Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 1, 185–190

INFLUENCE OF MgO (CaO) ON THE STRUCTURE OF SILICATE-PHOSPHATE GLASSES
TA and NMR study

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Thermal and structural properties of model silicate-phosphate glasses containing the different amounts of the glass network modifiers, i.e. Mg^{2+} and Ca^{2+} were studied. To explain the changes of the parameters characterizing the glass transition effect (T_g, Δc_p) and the crystallization process (T_c, ΔH) depending on the cations modifiers additions, analysis of the bonds and chemical interactions of atoms in the structure of glasses was used.

^{31}P MAS-NMR spectra of SiO_2–P_2O_5–MgO(CaO)–K_2O glasses show that the phosphate complexes are mono- and diphosphate. It has been found that increasing amounts of Mg^{2+} or Ca^{2+} cations in the structure of glasses causes the reduction of the degree of polymerization of the phosphate framework ($Q^1 \rightarrow Q^0$). The influence of increasing of modifiers in the structure of silicate-phosphate glasses on the number of non-bridging oxygens per SiO_4 tetrahedron and density of glasses was presented.

Keywords: *glass crystallization, glass structure, glass transformation, ^{31}P MAS-NMR, silicate-phosphate glasses*

Introduction

The progress in the study of glass is manifested in the search for new glasses with unconventional properties. Here belong, among others, the silicate-phosphate glasses, modified by addition of elements playing the role of macro- and microelements, indispensable in the biological processes of the growth of plants. They have the properties of slow-acting carriers of nutrients, released in a controlled way as they are absorbed by the plants, and hence as glassy fertilizers they can help the natural environment to restore its biogeochemical equilibrium as well as to protect it [1, 2].

The structure of these glasses is a spatial framework, formed by silicon and phosphorus oxides, which is possible due to the specific character of the glassy state. In the formation of such glasses the components, defined in the glass chemistry as modifiers (metals of alkalies and alkaline earths) play an important role. The more so that the chemical activity of such glasses in the biological environment is determined by the type and the amount of the components, occupying in the glass structure the positions outside the silicate-phosphate framework [3, 4].

In earlier investigations there has been analyzed the influence of phosphorus and potassium [5], calcium and magnesium [6] on the ability of the silicate-phosphate glasses to crystallize; these investigations, however were carried out on glasses with both Ca^{2+} and Mg^{2+} present in the composition of the glass. However their influence on the glass transformation effect of silicate-phosphate glasses was not analyzed then. The literature data referring to the above problem supply different information. According to [7] the increase in CaO and MgO content in the composition of phosphate glasses causes the increase in the characteristic temperature T_g. Similar dependencies have been observed for silicate [8] and silicate-phosphate glasses [10]. On the other hand, results of investigations [9] indicate that the increase of MgO content at the lost of CaO content in the structure of silicate-phosphate glasses causes the reduction of T_g temperature.

Considering the above statements, in the present study an attempt has been made to describe the effect of MgO and CaO additions on the thermal and structural properties of silicate-phosphate glasses.

Experimental

The composition of glasses from the SiO_2–P_2O_5–MgO–K_2O and SiO_2–P_2O_5–CaO–K_2O systems were selected so that the melted glasses contained: 2 and 7 mol% of P_2O_5, 6–18 mol% of K_2O, 12–36 mol% of CaO, 16–43 mol% of MgO and 45–91 mol% of SiO_2 (Table 1).

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1388–6150/$20.00

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The glasses were obtained by the traditional method of melting a mixture of pure materials, i.e. SiO_2, H_3PO_4, K_2CO_3, MgO and $CaCO_3$, in platinum crucibles, in the temperature range 1470–1600°C. The obtained amorphous material was refined to the grain size 0.1–0.3 mm.

To investigate the course of the phase transitions of the glasses during their heating, the thermal measurements were carried out using Perkin-Elmer DTA-7 thermoanalyzer, operating in heat flux DSC mode. In order to characterize the glass transformation effect, the sample of glass (60 mg) placed in platinum crucibles and dry nitrogen atmosphere were heated at a rate 10°C min^{-1} to the temperature of about 50°C above the transformation temperature, then cooled at the same rate and heated again. The transformation temperature T_g was registered in a half of the endothermal inflection on DSC curve. Crystallization temperature was registered as a maximum temperature of crystallization effect (T_{cryst}). Changes of Δc_p at the T_g point and enthalpy of crystallization (ΔH) were determined applying 7 Series/Pyris Thermal Analysis Software Library.

