transition effect (T_g) and crystallisation measurements.

The dissolution of the glasses in 2 mass% citric acid solution was determined according to the procedure of the fertilisers activity measurement method used in agrochemistry. Solubility in this solution is an indicator of assimilateness of fertiliser components by plants [3]. Moreover, the solubility of glasses in water was checked. The solubility of the chemical components of glasses was measured using inductively-coupled plasma atomic emission spectrography method (ICP-AES).

Changes of the glass surface generated by biological solutions were studied by scanning electron microscopy (SEM) with a chemical analyser (EDS).

Results and discussion

Thermal behaviour of silicate-phosphate glasses

It can be seen from the DSC curves (Figs 1 and 2) that during heating silicate-phosphate glasses typical glass crystalline transformations, such as glass transition effect (T_g) and crystallisation (T_{cryst}) take place.

The crystallisation of silicate glasses proceeds in one stage. The products of crystallisation are compounds of Mg_2SiO_4 and $K_2MgSi_3O_8$ composition. On the other hand, crystallisation of silicate-phosphate glasses has a multistage character. Glasses from the $K_2O-MgO-CaO-P_2O_5-SiO_2$ system start to crystallise at the glass transition temperature and Ca-phosphates are formed first. Mg_2SiO_4 crystallises next. Afterwards, above the softening temperature, $KAlSiO_4$ crystallises in the remaining glassy matrix if glass contains aluminium.

Weakening the framework in the structure of silicate-phosphate glasses by increasing the content of the components depolarising this framework (P_2O_5 , K_2O) present in their composition is manifested in the increasing tendency of these glasses for crystallisation. The ability of glasses for crystallisation is measured by values of the temperature and enthalpy of crystallisation and values of the thermal stability pa-

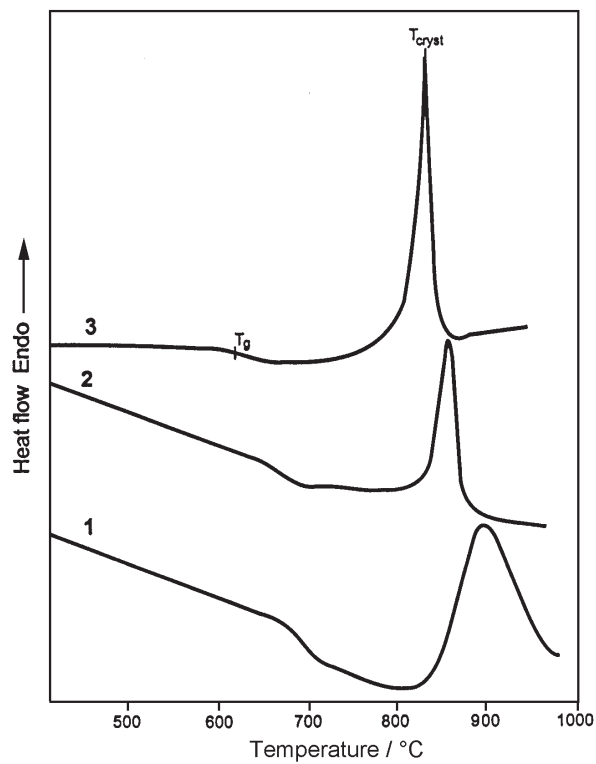


Fig. 1 DSC curves of glasses from the K_2O - MgO - CaO - SiO_2 system; 1, 2, 3 – numbers of glass (Table 1)

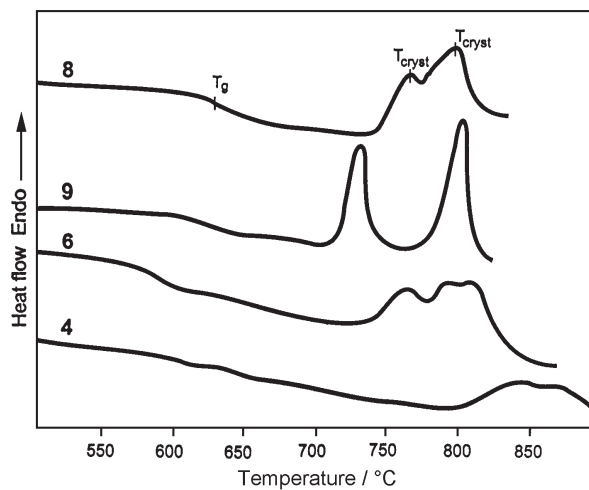


Fig. 2 DSC curves of glasses from the K_2O - MgO - CaO - P_2O_5 - SiO_2 system; 4, 6, 8, 9 – numbers of glass (Table 1)

parameter of glasses (ΔT). Lower values of temperatures and higher values of enthalpy crystallisation and lower values of thermal stability parameter (Table 1) indicate greater tendency of the glass for devitrification.

