Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

# Prediction of glass forming regions in mixed-anion phosphate glasses

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ARTICLE INFO

*Keywords:*
Fluoro-sulfo-phosphate glass
Glass-forming region
Thermodynamic method

ABSTRACT

Fluoro-sulfo-phosphate glasses with rich ligand situations and excellent thermal stability are promising host materials for optically active species, injection moulding and low-temperature sealing, which have received a significant amount of interest in recent years. Herein, the glass-forming regions of such inverted glass systems are predicted *via* the thermodynamic method. Based on this, the actual glass formation areas are further determined by the experiments. The liquidus and eutectic points of the binary systems are calculated and the deviations in composition between the calculated results and available phase diagrams are determined with a small deviation (< 6 mol%). Meanwhile, the glass-forming regions are derived quantitatively, which are relatively in agreement with the experimental results. These results demonstrate that it is practical to predict the formation regions of fluoro-sulfo-phosphate glass systems based on thermodynamic calculation, providing an effective and predictive method for the development of new glass systems.

## 1. Introduction

Fluoro-phosphate glasses are promising candidate materials for high-performance optics and laser devices owing to their low linear and nonlinear refractive index, large transmission range, high rare-earth (RE) ions solubility, and tailorable spectroscopic properties [1–4]. Previous research has already demonstrated that the introduction of sulfate anions can significantly improve the thermal stability of phosphate glasses in terms of both rheology and chemical properties [5–9]. Additionally, sulfate group was found to be responsible for increasing the radiative properties of RE-doped phosphate glass matrix [10], tailoring the local structure [11, 12] and enhancing the durability of phosphate glass in corrosion medium [13]. Inspired by these ideas, a new type of fluoro-sulfo-phosphate glass with rich ligand situations and excellent thermal stability was developed through simultaneously incorporating the sulfate and fluoride into the phosphate glass, demonstrating an interesting route for tailoring the structural dynamics and hosting the optically active cation species in the field of optical glass and fiber lasers [14, 15]. Besides, the fluoro-sulfo-phosphate glasses are potential materials in organic/inorganic conforming processes, injection moulding and low-temperature sealing [16, 17].

On the other hand, it is necessary to ensure that the glass composition locates at the stable glass-forming region in the phase diagram when developing novel glass compositions with special properties. The traditional way of determining glass-forming region was directly performed by a large number of experiments, which costs a lot on human and material resources. Our previous work has established a simple, rapid, and predictable research method for the prediction of glass-forming region using the thermodynamic theory [18–20]. The deviations between the computational and experimental composition of eutectics in binary silicate and borosilicate systems are < 7 mol% [20]. Furthermore, the optimized glass-forming regions in ternary systems can be predicted by identifying the eutectic points of corresponding binary systems.

In the present work, the glass-forming regions in ternary phosphate ($R_2O$–$Al_2O_3$–$P_2O_5$ (R = Li, Na, K), MO–$Al_2O_3$–$P_2O_5$ (M = Mg, Ca, Ba)), fluoro-phosphate ($MgF_2$–$AlF_3$–$Ba(PO_3)_2$, $ZnF_2$–$AlF_3$–$Ba(PO_3)_2$, $ZnF_2$–$AlF_3$–$Zn(PO)_3$) systems were calculated *via* the thermodynamic method and compared with the available experimental results [4, 21]. Moreover, the formation regions in fluoro-sulfo-phosphate ($AlF_3$–$R_2SO_4$–$RPO_3$) glass systems were predicted quantitatively using this method and determined experimentally.

## 2. The thermodynamic method

When two types of compounds are mixed without forming a new compound, the free energy of the mixed solutions ($G_M^L$) and solids ($G_M^S$) can be described as follows [22]:

$$G_M^L = RT(x_A \ln x_A + x_B \ln x_B) \quad (1)$$

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https://doi.org/10.1016/j.jnoncrysol.2018.08.012
Received 19 June 2018; Received in revised form 1 August 2018; Accepted 9 August 2018