To identify the crystal phases X-ray diffraction method (Diffractometer X'Pert PRO) was applied.

Structural examinations of the glasses were based on nuclear magnetic resonance (MAS-NMR) method. The ^{31}P MAS-NMR investigations were carried out at room temperature, using CMV-400 Chemagnetics pulse spectrometer with Bruker 9.4T Superconductive magnet. ^{31}P MAS-NMR spectra were obtained at 161.9 MHz. Pulses of Pi/2 followed by a 2.5 μs delay was used to record the ^{31}P spectra. 85% H_3PO_4 was used as a chemical shift reference.

Physical density of silicate-phosphate glasses was determined by pycnometric measurements, which were performed on grains from 0.1–0.3 mm. Five measurements on each glass were carried.

Results and discussion

Thermal analysis

The results of thermal investigations (Fig. 1) indicate that glasses of the K_2O–MgO(CaO)–SiO_2–P_2O_5 system (Table 1) as a result of heating undergo typical phase transitions such a glass transformation effect and crystallization. These transitions are characterized by the following parameters: T_g temperature, change in the specific heat at the T_g (Δc_p), temperature (T_{cryst}) and the enthalpy of crystallization (ΔH) as well as the thermal stability parameter ($\Delta T = T_{cryst} - T_g$).

The effect of changes in the chemical composition of the glasses on the parameters characterizing both transitions is shown in Table 1. The silicate-phosphate glasses containing a single modifier in the form of K^+ ions present in their composition, are characterized by low values of the T_g temperature and the jump-like change of the molar heat (Δc_p), lowering with the increase of the content of this modifier. These glasses do not show the ability to crystallize. On the other hand, introducing into their structure of increasing amounts of the modifiers in the form of Ca^{2+} and Mg^{2+} ions at the lost of Si^{4+} ions causes a gradual increase of the parameters characterizing the glass transformation effect. The modifier in the form of Mg^{2+} ions, present in the structure of the analyzed glasses, has a greater influence on the increase of T_g than the Ca^{2+} ions.

Table 1 Chemical composition, thermal and X-ray characteristics of silicate-phosphate glasses

No.	SiO_2	P_2O_5	K_2O	MgO	CaO	T_g/ °C	Δc_p/ J g^{-1} $°C^{-1}$	MgO/SiO_2 CaO/SiO_2	T_{crys}/ °C	ΔH/ J g^{-1}	ΔT/ °C	Type of cryst. compounds
	mol%											
1	91	2	7	–	–	561	0.31	–	–	–	–	–
2	87	2	11	–	–	559	0.27	–	–	–	–	–
3	84	2	14	–	–	544	0.19	–	–	–	–	–
4	80	2	18	–	–	502	0.13	–	–	–	–	–
5	76	2	6	16	–	710	0.39	0.21	–	–	–	–
6	69	2	6	23	–	722	0.50	0.33	–	–	–	–
7	63	2	6	29	–	725	0.55	0.46	–	–	–	–
8	57	2	6	35	–	728	0.61	0.61	1053	35.41	325	Mg_2SiO_4
9	51	2	6	41	–	729	0.85	0.80	1000	67.44	271	Mg_2SiO_4
10	80	2	6	–	12	673	0.31	0.15	–	–	–	–
11	74	2	6	–	18	698	0.49	0.24	1015	12.07	317	$Ca_3(PO_4)_2$
12	68	2	6	–	24	715	0.64	0.35	926	15.10	211	$Ca_3(PO_4)_2+Ca_2SiO_4$
13	63	2	6	–	28	718	0.87	0.44	904	34.30	186	Ca_2SiO_4

