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THERMAL METHODS APPLIED TO THE GLASS TRANSITION OF MIXED NETWORK $AlPO_4$–BPO_4–SiO_2 GLASSES

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Abstract

Glass transition effect of mixed network $AlPO_4$–BPO_4–SiO_2 glasses was studied. DTA/DSC and TMA measurements has been applied in the research. It has been found that glass transition effect has structurally sensitive properties. Glass transition temperature T_g, changes of specific heat (Δc_p) and thermal expansion coefficient (α) accompanying the process depend on the nature and the number of components forming the glassy framework. Character of chemical bonds combining them into the glass structure has an influence on the glass transition effect. Its course is dependent on the flexibility of the structure of glasses.

Keywords: DTA/DSC/TMA, glass transition, structure flexibility, structural relaxation

Introduction

During cooling and heating, glasses exhibit the structural strain relaxation phenomenon termed the glass transition effect. These strains result from the disordered structure of the glass and the random arrangements of the glass structure elements. Relaxation of strains in the glass structure at the transition temperature is connected with a sudden change of its properties, such as specific heat, expansion coefficient and viscosity from crystal-like to liquid-like values. The glass transition temperature (T_g) and the changes in glass properties with temperature that accompany this transition depend on the kind of glass and also, to a considerable degree, on its history and especially the rate of cooling of the melt. Glass transition effect is manifested by an endothermal reversible deflection in the DTA/DSC curves, illustrating jump-like changes in the specific heat (Δc_p).

The present study discusses the glass transition effect occurring in glasses from the $AlPO_4$–BPO_4–SiO_2 system. The influence of Na_2O and CaO on the glassy state in mixed network $AlPO_4$–BPO_4–SiO_2 glasses is determined.

The term ‘mixed network glasses’ is used when referring to glasses, the network of which is made of two or more different components or when a component is incorporated into the network in the form of various coordination polyhedra or as differently built molecules.

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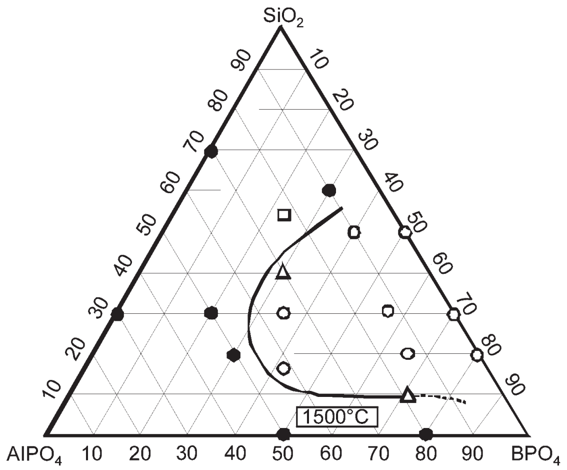

Fig. 1 Glass forming area of $AlPO_4$–BPO_4–SiO_2 system. o – glass, Δ – glass with beginning of crystallization, □ – glass with crytallization, ● – no glass

In the network of the examined glasses, $AlPO_4$ and BPO_4 form pairs of the tetrahedra $[AlPO_4]$ $[PO_4]$ and $[BO_4]$ $[PO_4]$, which geometrically correspond to the pairs $[SiO_4]$ $[SiO_4]$. $[AlPO_4]$ tetrahedra are easily incorporated into the network of silicates of crystalline structure and they substitute the anions $[SiO_4]^{4-}$ in the amount up to 50% of their fraction. They occur also in the glass framework (alumino-silicate glasses). SiO_2 and BPO_4 form solid solutions. SiO_2 in the form of a cristobalite accepts up to 10 mole% of BPO_4, while the structure of BPO_4 may accept 15 mole% of SiO_2 (Fig. 1).

Experimental

Materials

Glasses were melted in alumina crucibles from 100 g batches in the temperature range of 1400–1500°C. The melt was poured out on a steel plate to be glassified. Chemical pure components: $AlPO_4$, BPO_4, SiO_2, Na_2CO_3 and $CaCO_3$ were used to obtain the glass.

