

## **THERMAL ANALYSIS OF GEL-DERIVED BIOACTIVE PHOSPHO-SILICATE GLASSES**

*M. Ciecńska\**

Department of Glass and Enamel, Faculty of Material Science and Ceramics, University of Mining and Metallurgy, 30–059 Cracow, Poland

### **Abstract**

Thermal reactions of model phospho-silicate gels of simple composition has been studied. The investigations demonstrate that the kind of compounds introducing  $P_2O_5$  into the gel silicate network,  $H_3PO_4$ ,  $PO(OC_2H_5)_3$ ,  $POCl_3$  influence the course and temperature and the xerogel formation. The amount of interstitial water and xerogel porosity is dependent on the cations, amorphous structure modifiers (Ca, Na) used. Thermal analysis curves appear the convenient carriers of informations about the processes in gel pores and the formation of xerogel and glass.

**Keywords:** bioactive glasses, gels thermal reactions, phospho-silicate glasses, sol–gel glass synthesis, thermal analysis

### **Introduction**

Phospho-silicate glasses as well as glass–ceramics obtained by way of their crystallization, demonstrate bioactive properties, which enable their join to living osseous tissue. Their usefulness in surgery as implants and filling of osseous losses has been confirmed in numerous investigations and they are now more and more frequently applied in practice in hospitals [1].

The bioactive glasses used in surgery contain about 50 mass% of  $SiO_2$  and more than 5 mass% of  $P_2O_5$  as glass network formers. Glass modifiers are CaO and  $Na_2O$ . The glass known as Bioglass<sup>®</sup> is here an example [2].

The bioactive glass–ceramics (Ceravital<sup>®</sup>) is composed of apatite in glassy matrix and its principal chemical components are:  $SiO_2$  40–50 mass%,  $P_2O_5$  10–20% and CaO 30–35%. These materials are produced by melting the components at the temperature 1450–1600°C depending on glass composition, vitrification of the melt by slow cooling and crystallization of the obtained glass.

Recently more and more attention has been given to bioactive glasses formed by the sol–gel method. It has been found that they are better tolerated by the living tissue in comparison with glass of similar composition obtained by way of high temperature melting [3]. At the same time the interest has been arisen in new applications of

\* Author for correspondence: E-mail: [stoch\\_l@poczta.onet.pl](mailto:stoch_l@poczta.onet.pl)

bioactive materials as bioactive fibers for reinforcing the glass–ceramic implants [4] and implants as medicins carriers releasing them slowly. For this application the glasses produced by the sol–gel method may be particularly useful.

Increased bioactivity of gel glasses, resulting from their nature when compared with that of melted glasses, allows to increase  $\text{SiO}_2$  content in them. The traditional glasses containing more than 50% of  $\text{SiO}_2$  are regarded as being not sufficiently biologically active. As a consequence investigations have been undertaken on the sol–gel synthesis of phospho-silicate glasses which might be applied as bioactive materials in various forms. It has been found that in the traditional glasses the use of various acids ( $\text{H}_3\text{PO}_4$  or  $\text{HPO}_3$ ) as phosphate raw materials has an influence on their crystallization [5]. In consideration of this statement the influence of various phosphorus compounds on the glass synthesis by the sol–gel method has been investigated. The thermal analysis has proved very useful in these investigations. The application and usefulness of thermal analysis in the sol–gel synthesis of phospho-silicate glasses and the thermal reactions accompanying the gel–glass transition are the subject of the present study.