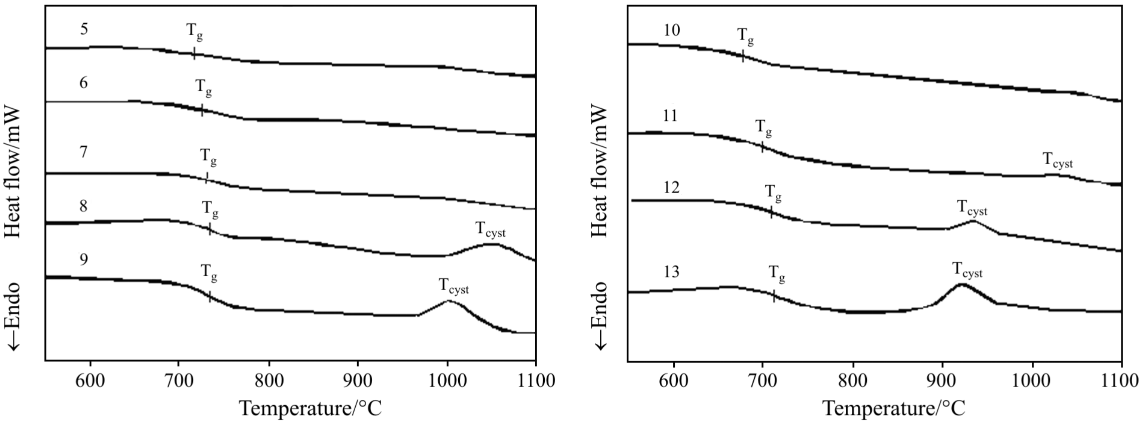

Fig. 1 DSC curves of silicate-phosphate glasses containing Mg^{2+} (No. 5–9) and Ca^{2+} (No. 10–13) as the modifier cations

On the basis of thermal investigations it has been found that the examined silicate-phosphate glasses which contain a single modifier in the form of Mg^{2+} or Ca^{2+} ions demonstrate a relatively low ability to crystallization. With increasing amount of the modifier in the glass structure their ability to crystallize, measured by values of thermal stability parameter (ΔT) and enthalpy of crystallization (ΔH), increases (Table 1).

In the glasses containing a modifier in the form of Mg^{2+} ions, their ability to crystallize appears at the value $MgO/SiO_2 = 0.61$. Crystallization has a one-stage character, and its product is magnesium silicate Mg_2SiO_4. In the glasses containing Ca^{2+} ions as a modifier, their ability to crystallize is observed already at the value $CaO/SiO_2=0.24$. Crystallization has a one-stage character, too (Fig. 1), but the crystallization products are more differentiated, and besides calcium phosphate $Ca_3(PO_4)_2$ there appears calcium silicate Ca_2SiO_4.The ability of glasses to crystallize, its progress as well as the type of the newly formed crystal phases depend thus on the mutual proportion between the components forming the glass structure.

The described changes of the parameters characterizing the glass transition effect and the crystallization process, confirm the effect of the nature of the chemical bonds present in the glass structure on the course of the above transitions [11], since they are connected with the breaking of the bonds or the rearrangement of the groups of atoms either for relaxation of the internal stresses induced by the disordered structure of the glass (glass transformation effect) or for transition from the amorphous into the crystalline state with ordered structure, specific for the state of thermodynamic equilibrium (crystallization process).

Characteristics of the bonds and of the chemical interactions of atoms in the structure of the examined glasses was based on parameters introduced by Görlich [12].

Introduction of increasing amount of K–O bonds, characterized by considerable ionicity ($i_G=0.823$), into the structure of silicate-phosphate glasses increases the elasticity of the structure of the examined glasses. At the same time the number of structural stresses ($L_{K–O}=1.340$), whose relaxation requires a small amount of energy, is decreasing. The glass transformation effect occurs thus at lower temperatures and is accompanied by a small change of the molar heat. At the same time relaxation of the small structural stresses can be realized through rotation or other rearrangement of the elements of the structure without disturbing the structure as a whole; hence silicate-phosphate glasses containing increasing amount of K_2O are characterized by great thermal stability.

Increasing amount of Mg–O and Ca–O bonds of low ionicity ($i_{G\ Mg–O}=0.670$; $i_{G\ Ca–O}=0.707$) causes that the structure of the glass becomes more rigid ($L_{Mg–O}=1.830$; $L_{Ca–O}=1.425$). The more covalent character of Mg–O and Ca–O bonds present in the structure of the examined glasses in comparison with the bonds of K–O type is thus responsible for the existence of considerable structural stresses in these glasses. Relaxation of these stresses requires more energy, hence higher T_g values which are correlated with increasing value Δc_p. At the same time relaxation process takes place through breaking some of the chemical bonds in the amorphous structure, and this in turn makes the crystallization of the glasses easier.