Table 1 Thermal characteristics of silicate-phosphate glasses

No. of glass	Content of P_2O_5 /mass%	Content of K_2O /mass%	$T_g/^\circ C$	$T_{cryst}/^\circ C$	Thermal stability parameter $\Delta T = T_{cryst} - T_g/^\circ C$	$\Delta H_{cryst}/J g^{-1}$
1	–	5.0	695	897	202	–
2	–	10.0	673	861	188	–
3	–	15.0	661	843	102	–
4	5.0	5.0	664	909	245	100.2
5	5.0	10.0	660	902	242	102.0
6	10.0	10.0	669	820	151	165.0
7	15.0	5.0	643	874	231	132.0
8	15.0	10.0	673	803	130	206.6
9	20.0	10.0	654	782	128	210.0

Solubility of silicate-phosphate glasses

The solubility of the particular components of K_2O – MgO – CaO – SiO_2 and K_2O – MgO – CaO – P_2O_5 – SiO_2 glasses in citric acid depends on the content of P_2O_5 and K_2O in their composition [4]. In glasses containing bigger amounts of P_2O_5 and K_2O , under ‘in vitro’

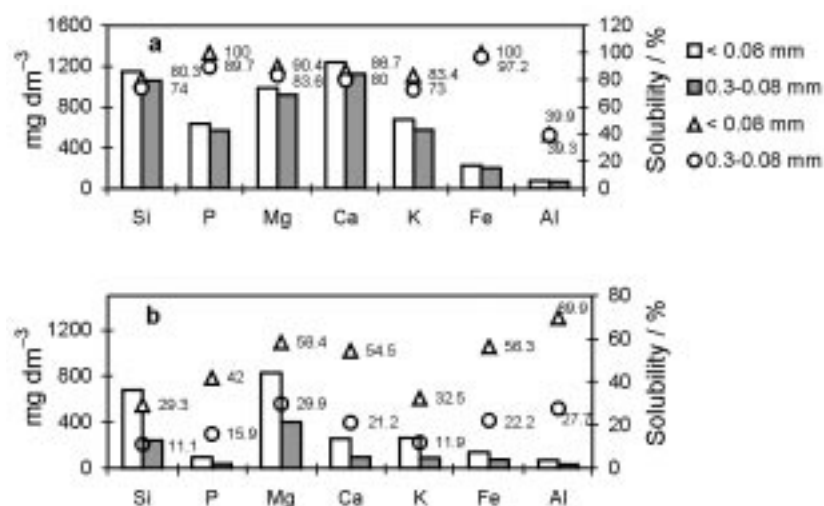


Fig. 3 Solubility of the chemical components of K_2O – MgO – CaO – P_2O_5 – SiO_2 glasses in citric acid; a – 15 mass% of P_2O_5 and 10 mass% of K_2O ; b – 5 mass% of P_2O_5 and 5 mass% K_2O

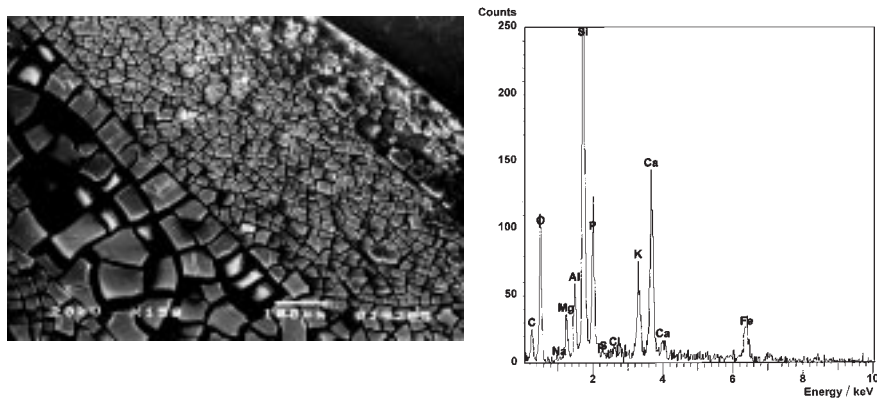


Fig. 4 SEM and EDS data of surface of silicate-phosphate glasses after 1 day citric acid etching

