Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 1, 255–260

CRYSTALLIZATION OF SILICO-PHOSPHATE GLASSES

M. Sitarz[*] *and M. Szumera*

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, 30-059 Cracow, Al. Mickiewicza 30, Poland

Silico-phosphate glasses of $Ca_{3/2}PO_4$–SiO_2 and $NaCaPO_4$–SiO_2 systems have been the topic of our studies. Microscopic and EDX investigations which have been carried out have shown that liquation occurs only in the case of glasses belonging to the $NaCaPO_4$–SiO_2 system. Additionally, it has been found that there are significant differences in the chemical compositions of the matrix and the inclusions. Based on the spectroscopic investigations it has been shown that the glasses of both series are characterized by complex domain composition and the structure of domains is close to that of the corresponding crystalline phase.

Interpretation of the DTA results has been based on the knowledge of the texture and the structure of the materials studied. It has been found that liquation of the glasses is a multi-step process in which the matrix and the inclusions crystallize separately. Multi-step crystallization of the glasses belonging to the $NaCaPO_4$–SiO_2 system has been confirmed by the high temperature XRD investigations.

Keywords: *direct crystallization, glass-ceramics, MIR spectra, phospho-silicate materials*

Introduction

The glassy-crystalline materials obtained via direct crystallization from the glassy state are one of the most interesting ceramics materials [1]. Glassy-crystalline materials combine advantages of crystalline materials (mechanical strength) and those of amorphous ones (easy processing, controllable properties). Composition, but also structure and texture of the glass have decisive influence on the type and the properties of glassy-crystalline materials.

Design of the controlled crystallization process of silico-phosphate glasses in order to obtain glassy-crystalline biomaterials has been the main goal of the work.

Glassy phospho-silicate materials are well-known biomaterials [2, 3]. Bioactive glasses containing 55 mol% SiO_2, up to 50 mol% CaO and up to 40 mol% P_2O_5 have been patented by Hench under the trademark Bioglass® [4–7]. Various types of bioactive glasses containing such additives as e.g. K^+, Mg^{2+}, Al^{3+}, B^{3+} are known at present [8–10]. Silicate glasses are becoming frequently used as precursors of glassy-crystalline materials prepared by controlled crystallization [1]. Crystallization significantly lowers the bioactivity degree of glasses [11, 12]; it can also turn the bioactive glass into an inactive material. Therefore in order to obtain a material of complex texture and chemical composition it is important to perform crystallization in a controlled way. To design such process properly it is necessary to know the texture and structure of the glassy precursor. Our previous work has made it possible to establish by spectroscopic studies that in silicate glasses there exists ordering which significantly exceeds a single tetrahedron – domains [13]. The type of ordering may differ and it depends on chemical composition of glass. In the case of v-SiO_2 the domains show the structure of low temperature crystoballite [13, 14]. In the case of complex silico-phosphate glasses this may indicate the presence of submicroheterogeneity. Submicroheterogeneity may lead to macroscopic phenomenon of liquation [15, 16]. Liquation areas and submicroheterogeneity of the glass may be treated as ‘crystallization nuclei’ which show decisive impact on the crystallization process.

Experimental

Glasses belonging to $Ca_{3/2}PO_4$–SiO_2 and $NaCaPO_4$–SiO_2 systems whose composition are given in Table 1 have been selected for the studies. The composition was se-

Table 1 The composition of samples [mol%]

$NaCaPO_4$–SiO_2 system		$Ca_{3/2}PO_4$–SiO_2 system	
I	10% $NaCaPO_4$ 90% SiO_2	Ia	10% $Ca_{3/2}PO_4$ 90% SiO_2
II	20% $NaCaPO_4$ 80% SiO_2	IIa	20% $Ca_{3/2}PO_4$ 80% SiO_2
III	30% $NaCaPO_4$ 70% SiO_2	IIa	30% $Ca_{3/2}PO_4$ 70% SiO_2
IV	40% $NaCaPO_4$ 60% SiO_2	IVa	40% $Ca_{3/2}PO_4$ 60% SiO_2
V	50% $NaCaPO_4$ 50% SiO_2	Va	50% $Ca_{3/2}PO_4$ 50% SiO_2

