Solution calorimetric investigation of $0.67[x\text{SiO}_2-(1-x)\text{P}_2\text{O}_5]-0.33\text{Na}_2\text{O}$ glasses at 298.15 K

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Abstract

New density, glassy temperature, mixing enthalpy measurements are presented on glassy sodium phosphosilicate oxides. Mixing enthalpies at 298.15 K are obtained by acidic solution calorimetry. Attractive and contraction behaviors are observed with the increasing silica content.

Keywords: Silicophosphate, solution calorimetry, density, glass transition temperature, Mixing enthalpy.

Introduction

Phosphosilicate glasses have received increasing attention for their various kind of applications. For biological applications, they may be used as degradable temporary implants in order to promote healing or the growth of the surrounding tissue and in order to avoid the need for secondary surgery to remove the implant [1, 2]. Moreover these materials have found applications in glass-to-metal seals, laser hosts, optical fibers and nuclear waste encapsulates [3]. Previous investigations in phosphosilicate glasses were mostly focused on their structural studies [4, 5]. The knowledge of the thermodynamical properties of the system, including the vitreous state, is necessary for design and improvement of industrial applications. For a better understanding of the thermodynamic stability, different techniques like DSC and acid solution calorimetry shall be further investigated under different environmental conditions. Based on these results, optimisations of parameters influencing the stability should be investigated. Acid solution calorimetry has proven to be a valuable technique for determination of enthalpies of formation of glasses [6, 7]. This technique produces highly precise data on small samples. This method provides mixing enthalpies by comparing the enthalpy of solution of the homogeneous glass and mechanical mixtures of end-members glasses. Accurate calorimetric measurements are valuable and helpful data for understanding the existence of miscibility gaps along the glass system.

In spite of the wide field of applications, there is a lack of knowledge of the thermodynamical properties of phosphosilicate glasses. Nevertheless, very few experimental thermochemical studies have been undertaken on borophosphate glasses [7, 8]. At the same time the presently investigated glassy system may be considered as a basic system for studies of multicomponent vitreous systems as SiO_2-P_2O_5-Na_2O-CaO, SiO_2-P_2O_5-Na_2O-CaO-MgO, displaying numerous industrial and biological applications as coating prosthesis; toothpaste, treatment of liquid waste [9-11]. The present study mainly investigates the relationships between the composition and the physical and thermochemical properties, such as density, glass transition temperature and mixing enthalpy of $0.67[x\text{SiO}_2-(1-x)\text{P}_2\text{O}_5]-0.33\text{Na}_2\text{O}$ glass system.

Experimental setup

Seven different molar compositions of the $0.67[x\text{SiO}_2-(1-x)\text{P}_2\text{O}_5]-0.33\text{Na}_2\text{O}$ system were prepared by the melt quenching technique. High-purity reagent grade SiO_2, Na_2CO_3 and $(\text{NH}_4)_2\text{HPO}_4$ were used to obtain glass compositions.

Amorphous state of the analyzed silicophosphate glasses was confirmed by X-ray diffraction method. The glass transition temperature of obtained glasses was determined by DSC measurements conducted on DSC 111 SETARAM operating in the heat flux DSC mode. The samples (about 50 mg) were heated in platinum crucibles at a rate of 5°C min^{-1} in argon atmosphere up to 700°C. The glass transition temperature (Tg) was determined from the inflection point on the enthalpy curve. Densities of glass samples were measured at 296.15 K by using a pycnometer with diethylphtalate (d = 1.118) as the immersion fluid. Measurements of the solution enthalpy, at 298.15 K, were performed using a calsol calorimeter. The calorimeter and standard procedures have been described previously [8, 12]. The solvent consists in a 25 mL HF (6M) and 25 mL HNO_3 (4M) mixture.

Result

All the experimental solution enthalpy values are reported in the appendix A. The solution enthalpies were extrapolated to infinite dilution. A constrained least-square method was applied to fit the data, taking account a linear variation of the slopes with the composition of the composite [10, 13]. Following this procedure, we obtained solution enthalpies at infinite dilution for the different materials, summarized in Ta-

ble 1. The density and the glass transition temperature values are also gathered in Table 1.

Table 1. Density (ρ), glass transition temperature (Tg) and solution enthalpy at infinite dilution ($\Delta_{sol}^{\infty}H$) of 0.67[xSiO$_2$-(1-x)P$_2$O$_5$]-0.33Na$_2$O glasses.

x	ρ (g.cm^{-3})	Tg (°C)	$\Delta_{sol}^{\infty}H$ (kJ.mol^{-1})
0	2.55	193	-65.7
0.1	2.67	321	- 63.9
0.3	2.73	501	-75.0
0.5	2.75	515	-77.1
0.7	2.74	534	-88.3
0.9	2.67	557	-129.4
1	2.62	503	-142.2
Experimental error	± 0.03	± 3	± 1.5

Figure 1. Mixing enthalpy for 0.67[xSiO$_2$-(1-x)P$_2$O$_5$]-0.33Na$_2$O glasses as a function of SiO$_2$ content at 298 K. Points, are the experimental data. The line represents a fit according Eq. (1). The errors bars are also indicated.