Methods

Thermal measurements were made with a Perkin Elmer DTA-7 apparatus with both DTA and DSC modes of operation. The temperature and heat calibrations of the instrument were performed using the melting temperature and melting enthalpy of high purity aluminium and gold. The samples of glasses (50 mg) placed in platinum crucibles and in dry nitrogen atmosphere were first heated at a rate of 10°C min^{-1} from room temperature to temperature ~50°C above the glass transition effect where they

Table 1 Thermal characteristics of glass transition effect of $AlPO_4$–BPO_4–SiO_2 glasses

Glass No.	Chemical composition of glass/mole%	Mole ratio	Temperature range of transformation $\Delta T=T_2-T_1$/°C	T_g/°C	Δc_p/ J g^{-1} °C^{-1}	α/°C^{-1}
1	$70BPO_4$–$30SiO_2$	$SiO_2/P_2O_5=0.21$	6	767	0.229	
2	$15AlPO_4$–$55BPO_4$–$30SiO_2$	$SiO_2/P_2O_5=0.21$ $Al_2O_3/B_2O_3=0.5$	30	678	0.322	$\alpha_{150}^{550}=42.7\cdot10^{-7}$
3	$35AlPO_4$–$35BPO_4$–$30SiO_2$	$SiO_2/P_2O_5=0.21$ $Al_2O_3/B_2O_3=2.0$	32	670	0.416	$\alpha_{150}^{550}=63.89\cdot10^{-7}$
4	$10AlPO_4$–$40BPO_4$–$50SiO_2$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	7	710	0.054	$\alpha_{50}^{450}=57.67\cdot10^{-7}$
5	$20AlPO_4$–$30BPO_4$–$50SiO_2$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.33$	13	707	0.086	

Table 2 Thermal characteristics of glass transition effect of $AlPO_4$–BPO_4–SiO_2 glasses with sodium

Glass No.	Chemical composition of glass/mole%	Mole ratio	Temperature range of transformation $\Delta T=T_2-T_1$/°C	T_g/°C	Δc_p/ J g^{-1} °C^{-1}	α/°C^{-1}
4	$10AlPO_4$–$40BPO_4$–$50SiO_2$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	7	710	0.00054	$\alpha_{50}^{450}=57.67\cdot10^{-7}$
6	$9AlPO_4$–$36BPO_4$–$45SiO_2$–$10Na_2O$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	18	566	0.334	$\alpha_{50}^{350}=73.49\cdot10^{-7}$
7	$8AlPO_4$–$30BPO_4$–$39SiO_2$–$23Na_2O$	$SiO_2/P2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	17	466	0.531	
5	$20AlPO_4$–$30BPO_4$–$50SiO_2$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.33$	13	707	0.086	
8	$18AlPO_4$–$27BPO_4$–$45SiO_2$–$10Na_2O$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.33$	15	556	0.212	$\alpha_{50}^{350}=66.23\cdot10^{-7}$
9	$15AlPO_4$–$23BPO_4$–$39SiO_2$–$23Na_2O$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.33$	15	462	0.430	$\alpha_{50}^{350}=79.37\cdot10^{-7}$
10	$20AlPO_4$–$20BPO_4$–$40SiO_2$–$20Na_2O$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.5$	16	476	0.381	
11	$25AlPO_4$–$25BPO_4$–$30SiO_2$–$20Na_2O$	$SiO_2/P_2O_5=0.3$ $Al_2O_3/B_2O_3=0.5$	20	478	0.538	

Table 3 Thermal characteristics of glass transition effect of $AlPO_4$–BPO_4–SiO_2 glasses with calcium

Glass No.	Chemical composition of glass/mole%	Mole ratio	Temperature range of transformation $\Delta T=T_2-T_1$/°C	T_g/°C	Δc_p/ J g^{-1} °C^{-1}	α/°C^{-1}
4	$10AlPO_4$–$40BPO_4$–$50SiO_2$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	7	710	0.054	$\alpha_{50}^{450}=57.67\cdot10^{-7}$
12	$9AlPO_4$–$36BPO_4$–$45SiO_2$–$10CaO$	$SiO_2/P_2O_5=0.5$ $Al_2O_3/B_2O_3=0.125$	22	631	0.228	$\alpha_{50}^{350}=61.64\cdot10^{-7}$

were both in structural and thermal equilibrium. The samples were then cooled through T_g to room temperature at a rate of 10°C min^{-1} and then reheated at a constant rate of 10°C min^{-1} through the glass transition region. The glass transition temperature T_g was determined from the inflection point in the rapidly rising part of the reheated enthalpy curve and the jump-like changes of the specific heat Δc_p accompanying the glass transition were calculated using the 7 Series/Unix Thermal Analysis Software Library.

Perkin Elmer TMA-7 apparatus was applied to determine the thermal expansion coefficient in glasses. Distressed glass samples, (8×8×8 mm), having the form of rectangular prisms and with their bases parallel to each other, were heated in argon atmosphere at a rate 10°C min^{-1}, applying the pressure force of 50 mN. Basing on the plot of changes of the sample linear dimensions as a function of temperature and using the 7 Series/Unix Thermal Analysis Software Library the coefficient of linear thermal expansion of the glasses has been determined.