## Experimental

The object of experiments were gel glasses from the systems:  $\text{SiO}_2$ – $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$ – $\text{P}_2\text{O}_5$ – $\text{NaO}$  and  $\text{SiO}_2$ – $\text{P}_2\text{O}_5$ – $\text{CaO}$ . As the  $\text{P}_2\text{O}_5$  precursor there were used compounds:  $\text{H}_3\text{PO}_4$ ,  $\text{PO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{POCl}_3$ . Ethyl alcohol  $\text{C}_2\text{H}_5\text{OH}$  was used as the solvent and the catalyser of the reaction was a water solution of hydrochloric acid  $\text{HCl}$  in the proportion 1:1. Na and Ca were introduced as sodium nitrate and calcium chloride water solutions. The final solutions were allowed to stay under ambient conditions until completion of gelation which occurred after a period from 0.5 h up to 14 days depending on the gel composition and first of all on the applied  $\text{P}_2\text{O}_5$  precursor.

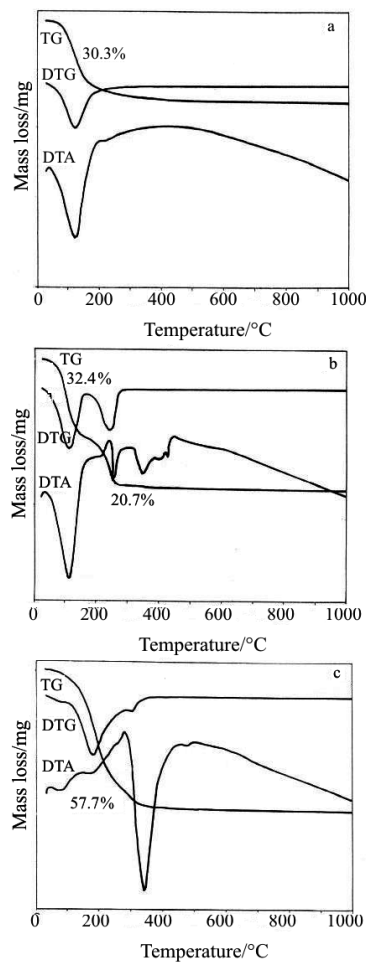
The gels were dried in ambient conditions for 2 weeks and next subjected to multi-stage thermal treatment, successively to 120, 400 up to 1000°C. Samples obtained in this way were subjected to DTA, TG, XRD and FTIR investigations. Thermal analysis was carried out with Derivatograph C (Hungarian Optic Works). Experiments conditions were, samples mass 50 mg, heating rate 10°C min<sup>-1</sup>, air atmosphere.

## Results

### *Thermal analysis*

DTA, TG and DTG curves of 80  $\text{SiO}_2$  20  $\text{P}_2\text{O}_5$  (mol%) gels obtained with the application of  $\text{H}_3\text{PO}_4$ ,  $\text{POCl}_3$  and  $\text{PO}(\text{OC}_2\text{H}_5)_3$  as the components introducing phosphorus are shown in Fig. 1. In the case when in order to obtain gel, phosphorus is introduced as  $\text{H}_3\text{PO}_4$ , on the thermal analysis curves there occurs one strong endothermic peak at 125.6°C. It is accompanied by 30.37 mass% loss of mass connected with the removal of the interstitial liquid and decomposition of tetraethyloxysilane (TEOS) which is continued till, the temperature reaches 400°C. On the other hand when phosphorus is

