

THERMAL ANALYSIS AND THERMOCHEMISTRY OF VITREOUS INTO CRYSTALLINE STATE TRANSITION

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Abstract

Thermochemistry and structural mechanism of crystallization of MgO–Al₂O₃–SiO₂ glasses with TiO₂ as crystallization activator were studied. Thermal and HREM investigation proved that near the T_g temperature crystallization is going by rearrangement of glass structure elements and part of its components redistribution like at disorder – order phase transition in solid bodies. Nanocrystals of Mg-titanate and high quartz structure solid solution are formed then. Next enstatite and cordierite are crystallizing. Thermochemical and chemical bonds strength analysis indicate that during multi-stage crystallization of glasses, kind and order of crystal phase formation, is determined by the glass structure decomposition progress and its particular components release accompanying increase of temperature. It has been proved that molar heat capacity change (ΔC_p) accompanying the glass transition is the significant measure of degree of changes in the structure of glass preceding crystallization.

Keywords: glass, glass transformation, nanocrystallization, thermal analysis, thermochemistry,

Introduction

The effect of the solid structure as a medium of reaction on its course is particularly complex. In solids the atoms are firmly localized, and in crystalline solids they occupy definite positions in their crystal lattice. The possibility of displacement of the reactants atom is very limited, what is expressed by their coefficients of diffusion.

The specificity of the chemical processes of crystal phase formation inside the amorphous structure of glass as a reaction medium, at conditions of changing mobility of the reactants caused by viscosity with temperature change, are the subject of the paper. Glass crystallization near the vitreous state transformation temperature makes possible formation of nanocrystalline glass-ceramic materials of specific properties. As it was indicated earlier [1] this process belongs to glass structure reconstruction and chemical components redistribution processes. The interaction of thermochemical and structural factors accompanying them has been studied.

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Experimental

Magnesium aluminosilicate glasses of polymeric structure have been taken as the subject of the study. These glasses were modifications of a basic glass which was the glass used to obtain tough nanocrystalline glass-ceramics. It had the composition: SiO₂-47.1, Al₂O₃-22.0, MgO-16.9, ZnO-1.7 and TiO₂-12.3 mass% [2]. The structure of the glass consists of three-dimensional network, formed by joined [SiO₄] and [AlO₄] tetrahedra (glass formers) and Mg²⁺ as glass modifiers. TiO₂ was added as a glass crystallization activator. To determine the influence of the particular components on phase transformation, the main components have been partly substituted by about 5 mass% of P₂O₅ (SiO₂), ZnO (MgO) and ZrO₂ (TiO₂). Mg-aluminosilicate glasses and TiO₂ crystallization activator are of common use in glass-ceramics technology and study of the mechanism their crystallization has a wider sense.

Thermal phase transitions in glasses were investigated on samples grained to 0.1 – 0.3 mm by the differential scanning calorimetry (DSC) and differential thermal analysis (DTA) methods (Perkin Elmer apparatus) at the heating rate 10°C min⁻¹.

The phase composition of crystallized glass was investigated using X-ray diffraction (XRD), DRON-1.5 apparatus and scanning electron microscopy (SEM) Philips XL30 with Oxford Instruments energy dispersive spectroscopy (EDS) system, as well as the transmission electron microscopy (TEM) and analytical electron microscopy (AEM), CM30 Ultra TWIN and CM20 TWIN with energy dispersive X-ray (EDAX) Phoenix system, respectively. Thin foils were prepared by dimpling followed by ion milling. SEM and TEM studies were carried out at the Institute of Metallurgy and Material Science of the Polish Academy of Science, Cracow. The early stages of crystallization were investigated using High Resolution Electron Microscopy (HREM) at the Eidgenössische Technische Hochschule in Zurich and at the Silesian University in Katowice.