---

[*] Author for correspondence: msitarz@agh.edu.pl

1388–6150/\$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

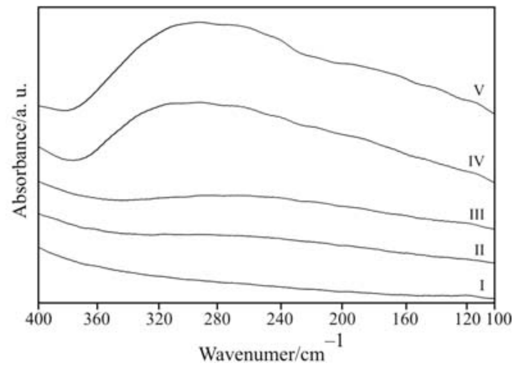

Fig. 1 FIR spectra of glassy samples from $NaCaPO_4$–SiO_2 system

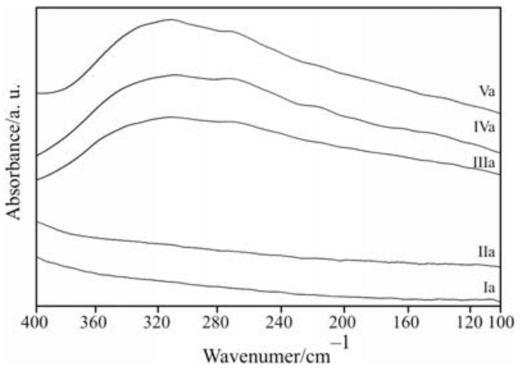

Fig. 2 FIR spectra of glassy samples from $Ca_{3/2}PO_4$–SiO_2 system

lected to compensate the negative charge of $[PO_4]^{3-}$ and $[SiO_4]^{4-}$ by Ca^{2+} cation or by couples of Na^+ and Ca^{2+} cations.

The standard sol-gel method [17] was selected to obtain the materials of the highest possible homogeneity. TEOS (SiO_2), $Ca(NO_3)_2{\cdot}4H_2O$ (CaO), $Na_3PO_4{\cdot}12H_2O$ (Na_2O) and H_3PO_4 (P_2O_5) were used to introduce particular oxides. All chemical used have been of analytical grade. The obtained gels were dried at room temperature (30 days) and then at the temperature of 60°C. After drying process all the gels were heated at 1380°C to obtain crystalline materials. To obtain the glassy samples the gels were melting in platinum crucible in the temperature 1730°C and rapidly cooled on the cast iron plate.

X-ray measurement of all samples were carried out using FPM Seifert XRD 7 with a step of 0.01° and collecting time –5 s.

EDX spectra were measured on a JEOL 5400 scanning microscope with microprobe analyser LINK ISIS (Oxford Instrument).

IR spectroscopic measurements (MIR – middle infrared and FIR – far infrared) of the resulting materials were made with a Bio-Rad FTS 60V spectrometer. MIR: transmission technique, samples as KBr pellets. Spectra were collected after 256 scans at 4 cm^{-1} resolution. FIR: polyethylene pellets. Spectra were collected after 2000 scans at 4 cm^{-1} resolution.

To study the thermal stability of glasses, differential thermal analysis measurements were made with Perkin Elmer DTA-7 system operating in heat flux DSC mode. The samples of glass (60 mg) placed in platinum crucibles and dry nitrogen atmosphere were heated at a rate of 10°C min^{-1}.

Results and discussion

In the first stage of the work glasses of the $Ca_{3/2}PO_4$–SiO_2 and $NaCaPO_4$–SiO_2 systems as precursors for glassy-crystalline materials have been prepared. Amorphous nature of the obtained materials has been confirmed by XRD and FIR studies. XRD patterns of all the samples contain exclusively the raised background typical of amorphous materials. In the FIR spectra (Figs 1 and 2) no intensive bands can be seen which unequivocally shows that the long-range order in the materials is lacking. All the prepared glasses have been untransparent which – with their confirmed amorphous nature – indicates occurrence of liquation.