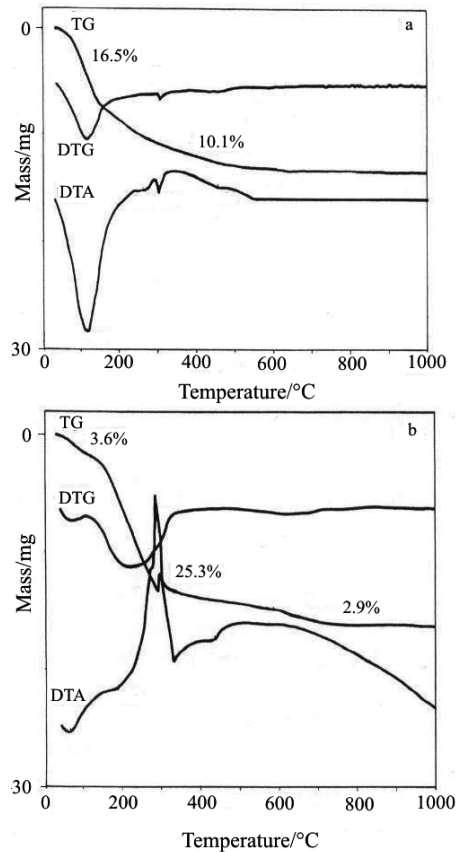
introduced as  $\text{POCl}_3$  this process proceeds in two stages. The first stage, at  $114.2^\circ\text{C}$ , is connected with 32.49 mass% loss. The second stage occurs within the range  $180\text{--}300^\circ\text{C}$ , and comprises the endo- and exothermic reactions which overlaps. It is accompanied by 20.76 mass% loss. At the temperatures  $348.9$  and  $410^\circ\text{C}$  there appear distinct endothermic transitions, not connected with a change of the sample mass. The exothermic effect can be interpreted as the organic compounds combustion. According to the FTIR results the endothermic effects at about  $400^\circ\text{C}$  can be interpreted as the reconstitution of the gel structure. It is connected with its transition into porous gel, free from the interstitial liquid (xerogel). The total loss of the gel mass accompanying the transition into a state free from the interstitial liquid is equal to 53.25 mass%.



**Fig. 1** DTA, TG, DTG curves of  $80\text{SiO}_2\cdot 20\text{P}_2\text{O}_5$  with different phosphorus compounds  
a –  $\text{H}_3\text{PO}_4$ , b –  $\text{POCl}_3$ , c –  $\text{PO}(\text{OC}_2\text{H}_5)_3$

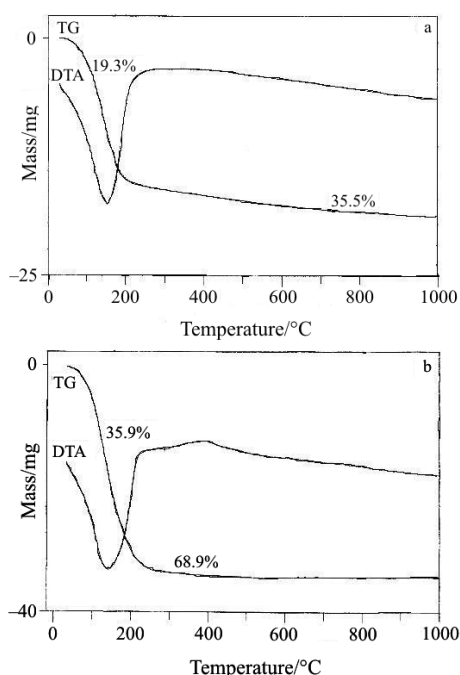
When phosphorus is introduced through the ester  $\text{PO}(\text{OC}_2\text{H}_5)_3$  the liquid removal takes place till the temperature reaches  $350^\circ\text{C}$ , and the total amount which becomes removed is 57.70 mass%. At  $281^\circ\text{C}$  there appears the exothermic reaction of ester oxidation. After this reaction and the removal of the volatile compounds there appear the endothermic effects of DTA indicating the reconstruction of the primary gel structure into amorphous phospho-silicate structure close to that of glass.

Introduction of 10 mol% of  $\text{Na}_2\text{O}$  at the expense of 10 mol% of  $\text{P}_2\text{O}_5$  in gel with  $\text{H}_3\text{PO}_4$  increased the range of the removal of the interstitial liquid up to  $600^\circ\text{C}$ , and its amount increased to 26.72 mass% (Fig. 2). On the DTA curve there appeared, as before, the endothermic effects at  $267$ ,  $304$  and  $1150^\circ\text{C}$ , but they were evidently weaker, which allows to assume that they derive from the phosphate component of the gel structure. In this case of gel containing the ester  $\text{PO}(\text{OC}_2\text{H}_5)_3$  in the presence of sodium, the loss of mass takes place up to  $32.02$  mass%. The temperature of the exothermic oxidations of ester does not change.