Results and discussion

Vitreous state transformation

DTA and DSC curves enable to determine the vitreous state transformation (glass transition) temperature (T_g), the crystallization temperature (T_c) and the glass melting temperature (T_m) as well as accompanying them thermal effects. They are sensitive to the changes in the chemical composition of the glass [3] as well as mode of its formation, melting or sol-gel process. Thermal properties and composition of the examined glasses as shown in Table 1.

In the course of cooling or heating the glass demonstrates the phenomenon of a jump-like change of the molar heat C_p (second derivative of free enthalpy ΔG function), similarly as in the phase transitions of the II-nd order according to Ehrenfest's thermodynamic classification [3]. The molar volume and some other physical properties of glass show similar changes. It is an external expression of the transition of the glass structure from the state of a rigid solid body into the viscoelastic state,

Table 1 Influence of chemical components substitution on ΔC_p value

Glass	Glass composition/mass%	$T_g/^\circ\text{C}$	$\Delta C_p/\text{J g}^{-1} \text{K}^{-1}$	$\Delta C_p T_g^{-1}/\text{J g}^{-1} \text{K}^{-2}/10^3$	$T_c=T_g/^\circ\text{C}$
G-O	47SiO ₂ 22Al ₂ O ₃ 17MgO 2ZnO 12TiO ₂	744	1.095	1.074	108
G-ZnO	47SiO ₂ 10Al ₂ O ₃ 22MgO 8ZnO 12TiO ₂	688	0.948	0.986	85
G-P ₂ O ₅	45SiO ₂ 5P ₂ O ₅ 21Al ₂ O ₃ 16MgO 2ZnO 12TiO ₂	723	0.745	0.748	95
G-ZrO ₂	51SiO ₂ 24Al ₂ O ₃ 18MgO 2ZnO 5ZrO ₂	784	1.210	1.145	130

what is the essence of glassy state transition. The temperature of this transition (T_g) is measured on the DSC curves at half of the ΔC_p step. It corresponds to the glass viscosity $10^{13.3} \text{dPa s}^{-1}$. The transition is induced by the relaxation of stresses, occurring in the disordered structure, through breaking of some of the chemical bonds. This process proceeds with temperature increase and its effect is the diminishing of the viscosity of glass. When the viscosity drops to $10^6\text{--}10^2 \text{dPa s}^{-1}$ the glass attains the ability of viscous deformation with oriented flow of preserved structural units. The dimensions of the units diminish with temperature and a corresponding parabolic decrease of viscosity takes place.

The structural changes in glasses induced by temperature increase correlate with the increase of the configuration entropy of glass (ΔS_{conf}) which can be expressed by the equation:

$$\Delta S_{\text{conf}} = \Delta S_{T_g} + \int_{T_g}^{T_m} \frac{\Delta C_p}{T} dT \quad \Delta S_0 \approx \Delta S_{T_g}$$

At the temperature 0°K the glass entropy is greater than zero and it has a value close to the entropy at the point T_g , when the primary structure of the melt becomes frozen as a result of its vitrification [5].

As it has been noticed earlier [6], the change in the value of C_p accompanying the glassy state transition (ΔC_p), determined from the DSC curves, is related with the degree of the rearrangement of the glass structure connected with this transition. It differs, among others, depending on the type of the modifiers and the resulting strength of their bonds with the components of the glass network. This is the subject of separate paper [7].

The oxide glasses obey the Kautzman principle that $T_g/T_m = 2/3$, while in metallic glasses this ratio is like $1/2$ [5]. This suggests also the influence of the nature of the chemical bonds on the vitreous state transformation, since it is connected with breaking some of the bonds and/or the displacement of atoms for the relaxation of structural strains.