Results and discussion

Glasses of mixed network from $AlPO_4$–BPO_4–SiO_2 system show the glass transition effect, clearly visible on the DSC curves (Fig. 2). Its temperature and the magnitude measured by the jump-like change of specific heat depend on the nature and the num-

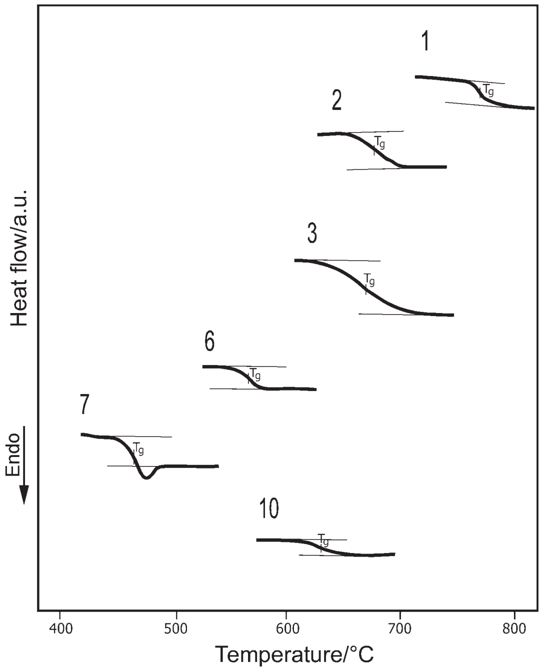

Fig. 2 DSC curves of the transition of the mixed network $AlPO_4$–BPO_4–SiO_2 structures 1–3, 6, 7, 10 – numbers of glass (Tables 1–3)

ber of the components forming the glassy framework. Two-component glass in the system BPO_4–SiO_2 (glass 1, Table 1) is characterised by the transformation temperature >700°C and a change in the specific heat of the order 0.2 J g^{-1} °C^{-1}. Introduction of aluminium into the structure of glass from the BPO_4–SiO_2 system (glasses 2–5, Table 1) causes broadening of the temperature range of transformation, decrease of the characteristic temperature T_g and increase of the linear thermal expansion coefficient α, on the other hand, transformation of the glassy state of such glassses is accompanied by greater changes in the specific heat. Such behaviour of glasses from $AlPO_4$–BPO_4–SiO_2 system is the indication of a higher degree of relaxation of their structure in comparison with the relaxation occurring in glasses from the BPO_4–SiO_2 system. The increase in the number of $[AlO_4]$ tetrahedra in the structure of such glasses at the lost of $[BO_4]$ tetrahedra, at the same ratio of the amount of SiO_2/P_2O_5 moles, induces the increase of the flexibility of the glassy framework, interpreted as the ability for the rearrangement of its structural elements without disturbing the continuity of the polymeric structure of the glass as a whole [1].

The increase in the flexibility of the glass structure appears to be determined by the strength of the chemical bonds between the cations present in the glass structure and the oxygen atoms. As a parameter characterizing the force of these interactions there has been used the so-called 'ionicity *i*' according to Görlich [2].

The greater number of aluminium cations in the glass structure as well as a more ionic character of their bonds with the network oxygen atoms (Al–O: 0.546) in comparison with the ionicity of the B–O bonds (B–O: 0.476) are responsible for the fact that the glass structure becomes more 'flexible' and requires less energy for its transition from the rigid state into a state characterised by smaller viscosity.

Introduction of the cation-modifiers in the form of Na_2O and CaO into the structure of $AlPO_4$–BPO_4–SiO_2 glasses exercises also the similar influence on the course of the glass transition (Tables 2, 3).

As it is known, introduction of the cation-modifiers into the glass structure causes the breaking of the oxygen bonds joining the framework components, and in this way weakening the glass framework. Ca and Na bonds with oxygen are characterised by high ionicity (Ca–O: 0.707; Na–O: 0.807). Hence, forming with the oxygen atoms much weaker and non-directional bonds they make flexibility of the glass structure increase which is manifested by lower T_g temperatures and increase of α as well as greater changes of Δc_p accompanying the relaxation of stresses in the structure of these glasses.

A factor increasing the structural flexibility of the examined glasses is also a change of the coordination number of aluminium atoms from 6 to 4, and that of the boron atoms from 4 to 3 due to the introduction into their structure of a modifier in the form of sodium ions. It has been observed on the ^{11}B and ^{27}Al NMR spectra of these glasses [3].

Conclusions

Glasses from the $AlPO_4$–BPO_4–SiO_2 system show a reversible glass transition effect, the course of which depends on nature and the number of cation modifiers with respect to the network formers, as well as the character and the strength of the chemical bonds between the modifiers and the network components. The greater number of modifiers in the glass and the more ionic their bonds with the network, the more flexible the structure is and correspondingly less energy-consuming the transition is from the state of a rigid body to the viscoelastic state.

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