**Fig. 2** DTA, TG, DTG curves of  $80\text{SiO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Na}_2\text{O}$  gels with different phosphorus compounds a –  $\text{H}_3\text{PO}_4$ , b –  $\text{PO}(\text{OC}_2\text{H}_5)_3$

Gel composed of 80SiO<sub>2</sub>, 10P<sub>2</sub>O<sub>3</sub>, 10CaO (mol%) with H<sub>3</sub>PO<sub>4</sub> gives also one endothermic peak at 151.7°C, accompanied by 19.32 mass% loss nearly as much is released gradually up to the temperature of 1000°C (Fig. 3). Together its amounts to 37.46 mass%. Gel with POCl<sub>3</sub> shows the endothermic peak at 142.7°C, accompanied by 35.92 mass% loss. It passes into a broad exothermic peak at 382.8°C. At this temperature the total loss of mass equals 68.93 mass%, increasing slowly up to 69.56 mass% at 1000°C. In both these cases, in spite of different initial content of the interstitial liquid and other components released during heating, the measure of which is the loss of mass after reaching the state of xerogel, the remainder left in its structure is the same and it is removed uniformly up to the temperature of 1000°C. It represents 48 mass% of the total content of thermally removed components.

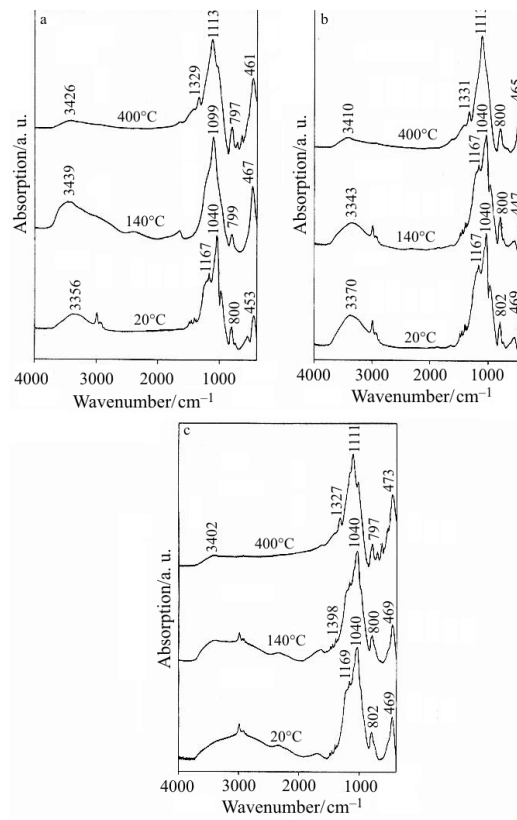


**Fig. 3** DTA, TG, DTG curves of 80SiO<sub>2</sub>·10P<sub>2</sub>O<sub>5</sub>·10CaO gels with different phosphorus compounds a – H<sub>3</sub>PO<sub>4</sub>, b – POCl<sub>3</sub>

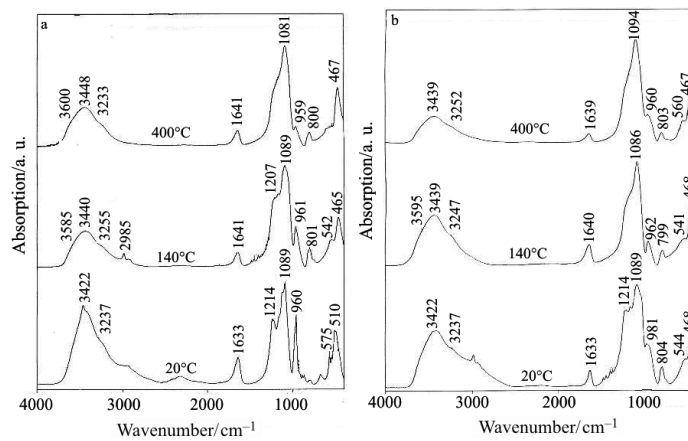
In all these gels, after the state of xerogel has been reached, with further increase of temperature, there can be observed a rather small, slow loss of mass connected with the gradual removal of OH groups combined with the phospho-silicate framework (silanol groups) and the progressing densification of the structure of glass.