The value of ΔC_p or $\Delta C_p/T_g$ determined from the DSC curves may be regarded as an indicator of the degree of the increase of configuration entropy, induced by changes in the structure accompanying the glass transition, as well as a measure of

Table 2 Formation of different stages of heating at various temperatures during 4 h

Temperature/ $^\circ\text{C}$	Glass crystallization stages
753	T_g –glass transition
725–825	$\text{MgTi}_2\text{O}_5 - \text{Al}_2\text{TiO}_5$ (s. s.) $\text{SiO}_2 - (\text{Al}, \text{Mg})$ (s. s.)
820–950	$\text{MgAl}_2\text{Si}_3\text{O}_{10} - \text{MgAl}_2\text{Si}_8\text{O}_{20}$ (s. s.), (<i>Mg-petalite</i>)
900–1100	MgSiO_3 (<i>enstatite</i>), Mg_2SiO_4 (<i>forsterite</i>)
1100–1200	$\text{Mg}_2\text{Al}_3 [\text{AlSi}_5\text{O}_{18}]$ (<i>cordierite</i>), Mg_2SiO_4 (<i>forsterite</i>)

the extent of these changes. The data presented in Table 1 and DTA curves (Fig. 1) show that this value is sensitive on relatively small changes in the chemical composition of the glass both in the network and among the modifiers, as well as to the type of the applied activator of crystallization. It is worth of notice that increase of ΔC_p value correlates with T_g and T_c temperature increase (Fig. 1, Table 1). It means that in this case the greater energetic impute is necessary. It confirms the ΔC_p of the glass transition as a significant measure of degree of changes in the structure of glass, preceding its crystallization.

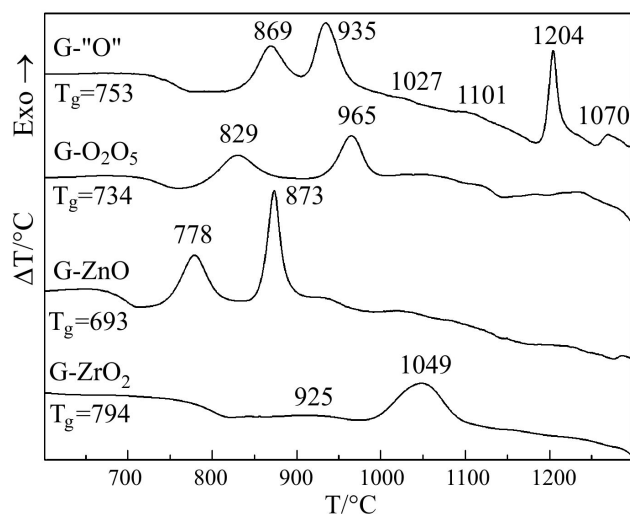


Fig. 1 DTA curves of glasses

Crystallization

The chemical composition of the examined glasses as regards the proportions of the content of the main components is to be found in the system of phase equilibria $MgO-Al_2O_3-SiO_2$ in the area of the primary crystallization of cordierite. It is situated near the triple point of cordierite – forsterite – enstatite co-crystallization. In equilibrium conditions these three phases should be the only products of crystallization of melted glass. However, when crystallization occurs during of heating the glass in a solidified state it takes a quite different course. Crystallization begins near the glass transition temperature. Solid solutions (s.s.) of varying composition are then formed. Through rearrangement of their structure combined with redistribution of the components the cordierite or its polymorphic modification: indialite is formed. The succession of the formation of these phases as a result of heating the glass samples at various temperatures during 4 h is shown in Table 2.

Crystallization at T_g begins with the formation of the Mg, Al-titanates s. s. Their crystals are formed by rearrangement of the components within the structure of the parent glass and their ordering into a crystal lattice. Prismatic shape of these crystals notice-

able from the very beginning of the process (Fig. 2a). The broadened boundary of diffusive character between the newly formed crystal lattice and the surrounding glass makes it coherent. This reduces the energetic barrier between them, which exists when crystallization occurs in a liquid in accordance with the standard nucleation – growth mechanism when the inter-phase boundary is sharp and incoherent. Coherent interphase makes the low temperature crystallization of glass possible.