Analysis of the values determining the strength of the oxygen bridges in silicate-phosphate glasses modified by an addition of increasing amounts of Mg^{2+} cations has shown smaller difference in the ionicity of the chemical bonds of oxygen bridges of Mg–O–Si ($\Delta i_G=0.242$) type in comparison with the bridges of Mg–O–P ($\Delta i_G=0.356$) type or the oxygen bridges binding the potassium cations with the framework forming components of the glasses ($\Delta i_{G\ K–O–Si}=0.395$; $\Delta i_{G\ K–O–P}=0.519$).

Assuming that in the crystallization process there participate those components of the glass structure whose bonds can be most easily broken, the prod-

Table 2 The values of ΔG of the formation of silicates and phosphates crystallizing in silicate-phosphate glasses [13]

Compounds	ΔG_f/kJ mol^{-1}	
	1200 K	1300 K
$2MgO \cdot SiO_2$	–2342	–2374
$3MgO \cdot P_2O_5$	–5584	–5691
$2MgO \cdot P_2O_5$	–4916	–5013
$2CaO \cdot SiO_2$	–2444	–2480
$3CaO \cdot P_2O_5$	–5737	–5849
$2CaO \cdot P_2O_5$	–5018	–5119

uct of crystallization of the considered glasses is the magnesium silicate of Mg_2SiO_4 type. It should be noted that the observed product of crystallization does not result from the value of the Gibbs free enthalpy of the formation of silicates and phosphates from oxides (ΔG) which should determine the probability of their formation (Table 2). Chemical affinity is thus not the only parameter determining the type of the crystallizing phase.

In silicate-phosphate glasses containing increasing amount of Ca^{2+} ions, the chemical affinity of the calcium ions to the phosphorus ions which is greater than that of the magnesium ions (Table 2) causes that formation of the crystallization product in the form of Ca_2SiO_4, which can be influenced by factors of crystallochemical nature, occurs only after a definite value of CaO/SiO_2 has been exceeded.

MAS-NMR study

The effect of the changes in the chemical composition of silicate-phosphate glasses on the character of the spectra ^{31}P MAS NMR is shown in Fig. 2.

The spectra of glasses with a single modifier present in their composition in the form of K^+ ions are characterized by a single peak whose position indicates that phosphorus is present in the structure of these glasses as a monophosphate complex (PO_4^{3-}) – Q^0 [14]. In turn, the character of ^{31}P MAS NMR spectra of glasses, into the structure of which increased amounts of modifiers in the form of Mg^{2+} or Ca^{2+} ions have been introduced at the lost of Si^{4+} ions, suggests that they are a superposition of two peaks being evidence of two different surroundings of the phosphorus atoms in the glass structure. Analysis of the ^{31}P MAS NMR spectra after the deconvolution (Fig. 3) has shown two resonances with chemical shifts of positive and negative values. They are attributed to monophosphate complexes (PO_4^{3-}) and diphosphate complexes ($P_2O_7^{4-}$) respectively. It has been found that the positions of resonances attributed to monophosphate complexes do not change, whereas their relative amount increases with the increasing amount of Mg^{2+} or Ca^{2+} ions in the glass structure. In turn, the values of the chemical shifts of the diphosphate complexes are lowered and their relative amount in the structure of the examined glasses decreases. The mentioned evolution of the ^{31}P diphosphate chemical shifts with the increasing amounts of Mg^{2+} and Ca^{2+} ions in the glass structure can be taken as a result of screening effect of the Mg^{2+} and Ca^{2+} ions.

On the other hand, their increasing amount in the glass structure causes breaking of the chemical bonds of the oxygen bridges P–O–P occurring in the structure of diphosphate complexes and thereby the reduction of the degree of polymerization of the phosphate framework ($Q^1 \rightarrow Q^0$). The more ionic character of Ca–O bonds in comparison with Mg–O bonds seems to be responsible for the higher degree of depolymerization of the phosphate framework.