Detailed microscopic studies have made it possible to conclude that liquation takes place only in the case of glasses belonging to the $NaCaPO_4$–SiO_2 system (Fig. 3). In the SEM images of these glasses distinct spherical inclusions in the matrix are visible. In the case of glasses belonging to $Ca_{3/2}PO_4$–SiO_2 system no inclusions can be seen. Lack of transparency of these glasses results from the presence of gas bubbles. EDX studies have shown that the inclusions are practically pure silico-calcium phase, whereas the matrix is enriched in sodium, calcium and phosphorus (Figs 4a and b). The results obtained for the samples of high SiO_2 content are particularly interesting (Fig. 3 II and III samples). In the case of these materials spherical inclusions are of nanometer size. XRD and FIR studies carried out have made it possible to establish that both, the inclusions and the matrix, are amorphous. Significant difference in the chemical composition of the matrix and the inclusions (Figs 4a and b) should cause – upon the appropriate thermal treatment – the crystallization of either the matrix or the inclusions (controlled crystallization).

As have been already stated, in order to prepare glassy-crystalline materials by controlled crystallization it is necessary to know both, texture and structure of the precursor glass. Detailed spectroscopic studies in the MIR range as well as NMR investigations of glassy materials belonging to the $NaCaPO_4$–SiO_2 system have made it possible to establish that they exhibit domain structure. It has been shown that the short range ordering in those materials is similar to that characteristic for the corresponding crystalline materials [15, 16]. Of course, MIR spectrum gives the