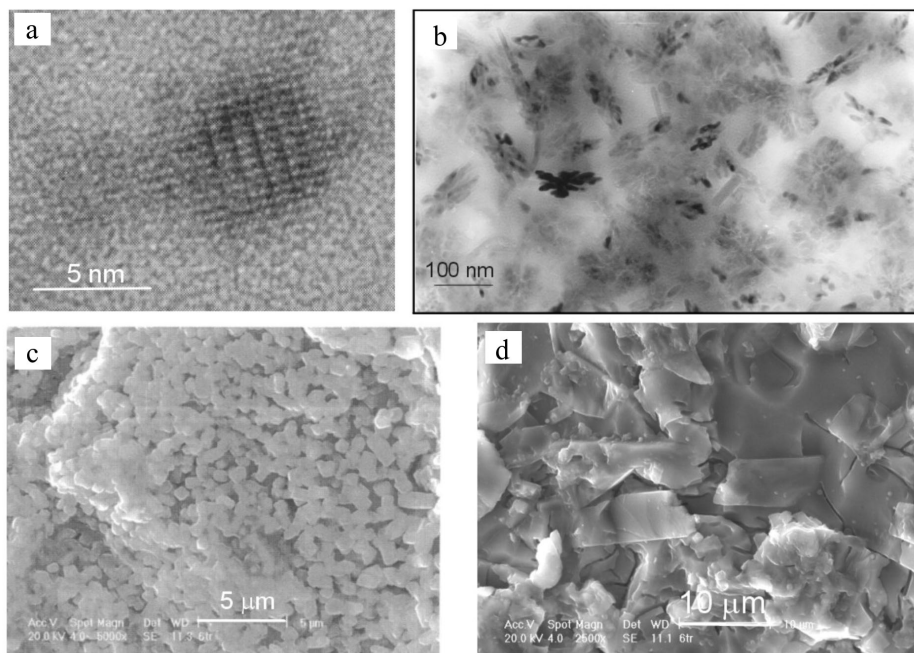


Fig. 2 Electron microscopy pictures of glass G – O samples heated for 4 h at different temperatures, a – HREM of sample heated at 725°C, b – TEM sample heated at 825°C, c – SEM of sample heated at 820°C, d – SEM of sample heated at 920°C

The possibility of glass crystallization by way of a rearrangement of its structure according to the model of phase transition in solid bodies of the disorder-order type has been reported in [8]. The present HREM investigations have confirmed this statement. Up to now it has been believed that TiO_2 acts as a nucleator of glass crystallization by inducing segregation of the components and their separation into two glasses (spinodal decomposition). The glassy phase, rich in TiO_2 , appears, and surface of its droplets plays the role of the nucleator of bulk crystallization of the main phase corresponding to the glass composition [1].

As it is shown in Fig. 2b, the titanate crystals (black) while growing take the form of star-shaped dendrites, around which the silicate phase (gray) is crystallizing. Results of XRD investigations indicate that it is a solid solution of high-quartz

structure which contains Al^{3+} substitutions replacing Si^{4+} as well as Mg^{2+} inside the silico-oxygen rings. It is a magnesium aluminosilicate equivalent of petalite ($\text{Li}[\text{AlSi}_4\text{O}_{10}]$) and it crystallizes only in artificial conditions, from the amorphous phase. Its crystals attained nanometric dimensions (20–100 nm).