**Table 1**
The melting points and $P_2O_5$ content of the eutectic points in binary systems.

| System | Subsystem | Melting point (°C) | $P_2O_5$ content (mol %) |
|---|---|---|---|
| $Li_2O–P_2O_5$ | $Li_2O·P_2O_5–2Li_2O·P_2O_5$ | 600 [35] | 43.9 [35] |
| | $2Li_2O·P_2O_5–3Li_2O·P_2O_5$ | 870 [35] | 30.9 [35] |
| $Na_2O–P_2O_5$ | $Na_2O·P_2O_5–2Na_2O·P_2O_5$ | 490 [36] | 43.5 [36] |
| | $2Na_2O·P_2O_5–3Na_2O·P_2O_5$ | 943 [36] | 30.1 [36] |
| $K_2O–P_2O_5$ | $K_2O·P_2O_5–2K_2O·P_2O_5$ | 610 [37] | 43.4 [37] |
| | $2K_2O·P_2O_5–3K_2O·P_2O_5$ | 1025 [37] | 29.4 [37] |
| $MgO–P_2O_5$ | $MgO·P_2O_5–2MgO·P_2O_5$ | 1150 [38] | 47.5 [38] |
| | $2MgO·P_2O_5–3MgO·P_2O_5$ | 1282 [38] | 27.6 [38] |
| $CaO–P_2O_5$ | $P_2O_5–CaO·2P_2O_5$ | 488 [39] | 91.0 [39] |
| | $CaO·2P_2O_5–CaO·P_2O_5$ | 740 [39] | 63.0 [39] |
| | $CaO·P_2O_5–2CaO·P_2O_5$ | 980 [39] | 48.8 [39] |
| | $2CaO·P_2O_5–3CaO·P_2O_5$ | 1302 [39] | 30.8 [39] |
| | $3CaO·P_2O_5–CaO$ | 1577 [39] | 21.9 [39] |
| $BaO–P_2O_5$ | $BaO·P_2O_5–2BaO·P_2O_5$ | 870 [40] | 47.4 [40] |
| | $2BaO·P_2O_5–3BaO·P_2O_5$ | 1415 [40] | 30.0 [40] |
| | $3BaO·P_2O_5–10BaO·3P_2O_5$ | 1570 [40] | 23.7 [40] |
| | $10BaO·3P_2O_5–BaO$ | 1480 [40] | 21.4 [40] |
| $Al_2O_3–P_2O_5$ | $Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5$ | 1212 [41] | 67.5 [41] |
| | $Al_2O_3·P_2O_5–3Al_2O_3·P_2O_5$ | 1881 [42] | 32.5 [42] |
| | $3Al_2O_3·P_2O_5–Al_2O_3$ | 1847 [42] | 23.5 [42] |
| $Li_2O–Al_2O_3$ | $Li_2O–Li_2O·Al_2O_3$ | 1055 [43] | – |
| | $Li_2O·Al_2O_3–Li_2O·5Al_2O_3$ | 1652 [43] | – |
| | $Li_2O·5Al_2O_3–Al_2O_3$ | 1915 [43] | – |
| $Na_2O–Al_2O_3$ | $Na_2O–Al_2O_3$ | 1540 [44] | – |
| $K_2O–Al_2O_3$ | $K_2O·Al_2O_3–Al_2O_3$ | 1450 [45] | – |
| $MgO–Al_2O_3$ | $MgO–Al_2O_3$ | 1996 [46] | – |
| $CaO–Al_2O_3$ | $CaO–Al_2O_3$ | 1371 [47] | – |
| $BaO–Al_2O_3$ | $BaO–3BaO·Al_2O_3$ | 1425 [48] | – |
| | $3BaO·Al_2O_3–BaO·Al_2O_3$ | 1480 [48] | – |
| | $BaO·Al_2O_3–BaO·6Al_2O_3$ | 1620 [48] | – |
| | $BaO·6Al_2O_3–Al_2O_3$ | 1875 [48] | – |

$$G_M^S = -(x_A \Delta G_{f,A} + x_B \Delta G_{f,B}) \tag{2}$$

$$\Delta G_{f,A} = \Delta H_{f,A}\left(1 - \frac{T}{T_A}\right) \tag{3}$$

$$\Delta G_{f,B} = \Delta H_{f,B}\left(1 - \frac{T}{T_B}\right) \tag{4}$$

where $x_A$ and $x_B$ are the molar fraction of components $A$ and $B$, respectively; $T_A$ and $T_B$ are the melting temperatures of compounds $A$ and $B$, respectively; $\Delta H_{f,A}$ and $\Delta H_{f,B}$ are the fusion heats of compounds $A$ and $B$, respectively; $R$ is the gas content.

In order to reduce the computation complexity, Eq. (1) is simplified to a parabolic equation as follows [20]:

$$G_M^L = 2.3x(x-1)RT - 0.1181RT \tag{5}$$

When the liquid phase and solid phase achieve an equilibrium, namely, $G_M{}^L = G_M{}^S$. The temperatures of both phases are equal and the function $T(x)$ can be obtained by simultaneously solving Eqs. (2) and (5) in form of [20]:

$$T = \frac{(\Delta H_{f,A} - \Delta H_{f,B})x_B - \Delta H_{f,A}}{2.3Rx_B^2 + \left(\frac{\Delta H_{f,A}}{T_A} - \frac{\Delta H_{f,B}}{T_B} - 2.3R\right)x_B - 0.1181R - \frac{\Delta H_{f,A}}{T_A}} \tag{6}$$

Then the eutectic temperature $T_E$ and composition $x$ of the binary system can be calculated by solving the minimum of function $T(x)$.