Discussion

As given in the Table 1, the densification of the glass with SiO$_2$ composition agrees with the observed increase in Tg. So, the structure of oxide glasses is thought as a polymer where the oxygen link atoms with covalent bounds. The substitution of SiO$_2$ in the phosphate network results in an increase in the connectivity and closeness of the packing in the glass [13, 15]. The cross-link density is then at the highest in the richest silicate glass. In the same manner it can be observed that Tg changes from 200 K to 500 K in the 0< x <1/3 range and of about only 50 K in the 1/3< x <1 domain. That points out the complex anion [Si$_2$P$_8$O$_{27}$]$^{-6}$ corresponding to the x =1/3 composition. The substitution of silicate to phosphate induces the formation of that anion which increases drastically the connectivity of the glass. The corresponding mixing enthalpy values are displayed in Fig.1. They are significantly negative over the whole composition range and may be described by the equation:

$$\Delta_{mix}H = x(1-x)(130\,x^2 - 251\,x - 18) \text{ in kJ/mol} \qquad (1)$$

where x is the molar fraction of SiO$_2$.

As shown in Fig.1, the fitted curve is asymmetric and displays a minimum value of about (-29.2 ± 4.5) kJ.mol^{-1} at x = 2/3. According to usual interpretation, negative mixing enthalpies are understood as a lack of immiscibility behaviour.
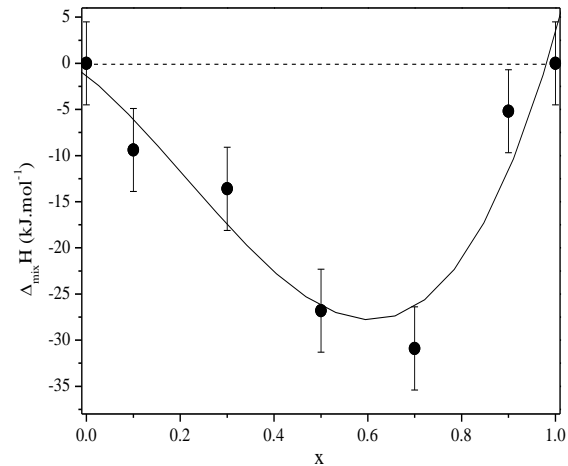
Mixing enthalpy is a sensitive tool providing valuable information about interactions between two species in solution as pure ionic, molecular or ion-solvent interactions. For the studied glasses, the mixing enthalpy values at 298.15 K shows relatively strong exothermic mixing enthalpy referred to the two glass former end members. The minimum is observed at about the x =2/3 concentration which corresponds to the [Si$_4$P$_4$O$_{21}$]$^{-6}$ complex anion. It can be noticed that this maximum of energetic stability do not correspond to the minimum of steric compacity. That means that the calculus of configurational entropy cannot be deduced from only energetic considerations and must integer fine structural observations.

Conclusion

Density, glass transition temperature (Tg) and mixing enthalpy were investigated in the 0.67[xSiO$_2$-(1-x)P$_2$O$_5$]-0.33Na$_2$O glassy system. An increase in Tg and density upon substitution of SiO$_2$ on P$_2$O$_5$ species have been observed. These variations indicate that more compactness and reticulation of the glass network is observed with the addition of SiO$_2$, the maximum being rather observed at the x = 1/3 composition. Elsewhere, it is shown that a strong negative interaction occurs at the x = 2/3 composition. Both these observations must be accounted for the calculus of the entropy of the solution.

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Bibliographies

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Acknowledgments

Appendix

Experimental solution enthalpies $\Delta_{sol}H$ of 0.67[xSiO$_2$-(1-x)P$_2$O$_5$]-0.33Na$_2$O glasses in HF(6M) + HNO$_3$(4M) at 298.15 K.

x	Concentration of the solute in 50 mL of solvent (mmol.L^{-1})	$\Delta_{sol}H$ (kJ.mol^{-1})
0	2.574	-64.14
	2.043	-65.78
	2.824	-67.02
	1.788	-64.20
	2.643	-65.99
	2.147	-67.05
	1.316	-65.45
0.1	1.618	-65.62
	2.758	-61.27
	2.299	-63.57
	2.465	-64.27
	2.052	-64.72
	1.660	-64.66
	1.970	-63.05
0.3	1.579	-75.46
	2.242	-75.08
	1.957	-74.70
	2.399	-74.96
	2.144	-75.12
	2.056	-74.76
0.5	2.699	-77.07
	1.672	-76.94
	2.120	-77.69
	2.440	-77.84
	2.320	-76.71
	2.577	-76.27
0.7	1.356	-88.71
	2.833	-87.16
	3.149	-90.24
	2.656	-87.33
	2.366	-90.13
	2.788	-86.17
0.9	4.061	-129.63
	2.091	-129.91
	3.221	-128.81
	3.427	-129.81
	3.058	-128.83
	2.614	-129.30
1	3.521	-142.82
	3.359	-141.60
	3.188	-141.29
	3.745	-141.52
	3.975	-142.63
	3.597	-142.50
	3.517	-142.98