#### *Infrared spectroscopy*

Comparison of FTIR spectra of samples heated to various temperatures facilitates the determination of the processes inducing the TG, DTG and DTA thermal effects (Figs 4, 5).



**Fig. 4** FTIR spectra of 80SiO<sub>2</sub>·20P<sub>2</sub>O<sub>5</sub> gels with different phosphorus compounds  
a – H<sub>3</sub>PO<sub>4</sub>, b – POCl<sub>3</sub>, c – PO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>



**Fig. 5** FTIR spectra of 80SiO<sub>2</sub>·10P<sub>2</sub>O<sub>5</sub>·10CaO gels with different phosphorus compounds  
a – H<sub>3</sub>PO<sub>4</sub>, b – POCl<sub>3</sub>

The FTIR spectra of 80SiO<sub>2</sub>, 20P<sub>2</sub>O<sub>5</sub> (mol%) gels are characterized by a broad band at about 3500 cm<sup>-1</sup> from the OH groups of water (H–O–H vibrations) and at 980 cm<sup>-1</sup> (Si–OH and P–OH vibrations). Three main bands at about 1100, 800 and 450–470 cm<sup>-1</sup> are characterized of the vibrations of the Si–O–Si groups which are evidence of developed polymerization of SiO<sub>4</sub> tetrahedra in gel [6, 7]. In this area there may be also present the P–O–P and P–O–Si bands. In the spectrum of gel there appears also a series of sharp bands characteristic of the organic groups RO of tetraethoxysilan (TEOS) 2958, 2914, 1481, 1396, 1167 cm<sup>-1</sup>.

The thermal stability of these groups depends on the kind of the compound used to introduce phosphorus. In the presence of H<sub>3</sub>PO<sub>4</sub> they decay already at 140°C and are replaced by water bands at 3439 and 1641 cm<sup>-1</sup>. In the presence of POCl<sub>3</sub> and the ester PO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> the Si–OR groups retain their stability still at 140°C (the range of the first endothermic peak).

Removal of organic compounds from the gel structure, and in the case of using ester PO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> also from P–OR groups, results of the formation of gel of amorphous structure identical with the structure of phospho-silicate glass. When H<sub>3</sub>PO<sub>4</sub> has been applied, this phenomenon takes place already at 140°C, and the interstitial voids are filled only with water (bands at 3439 and 1641 cm<sup>-1</sup>). In the case of the other phosphorus compounds (phosphorus ester and POCl<sub>3</sub>) this process is completed at 400°C. At the temperature of 400°C a polymerized amorphous structure is formed, the framework of which comprises the [SiO<sub>4</sub>] tetrahedra (band at about 1113 cm<sup>-1</sup>) and [PO<sub>4</sub>] giving shoulder on the principal band Si–O–Si at about 1120 cm<sup>-1</sup> and a band at about 800 cm<sup>-1</sup> from the Si–O–P bridges combining both tetrahedra [7]. In the structure of xerogel part of the double bond P=O (1330 cm<sup>-1</sup>) is retained, as well as the OH groups as Si–OH. In the course of heating they become stepwise released up to temperature 1000°C.

Introducing of sodium in the form of NaNO<sub>3</sub> into gel was significantly manifested in the FTIR spectrum. There appeared sharp bands of NO<sub>3</sub> groups (at 1790, 1385, 802 cm<sup>-1</sup>). They appear still at the temperature 140°C. Bands connected with Si–RO groups decayed, and the band of the OH groups was shifted to 3464 cm<sup>-1</sup>. This means that already at 20°C sodium reacts with the gel components. As a result the RO groups are removed at 140°C and their bands are no longer present in any kind of the compounds used to introduce phosphorus.