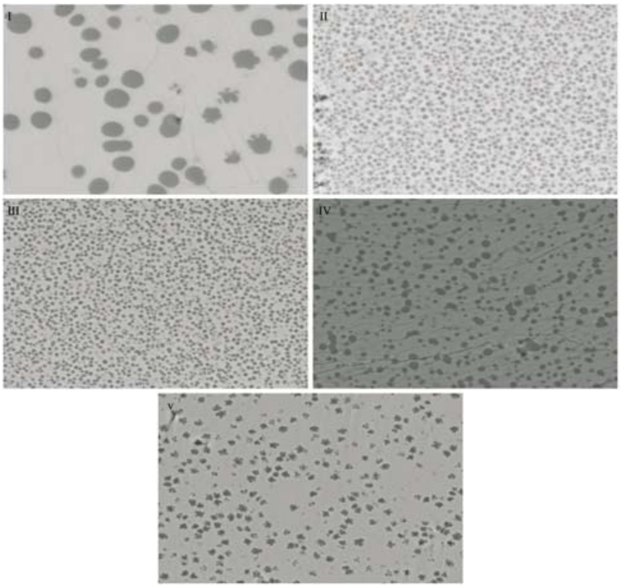

Fig. 3 SEM microphotograph of samples from $NaCaPO_4$–SiO_2 system

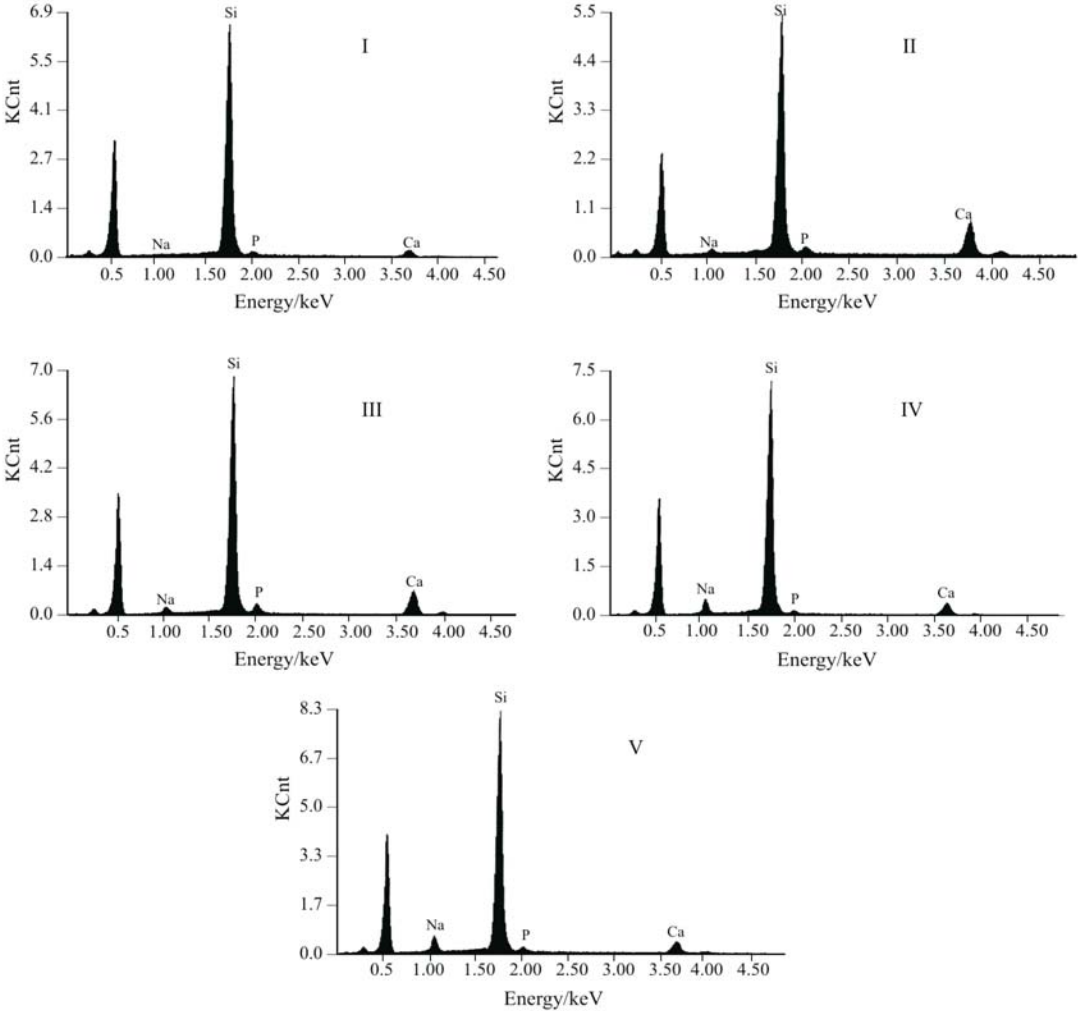

Fig. 4a EDX spectra of I–V samples (inclusions)