Generally, the thermodynamic parameters of the common compounds are available from related manuals. While the fusion heats of the certain substances and congruently melting compounds might be obtained from the phase diagrams. In this case, based on the phase diagram and thermodynamic theory, the fusion heat can be estimated using the freezing-point depression method by the following equation [20]:

$$\Delta H_m = \frac{R(T_m)^2}{\Delta T_m} x_B (xB << 1) \tag{7}$$

where $T_m$ is the melting point of component $A$ and $\Delta H_m$ is the molar fusion heat of component A; $R$ is the gas constant. Additionally, if the melting point and fusion heat of some compounds cannot be evaluated or queried, they can be obtained by measuring their thermodynamic parameters by differential scanning calorimetry (DSC) in experiment.

Based on the aforementioned thermodynamic method, the glass forming regions in ternary phosphate ($R_2O–Al_2O_3–P_2O_5$ and $MO–Al_2O_3–P_2O_5$) and fluoro-phosphate ($MgF_2–AlF_3–Ba(PO_3)_2$, $ZnF_2–AlF_3–Ba(PO_3)_2$ and $ZnF_2–AlF_3–Zn(PO_3)_2$) systems were calculated and compared with the experimental results reported [4, 21]. Table 1 summarizes the melting temperature and the glass former (*i.e.* $P_2O_5$) content of the eutectic points in binary systems. The binary subsystems

**Table 2**
The thermodynamic parameters, the calculated and experimental eutectic compositions of the binary subsystems in phosphate glass systems.

| | System | | Melting point $T_m$ (K) | | Fusion heat (J/mol) | | Eutectic composition $x_B$ (mol%) | | $T_g/T_L$[d] |
|---|---|---|---|---|---|---|---|---|---|
| | *A* | *B* | $T_A$ | $T_B$ | $\Delta Hf_{,A}$ | $\Delta Hf_{,B}$ | Calculated | Measured | |
| $Li_2O–Al_2O_3–P_2O_5$ | $2Li_2O·P_2O_5$ | $Li_2O·P_2O_5$ | 1158 [35] | 938 [35] | 27118[a] | 21,819 [49] | 44.4 | 43.9 [35] | – |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(2Li_2O·P_2O_5–Li_2O·P_2O_5)$[c] | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 873 [35] | 1485 [41] | 23594[b] | 27,349 [b] | 15.5 | – | – |
| $Na_2O–Al_2O_3–P_2O_5$ | $2Na_2O·P_2O_5$ | $Na_2O·P_2O_5$ | 1263 [36] | 900 [36] | 21190[a] | 27,040 [49] | 44.5 | 43.5 [36] | 0.49 |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(2Na_2O·P_2O_5–Na_2O·P_2O_5)$ | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 813 [36] | 1485 [41] | 25051[b] | 27349[b] | 10.0 | – | – |
| $K_2O–Al_2O_3–P_2O_5$ | $2K_2O·P_2O_5$ | $K_2O·P_2O_5$ | 1377 [37] | 1096 [37] | 20147[a] | 55,491 [49] | 43.8 | 43.4 [37] | 0.60 |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(2K_2O·P_2O_5–K_2O·P_2O_5)$ | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 883 [37] | 1485 [41] | 20148[b] | 27349[b] | 18.5 | – | – |
| $MgO–Al_2O_3–P_2O_5$ | $2MgO·P_2O_5$ | $MgO·P_2O_5$ | 1655 [38] | 1438 [38] | 55295[a] | 80,577 [49] | 43.3 | 47.5 [38] | 0.45 |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(2MgO·P_2O_5–MgO·P_2O_5)$ | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 1423 [38] | 1485 [41] | 70464[b] | 27349[b] | 61.0 | – | – |
| $CaO–Al_2O_3–P_2O_5$ | $CaO·P_2O_5$ | $CaO·2P_2O_5$ | 1263 [39] | 1073 [39] | 57,166 [49] | 30662[a] | 62.6 | 63.0 [39] | 0.68 |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(CaO·P_2O_5–CaO·2P_2O_5)$ | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 1013 [39] | 1485 [41] | 37125[b] | 27349[b] | 29.5 | – | – |
| $BaO–Al_2O_3–P_2O_5$ | $2BaO·P_2O_5$ | $BaO·P_2O_5$ | 1703 [40] | 1143 [40] | 54123[a] | 57,269 [49] | 48.4 | 47.4 [40] | 0.54 |
| | $Al_2O_3·3P_2O_5$ | $Al_2O_3·P_2O_5$ | 1762 [41] | 2273 [41] | 20176[a] | 48307[a] | 31.4 | 35.2 [41] | 0.63 |
| | $e(2BaO·P_2O_5–BaO·P_2O_5)$ | $e(Al_2O_3·3P_2O_5–Al_2O_3·P_2O_5)$ | 1123 [40] | 1485 [41] | 41266[b] | 27349[b] | 37.5 | – | – |

[a] Data calculated based on the freezing-point depression method.
[b] Data evaluated by the summation of fusion heats of two corresponding compounds.
[c] $e(2Li_2O·P_2O_5–Li_2O·P_2O_5)$ means the deepest eutectics of binary system $2Li_2O·P_2O_5–Li_2O·P_2O_5$, and so on.
[d] $T_g$ is referenced from [4] and $T_L$ is the eutectic temperature.