At the temperature of about 820°C there begins the growth of the newly formed crystals, taking the prismatic form measuring about $1\ \mu\text{m}$ (Fig. 2c). It is accompanied by the exothermic effect at about 869°C . The exothermic peak at 935°C corresponds to recrystallization of the earlier formed phases and the formation of enstatite, forsterite and the beginning of the formation of cordierite. The crystals increase their dimensions to $20\ \mu\text{m}$ and more (Fig. 2d). The successive exchange of crystal phase and glass composition and transition into cordierite takes place above 1100°C (DTA peak at 1204°C). Introducing of 5 mass% P_2O_5 into the glass network reduces the temperature of the first crystallization stage. A similar effect is observed when ZnO is introduced, however then willemsite (Zn_2SiO_4) is formed in place of enstatite. This is due to the weakening of the silicate framework (P_2O_5) and a weaker bond between ZnO and silicate framework in comparison with MgO . Replacement of the crystallization activator TiO_2 by ZrO_2 makes the temperature of the beginning of crystallization move upwards, the stage of the formation of intermediate phases through rearrangement of the structure is overleaped and cordierite is formed. Zr crystallizes in the form of ZrO_2 in spite of silicate surroundings and only later ZrSiO_4 is formed from it. DTA studies supported TEM and SEM investigations allowed to establish that the optimal materials to obtain nanocrystalline glass-ceramics, besides the basic glass, are glasses with ZnO and P_2O_5 additions.

Factors determining vitreous into crystalline state transition

In the case of crystallization of glass in the state of a liquid of small viscosity, the course of the formation of the crystalline phases is determined by the concentration of the components and the free enthalpy of compounds synthesis ΔG_r which, expressing the tendency of the system to attain the minimum of energy, shows the probability of formation of a particular crystal phase. This function expresses simultaneously the force of chemical interactions between the components, defined in the classical chemistry as chemical affinity. According to Prigogine [9] ΔG_r of reaction is a thermodynamic measure of the substrates affinity.

Results of the investigations presented above indicate that in the case of crystallization in the T_g temperature range when structure of the parent glass is preserved and crystals are formed by rebuilding this structure, it is necessary to consider additionally the influence of factors of structural nature. They are the character and the strength of bonds between oxygen and the network forming cations on the one hand, and bond of the same oxygen atoms and the cations modifiers on the other hand. It can be assumed that in the silicate glass similarly to the structure of silicates crystals, the oxygen atoms like bridges combine the network and the out of network components into a joint spatial network.

A simple parameter defining the character and the strength of the chemical cations-oxygen bonds is the ionicity of these bonds. The ionicity commonly used is calculated from Pauling's electronegativity. In the present study, however, Görlich's ionicity has been used [10]. The values both of these ionicity scales well correlate [1]. The difference in ionicity of the cation – oxygen bonds forming a bridge determines the local chemical affinity of these cations to the bridging oxygen, and at the same time acid-base interactions between bridge forming ions.

The oxygen atoms in the glasses behave as Lewis' bases and transfer part of their negative charge to the cations [1, 10]. The ability of oxygen to transfer the negative charges is the greatest, when it is situated in the surroundings of weak cations such as the alkalis. When oxygen forms bonds with strong cation, as Si^{4+} in the $[\text{SiO}_4]$ or other network – former tetrahedra, its ionicity is much lower, it is supposed to be acidic component of glass, and the possibility of transferring part of the charge to the metal cation is also smaller than in case of weak cations forming bonds of high ionicity, like alkalis. The acid-base interactions determine also the mutual chemical affinity between the components, which is the greater, the more they differ in their ionicity.

In the case of the examined glass there is no correlation between the succession of crystallization of the particular phases and ΔG_r for reaction of their synthesis from the oxides. This is illustrated by the values of free enthalpy for reaction of the synthesis from oxides compounds which can crystallize in examined glasses at 1200 K (ΔG_{r1200K} kJ mol⁻¹) basing on the available thermodynamic data [11]. They form the following series:

MgTi_2O_5 (-21.67)- $\text{SiO}_2(\text{Al, Mg})$ s.s. (not known) - MgSiO_3 (-44.25) - Mg_2SiO_4 (-60.25)- $\text{Mg}_2\text{Al}_3[\text{AlSi}_5\text{O}_{18}]$ (-18.00).

This means that the succession of crystallization in the examined glass occurs revers to the assumed direction, i.e. starting from the synthesis of Mg-titanate which has the smallest negative value ΔG_{r1200K} . Similar regularity has been observed already earlier in the case of silicate-phosphate glasses [6].