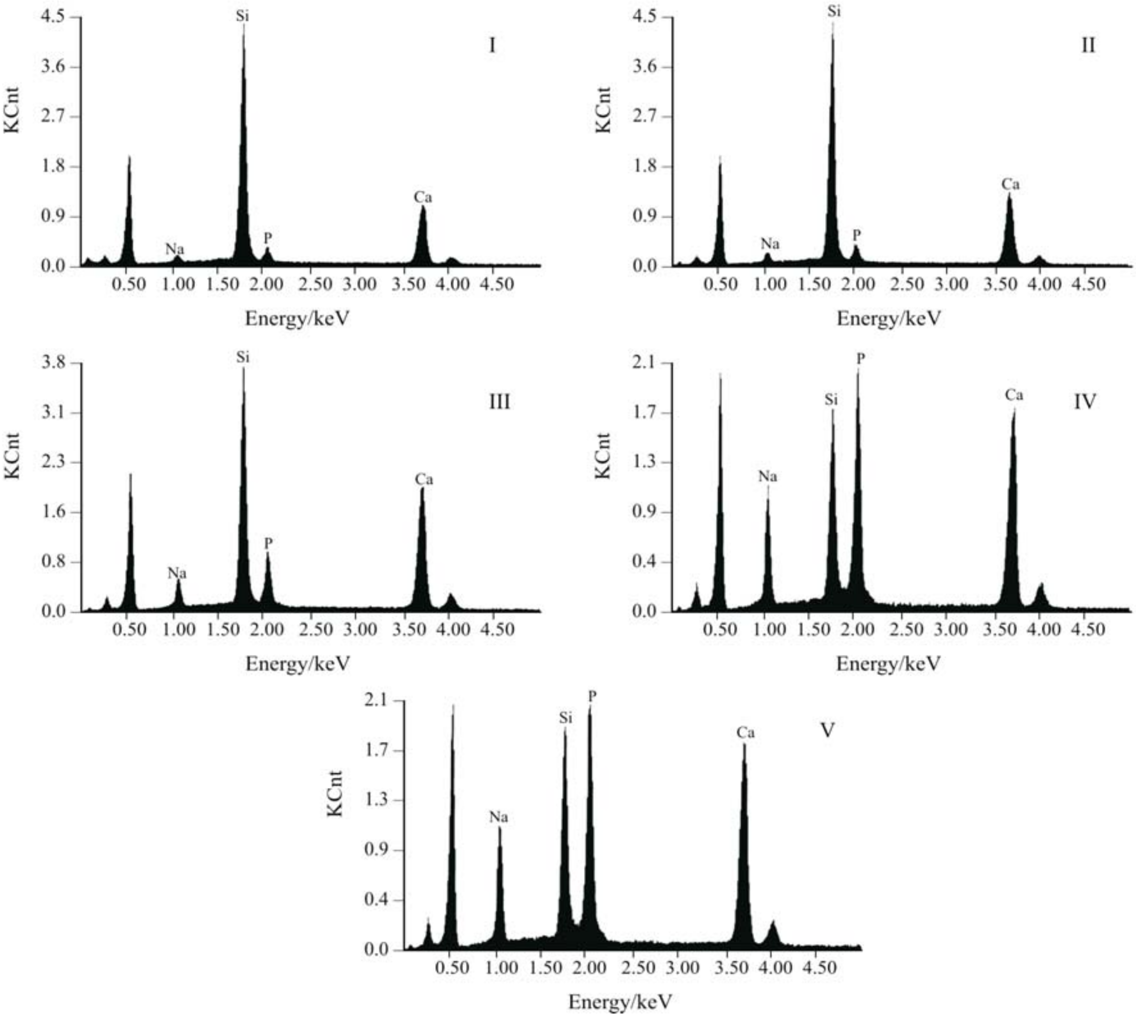

Fig. 4b EDX spectra of I–V samples (matrix)

average information on inclusions and the matrix. Due to nanometric size of inclusions it is not possible to carry out spectroscopic studies of the inclusion and the matrix separately. MIR studies combined with EDX results indicate, however, that the structure of inclusion domains is that typical of α-crystoballite, whereas the structure of matrix domains – silico-phosphate [15]. The $Ca_{3/2}PO_4$–SiO_2 system is less complex owing to lack of liquation. Figure 5 shows the MIR spectrum of the glasses belonging to this system as well as the v-SiO_2 spectrum. Based on the spectra similarities it is clear that the glasses which contain large amounts of SiO_2 (Ia and IIa) show–similarly to v-SiO_2 – structure of α-crystoballite. Shape of the spectra corresponding to the glass of low SiO_2 content (IIIa–Va) differs significantly from that due to amorphous silica. Significant shifts of the main bands towards lower wavenumbers as well as the appearance of several additional bands can be observed. It can be supposed that these glasses will show the domain structure similar to that of the respective phosphates and silicates – submicroheterogeneity. In the MIR