The presence of sodium, on the other hand, is accompanied by the increase in the intensity of the bands of (OH) groups (3464 cm<sup>-1</sup>) and water (1643 cm<sup>-1</sup>) in the spectra of samples heated to 140°C as well as to 400°C.

The presence of sodium causes the decay of the double bonds P=O at 400°C which is an indication that already at this temperature the amorphous structure of xerogel has been formed in its characteristic form with incorporated Na cation. This is also evidence by the shifting of the Si–O–Si band to 1088 cm<sup>-1</sup> which is characteristic of silicate glasses. There appeared also a band at 966 cm<sup>-1</sup>. The introducing of Ca into gel is accompanying by the increase in the intensity of the bands of (OH) groups (3422 cm<sup>-1</sup>) and water (1639 cm<sup>-1</sup>) as compare with Na containing gels (Fig. 5). They are visible even in 1000°C.

## Conclusions

The performed investigations of the thermal reactions of selected model gels of simple composition enabled to determine the temperatures and the character of the processes occurring in the gel pores and in its structure which lead to the removal of the interstitial liquid and the organic radicals as well as the transition of gel into xerogel and next into phospho-silicate glass.

From the thermal investigations it follows that the kind of the compound introducing phosphorus used in the synthesis of gel has influence on the amount of the interstitial liquid and on the temperature needed for its removal, i.e. on the temperature of the formation of the xerogel. This temperature is the lowest (about 300°C) when  $H_3PO_4$  is used, when compared with  $POCl_3$  and  $PO(OC_2H_5)_3$  as the compounds introducing phosphorus.

The amount of the interstitial liquid increases and the temperature of the transition into gel increases considerably as well when besides the framework forming components ( $SiO_2$ ,  $P_2O_5$ ) the modifiers ( $Na_2O$ ,  $CaO$ ) are introduced in the form of water solutions of their salts. This observation can be explained if it is assumed that they are present in the interstitial spaces of gel at the form of hydrated cations surrounded by  $H_2O$  molecules. The water of the hydrating envelopes is retained up to considerably high temperatures. It is released when the gel structure collapses and then this water becomes removed, and the cation combines with the phosphate-silicate framework of xerogel which next becomes transformed into glass.

Thermal analysis allows to obtain in a simple way a series of data essential for the study of the synthesis of gel-derived glasses, including such specific as the biologically active phospho-silicate glasses.

It is particularly helpful in the determination of the mechanism and the role of gel reconstruction into xerogel and next to glass and the temperature of the completion of these processes. Judging by the amount of the removal interstitial liquid it is possible to estimate the total porosity of gel at any arbitrary stage during this process. On this basis one can predict the shrinkage of gel and xerogel. It is also possible to establish the amount of the retained OH groups depending on the vitrification temperature. Their presence is one of the factors responsible for the bioactivity of the glass. This facilitates the examination of the effect of the kind of the compounds used to introduce the framework forming compounds and the kind of the cations modifiers on the above reactions and the thermal transitions responsible for glass formation from gel. The latest belongs to the internal structure rebuilding processes which mechanism is not good recognized yet [8–10].

The obtained  $80SiO_2$ ,  $10P_2O_5$ ,  $10CaO$  (mol%) glass shows good thermal stability; it can be produced already at the temperature 900–1000°C. When obtained by melting it requires the temperature of above 1500°C, it is easily crystallizing and its biological activity is poor. Laboratory test have confirmed the gel-derived glass activity with simulated body fluids (SBF). It is planned to apply the control thermal analysis in the synthesis of bioactive phospho-silicate glasses containing Na, Mg, K and Ca study.



This work was supported by the National Committee for Scientific Research of Poland grant 7T08D01018.

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