As the indicator of the energy of binding extra-network cations (modifiers, activators) with the silica network there have been used ΔG_r value of the reaction of synthesis of the selected silicate compounds divided by the amount of SiO_2 molecules in their chemical formula ($\Delta G_{r1200K}/\text{SiO}_2$). To characterize the interactions between the atoms of acid-base nature in the silicates and at the same time the chemical affinity to the oxygen modifier and the network Si, forming the oxygen bridge, there has been proposed ionicity factor of compound (i_{comp}). It is equal difference of ionicity of the O–Si bond, multiplied by number of Si atoms in chemical formula of the compound, minus sum of ionicity of out of network cations with oxygen bonds (O–Me) divided by the sum of valence of these cations. In this factor nominative as a difference of ionicity of acidic component of the compound (silica network) and basic component (out of network cations) ionicity is an indicator of basicity of the compound. It is related to the number of Me–O–Si bridges which is equal to the sum of cations valency. The obtained values are listed in Table 3. Both these parameters show a convergent tendency to diminishing of their values. The

$\Delta G_{r1200K}/\text{SiO}_2$ values can be used as a measure of stability of bonds, joining the cations and silicate network. They correspond well the i_{comp} based on the ionicity which is a crystal-chemical parameter.

It can be assumed that chemical interactions of components in crystalline silicates and in glasses are the same. They differ only in the order of the distribution in their internal structure. Even so, on the basis of data in Table 3 one can conclude, that at stage of crystallization near T_g , the first which are formed are the compounds of components most weakly connected with the silicate network, i.e. the activators of crystallization (TiO_2 , ZrO_2). Bridges Ti–O–Si and Zr–O–Si has much lower value of ionicity (0.013 and 0.073) as compare with Mg–O–Si (0.240). Only at higher temperatures, when the glass structure is sufficiently depolymerized, the magnesium silicates are formed. Lack of data on the value ΔG_r of the formation of a solid solution SiO_2 (Mg, Al) does not allow to estimate its position in the postulated series. Electron microscope observations suggest that it is formed through rearrangement of the glass network and a small displacements of its components, thus similarly as the Mg, Al titanates formation, and is going almost simultaneously with them. The magnesium silicates probably occur as a result of a decomposition of a high quartz solid solution.

Table 3 Parameters characterizing chemical bonds between cations and silica framework in structure of silicates

Silicate	$\Delta G_{r1200K}/\text{SiO}_2$ kJ mol ⁻¹	i_{comp}
Polymeric silica framework		
K_2SiO_3	-251.97	0.609
Na_2SiO_3	-235.72	0.593
$\text{K}_2\text{Si}_2\text{O}_5$	-195.60	0.395
$\text{Na}_2\text{Si}_2\text{O}_5$	-119.47	0.379
CaSiO_3	-90.36	0.140
MgSiO_3	-44.25	0.121
PbSiO_3	-20.46	0.121
Separated $[\text{SiO}_4]$ tetrahedra		
MgSiO_4	-61.76	0.228
Zn_2SiO_4	-27.84	0.212
$\text{Al}_6\text{Si}_3\text{O}_{12}$	-6.24	0.130
ZrSiO_4	-4.05	0.018

Conclusions

The presented results indicate that crystallization of Mg – aluminosilicate glass activated with TiO_2 admixture, at its low temperature, near T_g stage, has

intrastructural character. Its order is determined by the decomposition of the glass structure accompanying the temperature increase. Components of less stable chemical bonds with silica network, like TiO_2 form crystal phases first. The result is a multi-stage crystallization in which the components participate successively when their bonds with the network are broken and the depolymerization of the silicate network itself is in progress. For this reason introduction of components weakening the structure of glass (P_2O_5 , ZnO) reduce the crystallization temperature. Cordierite, compound containing all the main glass components and has a complex ring-shaped structure, is not formed until at the highest temperature when the decomposition of the primary glass structure is fairly advanced and the degree of the release of its components is the highest.

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