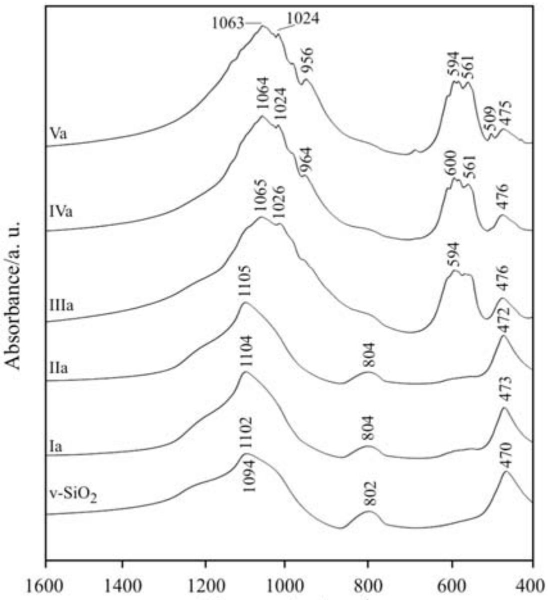

Fig. 5 MIR spectra of glassy samples from $Ca_{3/2}PO_4$–SiO_2 system

spectra – owing to the mixing of vibrations – it is difficult to differentiate between the bands due to $[SiO_4]^{4-}$ from those corresponding to $[PO_4]^{3-}$ tetrahedra. XRD investigations of crystalline materials have made it possible to establish that whitlockite – $Ca_3(PO_4)_2$ is the dominant phase for samples IIIa–Va. In the MIR spectrum corresponding to this phosphate the triplet in the range of 640–550 cm^{-1}, the bands at ca. 725 and 970 cm^{-1} as well as the group of bands at 1093–1030 cm^{-1} are most characteristic [18]. Analysis of the MIR spectra obtained for IIIa-Va samples makes it possible to distinguish the bands typical of whitlockite. Based on this it can be stated that the domain structure of glasses belonging to $Ca_{3/2}PO_4$–SiO_2 system containing the low amount of SiO_2 will be of whitlockite and α-crystoballite type.

In order to plan the controlled crystallization process it is necessary to determine the temperature values characteristic for the glassy state, in particular the devitrification temperature. For these studies glass II of the $NaCaPO_4$–SiO_2 system has been selected for which the existence of nanoliquation has been established as well as corresponding to its glass IIa of $Ca_{3/2}PO_4$–SiO_2 system. Figures 6 and 7 show DTA results for selected glasses. In the case of glass II (Fig. 6) two exothermic effects at 826 and 892°C are visible. They prove crystallization of the sample. Existence of the second exothermic effect can be connected either with the polymorphic transformation of the previously crystallized compound or with the appearance the additional crystalline phase. Liquation which has been previously established, makes it possible to suppose, however, that the existence of two exothermic effects can be connected with the crystallization of inclusions and the matrix occurring at various temperatures.

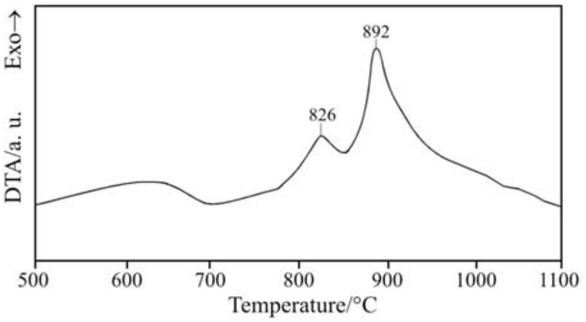

Fig. 6 DTA of II sample

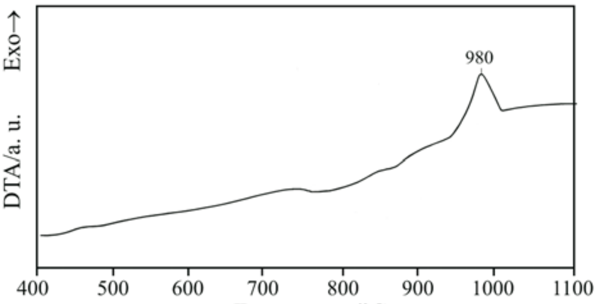

Fig. 7 DTA of IIa sample

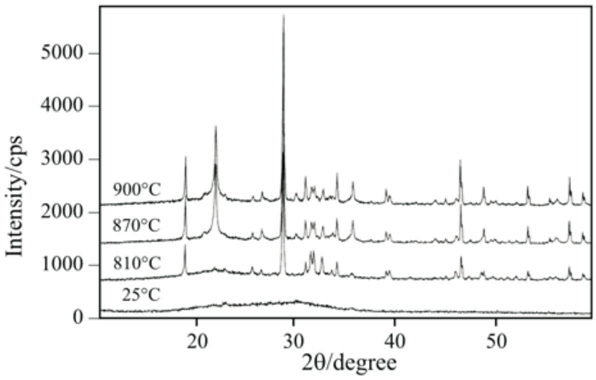

Fig. 8 X-ray diffraction patterns of sample II after heating

On the DTA curve of IIa (Fig. 7) glass only one exothermic effect at 980°C is visible. This indicates that simultaneous crystallization in the whole volume of the sample takes place.

Based on the DTA studies it can be concluded that controlled crystallization of glass II should be carried out at the temperature of 810 and 870°C. In order to establish the origin of two exothermic effects in situ XRD studies using high temperature camera have been carried out. Figure 8 shows the XRD patterns obtained after heating the glass at 810°C (heating time: 2 h), at 870°C (heating time: 2 h) and at 900°C (heating time: 2 h). As can be easily seen after heating of the sample at 870°C additional phase crystallizes; apart from the existing ones new peaks appear. Based on this it can be unequivocally concluded that the two DTA peaks result from crystallization of two different crystalline phases. After polymorphic crystallization the phase crystallizing at lower temperature should disappear.