From the performed investigations it follows that the average number of non-bridging oxygens per SiO_4 tetrahedron (NBO/T), determined on the basis of the

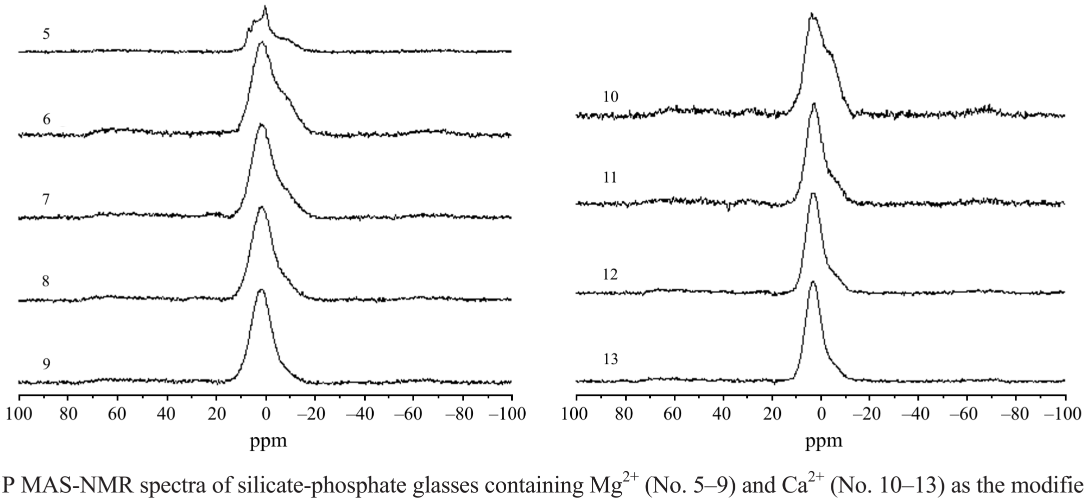

Fig. 2 ^{31}P MAS-NMR spectra of silicate-phosphate glasses containing Mg^{2+} (No. 5–9) and Ca^{2+} (No. 10–13) as the modifier cations

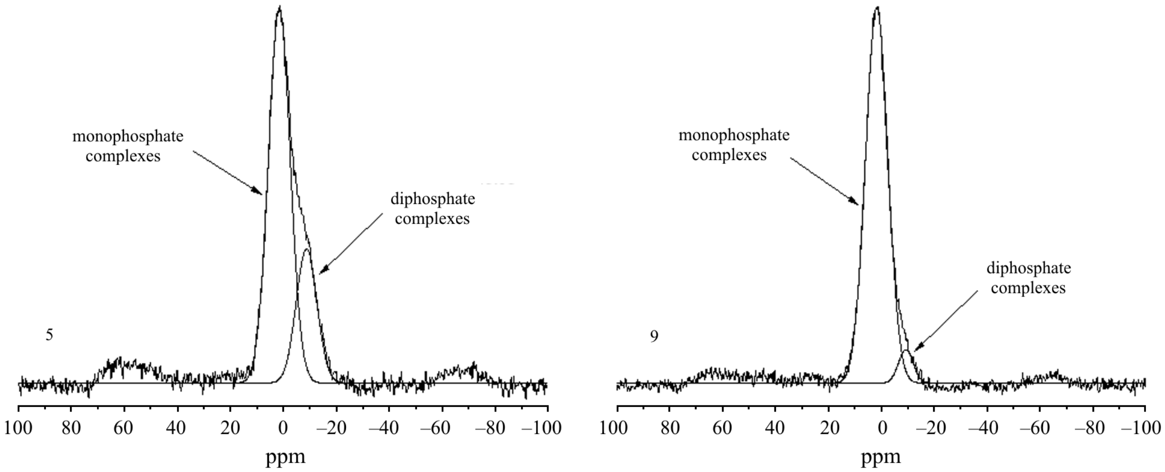

Fig. 3 ^{31}P MAS-NMR spectra of silicate-phosphate glasses containing MgO No. 5 (16 mol%) and No. 9 (41 mol%), after deconvolution process