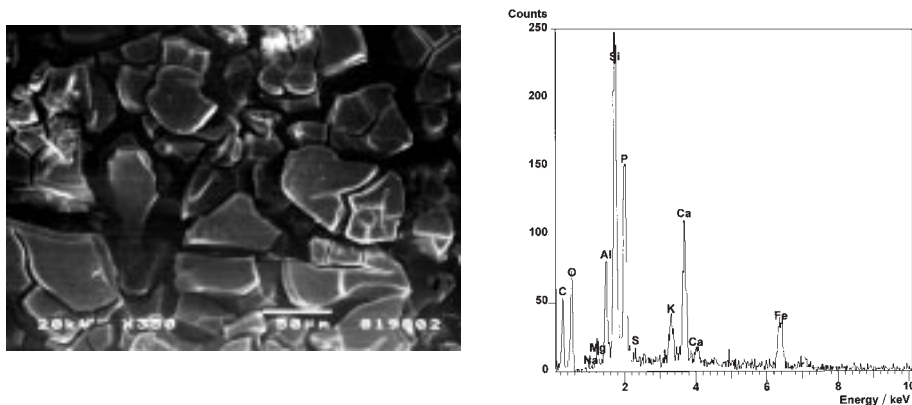


Fig. 5 SEM and EDS data of surface of silicate-phosphate glasses after soil (pH=5) etching

experiments about 70 to 85 mass% of their main components, i.e. Mg, Ca, K and Si are released, while the release of P may attain as much as 90 mass% of its total content (Fig. 3a). Reduction of P_2O_5 and K_2O content in the glasses diminishes their solubility (Fig. 3b).

Glasses from the K_2O -MgO-CaO-SiO₂ and K_2O -MgO-CaO-P₂O₅-SiO₂ systems are sparingly soluble in water, however they cause its alkalinisation.

The network of glasses of the K_2O -MgO-CaO-SiO₂ and K_2O -MgO-CaO-P₂O₅-SiO₂ systems is made up silicate and phosphate clusters linked by the bivalent cations. These cations may form both stable silicates and phosphates. The presence of phosphate clusters in the silicate framework makes it weaker and causes the solubility of these glasses to increase with its percent share. The solubility of silicate-phosphate

glasses also increases with the content of K_2O , which can be explained by their depolymerising influence on the framework, especially its silicate part. The more ionic character of K–O bonds (according to Görlich's scale [5] equals 0.823) in comparison with Ca–O bonds (0.707) is also responsible for the increasing solubility of these glasses with replacing CaO by K_2O .

The surface of silicate-phosphate glasses exposed to citric acid or soil solutions undergoes corrosion visible in the form of cracks and corrosion centers increasing with the time of acid action. On the surface of these glasses a layer of amorphous silica is formed retaining in its composition K, Mg as well as Ca and P probably as the calcium phosphates (Figs 4 and 5). Their content in the silica gel decreases with the dissolution time as they diffuse gradually towards the inside of the solution [6].

Conclusions

The dissolution rate of the particular components of silicate-phosphate glasses in biological solutions depends on their chemical composition and structure of the glass network, especially by the degree of its cross-linking and the strength of the chemical bonds between the modifiers cations and the components of the network. The more ionic character of Me–O bonds decreases the strength and chemical resistance of the glass structure. On the other hand, weakening the framework in the structure of silicate-phosphate glasses causes an increase in their ability for crystallisation which can be measured by thermal methods.

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References

- 1 J. V. Valartelli and R. Guardani, *Fertilizantes*, 3 (1981) 4.
- 2 P. Knott, *Glastechnische Berichte*, 62 (1989) 29.
- 3 T. Lityński, H. Jurkowska and E. Górlach, *Chemical Analysis for Agriculture*, Warszawa 1976 (in Polish).
- 4 I. Waclawska and L. Stoch, *Polish Ceramic Bulletin* 15, *Ceramics*, 53 (1997) 129.
- 5 E. Görlich, *The effective nuclear charges and the electronegativity*, Polish Academy of Arts and Science, Craców 1997.
- 6 I. Waclawska, L. Stoch and J. Ostrowska, *Glassy fertilisers composition and biochemical activity*, Proc. of the 5th ESG Conference, Prague 1999, B1-57.