Results of DTA and in situ XRD investigations make it possible to conclude that using appropriate thermal treatment crystallization of inclusions can be carried out in the controlled way while retaining the amorphous nature of the matrix (or vice versa). Therefore it can be hoped that glassy-crystalline materials (or nanomaterials) showing very interesting properties can be obtained.

Conclusions

- Microscopic and EDX investigations of glasses belonging to the $Ca_{3/2}PO_4$–SiO_2 and $NaCaPO_4$–SiO_2

systems have made it possible to conclude that only for the latter liquation occurs.

- Structural studies (MIR) of the obtained glasses have led to the determination of the domain structure type for the glasses belonging to the $Ca_{3/2}PO_4$–SiO_2 system. Domains of these glasses containing the high amount of SiO_2 exhibit the a-crystoballite type structure, whereas the glasses containing the low amount of SiO_2 – that of whitlockite and α-crystoballite.
- Analysis of DTA results has made it possible to establish that crystallization of the glasses belonging to $NaCaPO_4$–SiO_2 system is a multistep process. In contrast, crystallization of the glasses belonging to $Ca_{3/2}PO_4$–SiO_2 system occurs in one step.
- In situ XRD studies combined with high temperature cell have shown that crystallization of the matrix and inclusions for the glasses belonging to $NaCaPO_4$–SiO_2 system takes place at various temperatures.
- Crystallization of exclusively the matrix or exclusively the inclusions should be possible.

Acknowledgements

This work is supported by Ministry of Science and Higher Education under grant no. 3T 08D 033 27.

References

1 H. G. Kim and T. Komatsu, J. Mater. Sci. Lett., 17 (1988) 1198.
2 R. D. Rawlings, Clinical Mater., 14 (1993) 155.
3 P. Li, I. Kangasniemi, K. Groot, T. Kokubo and A. U. Yli-Urpo, J. Non-Cryst. Solids, 168 (1994) 281.
4 L. L Hench, R. J. Splinter, T. K. Greenlee and W. C. Allen, J. Biomedical Res. Symposium, 2 (1971) 117.
5 L. L Hench, R. J. Splinter, W. C. Allen and T. K. Greenlee, J. Biomed. Res., 5 (1972) 117.
6 L. L Hench and H. A. Paschall, J. Biomed. Res. Symposium, 4 (1973) 25.
7 G. Piotrowski, L. L Hench and W. C. Allen, J. Biomed. Res., 9 (1975) 47.
8 W. Vogel and W. Holand, J. Non-Cryst. Solids, 123 (1990) 349.
9 O. H. Anderson, J. Mater. Sci., 3 (1992) 326.
10 P. Li, I. Kangasniemi, K. Groot, T. Kokubo and A. U. Yli-Urpo, J. Non-Cryst. Solids, 168 (1994) 281.
11 O. Petil, G. Torre and L. L. Hench, J. Biol. Mater. Res., 30 (1996) 509.
12 P. Li, F. Zhang and T. Kokubo, J. Mater. Sci. Mater. Med., 3 (1992) 452.
13 M. Sitarz, W. Mozgawa and M. Handke, J. Mol. Struct., 511–512 (1999) 281.
14 E. Goerlich, Rev. Int. Htes Temp. Refract., 14 (1977) 201.
15 M. Sitarz, M. Rokita, M. Handke and E. Galuskin, J. Mol. Struct., 651–653 (2003) 489.
16 M. Sitarz, M. M. Handke Z. Fojud and S. Jurga, J. Mol. Struct., 744–747 (2005) 621.
17 M. Sitarz, W. Mozgawa, M. Rokita and M. Handke, Polish Ceramic Bull., 66 (2001) 232.
18 J. A. Gadsden, Infrared Spectra of Minerals and Related Inorganic Compounds, USA 1975.

Received: February 1, 2007
Accepted: April 4, 2007
OnlineFirst: July 11, 2007

DOI: 10.1007/s10973-007-8374-3