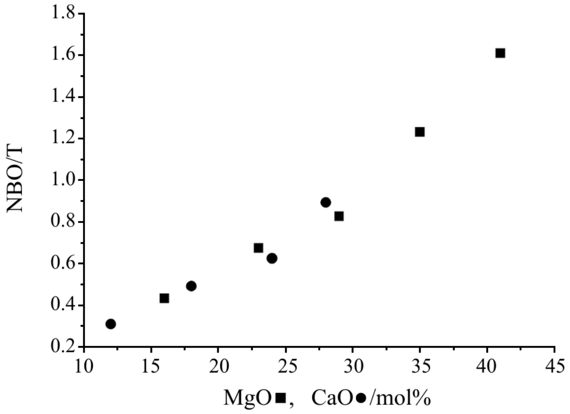

Fig. 4 The relation between NBO/T and the amount of MgO or CaO in the structure of silicate-phosphate glasses

molar proportions of mono- and diphosphate complexes [10], calculating from deconvolution of ^{31}P MAS-NMR spectra, being a measure of the degree of polymerization of the silicate framework, increases with the increase of the modifiers in the glass structure, and this increase is more distinct in case of increasing amount of CaO (Fig. 4). It has been found that the increase in the amount of Mg^{2+} and Ca^{2+} in the structure of examined glasses correlates with the increase of their density (Fig. 5).

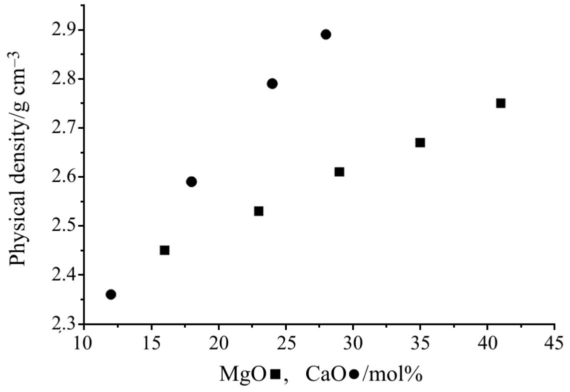

Fig. 5 The relation between physical density of glasses and the amount of MgO or CaO in their structure

Conclusions

The presence of increasing amounts of modifiers in the form of Mg^{2+} or Ca^{2+} cations in the structure of silicate-phosphate glasses causes the reduction of the degree of polymerization of their framework which brings about the increase of the glass density. At the same time the glass structure becomes more rigid which is manifested by the increase of T_g and Δc_p, as well as greater ability of the glasses to crystallize.

Acknowledgements

The authors want to express their thanks for help in MAS-NMR studies to PhD Zbigniew Olejniczak of The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Science, Krakow.

The work was supported by Grant 3 T0 8D 01427 of the Ministry of Science and Informatisation of Poland.

References

1 L. Stoch, I. Wacławska and A. Lis-Krzyścin, Chem. Agriculture, 2 (2001) 74.
2 I. Wacławska, M. Szumera and J. Ostrowska, Chem. Agriculture, 3 (2002) 303.
3 I. Wacławska, L. Stoch and J. Ostrowska, Ceramika/Ceramics, 57 (1998) 221.
4 M. Szumera, I. Wacławska, W. Mozgawa and M. Sitarz, J. Mol. Struct., 744–747 (2005) 609.
5 I. Wacławska and L. Stoch, J. Therm. Anal. Cal., 65 (2001) 141.

6 I. Wacławska and M. Szumera, J. Therm. Anal. Cal., 72 (2003) 1065.

7 G. Walter, J. Vogel, U. Hoppe and P. Hartmann, J. Non-Cryst. Solids, 296 (2001) 212.

8 F. Branda, A. Costantini, G. Luciani and G. Laudisiom, J. Therm. Anal. Cal., 64 (2001) 1017.

9 J. M. Oliveira and R. N. Correia, Proc. XVIII ICG in San Francisco, 1998, D-3.

10 M. W. G. Lockyer, D. Holland and R. Dupree, J. Non-Cryst. Solids, 188 (1995) 207.

11 L. Stoch, J. Therm Anal. Cal, 54 (1998) 9.

12 E. Görlich, The effective charges and the electronegativity, 1997, Polish Academy of Art. and Science, Krakow.

13 I. Barin and O. Kuache, Thermochemical properties of Inorganic Substances, 1973, Springer-Verlag.

14 H. Grussaute, L. Montagne, G. Palavit and J. L. Bernard, J. Non-Cryst. Solids, 263–264 (2000) 312.

DOI: 10.1007/s10973-005-7183-9