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Calculation of phase diagrams for the binary systems BaF_2–KF and KF–ZrF_4 and the ternary system BaF_2–KF–ZrF_4

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Abstract

This paper presents the thermodynamic modeling of excess functions and the phase diagram calculation of the ternary system BaF_2–KF–ZrF_4 based on the Hoch–Arpshofen model. The information required was the thermodynamic quantities relative to the three pure salts and the three limiting binary mixtures. The calculated position of the "deep" ternary eutectic allows the prediction of the composition glass range.

Keywords: Glass; Heat of mixing; Phase diagram

1. Introduction

The discovery in 1975 of the fluoride glasses (fluorozirconates) [1–3] was of great interest to scientists, especially with regard to their remarkable optical properties. Indeed, in the infrared, their transparency is about one hundred times better than that of silicate-based glasses [4]. In the past twenty years, many studies have investigated their structures [5–7], physical properties (optical [1,2], electrical [8–10], viscosity [11]), and physico-chemical behaviour (influence of composition on glass properties [12], recrystallization phenomena [13, 14], etc.).

It is now well known that the binary mixture BaF_2–ZrF_4 is a glass-forming system [9]. The addition of other fluorides to this system makes it more difficult to study the vitrification range. In a recent paper we proposed a correlation between the phase diagram of the BaF_2–NaF–ZrF_4 ternary system and the probable vitrification range

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[15]. Some years ago, Kaufman et al. [16] made the first attempt to calculate this ternary phase diagram.

The results obtained were very encouraging since the ternary eutectic points with relatively low fusion temperatures, are located around the vitrification area, as previously published [17].

The glass-forming region in ZrF_4–BaF_2–MF (M is Na [17] or Cs[18]) glass systems has been determined and it appears to be larger in the system containing CsF. The glass-formation range, glass-forming ability and crystallization kinetics have been studied with alkali-containing fluoride systems of composition $(100-x)(0.6ZrF_4$–$0.1AlF_3$–$0.3BaF_2)x(MF)$ with M being Li, Na, K, Cs [19]. From this study it appears that the glass formation decreases with increasing size of alkali ion. These conclusions are inconsistent.

The effect of alkali fluoride on the short-range structures of ZrF_4–BaF_2-based glasses has been studied by XAFS [20]; unfortunately, this paper gave no information on glass-forming ability.

The BaF_2–CsF–ZrF_4 phase digram is not known and its calculation is actually impossible because thermodynamic information concerning the liquid phase is not available. This information is necessary to localize the ternary eutectic points and to compare their position with corresponding points in the BaF_2–NaF–ZrF_4 system.

Therefore, in the present study, we have applied the same calculation procedure to the melted ternary BaF_2–KF–ZrF_4 as enthalpies of formation and the phase diagram of the three adjacent binaries are known; for the ternary system however, only the enthalpies of formation are known [21].

This paper presents a modeling of the enthalpies of formation of this ternary, either from excess enthalpies of the three adjacent binaries, or from the excess enthalpies obtained from some sections of the ternary, the calculation of the phase diagram, and the investigation of the ternary eutectic points with a relatively low temperature of fusion.

2. Constraints of theory

2.1. Modeling

The Hoch–Arpshofen model has been described in detail in previous publications [22, 23] and applied to molten salt systems [15, 24]. For the sake of clarity, we will briefly recall the main analytical expressions of the excess Gibbs free energy deduced from this model.

Let a solution contain components (A, B, C); the contribution of the A–B binary system to the solution is

$$\Delta_{\mathrm{mix}} G_{\mathrm{AB}} = n_{\mathrm{AB}} W_{\mathrm{G,AB}}\, x(1-(1-y)^{n-1}) \tag{1}$$

where x is the ternary mole fraction of A (or B), y is the ternary mole fraction of B (or A), $W_{\mathrm{G,AB}}$ is the interaction parameter, and n_{AB} is an integer (2, 3, 4, etc.).

The interaction parameter W_G was assumed to be either constant, or linearly temperature-dependent: $W_G = W_H + \Delta W T$. The enthalpic part, W_H, is determined from experimental enthalpy data.

The total Gibbs free energy of a ternary system is the sum of the each contribution A–B, A–C and B–C

$$\Delta_{mix} G = \Delta_{mix} G_{AB} + \Delta_{mix} G_{AC} + \Delta_{mix} G_{BC} \qquad (2)$$

Every enthalpic term W_H (A, B), W_H (A, C) and W_H (B, C) can be obtained either from the experimental heat of mixing binary data by using relation (1) (where $x + y = 1$), or from the experimental heat of mixing ternary data by using relation (2).

2.2. Phase diagram calculation

The equilibrium between the liquid and the solid compound (A, B, C, $A_{x(A,s)}B_{x(B,s)}$ or $A_{x(A,s)}C_{x(C,s)}$) is described by the relation [15]

$$G_{form} = \sum x(i, s) \{(T_{fus}(i) - T) S^*_{fus(i)} + T \ln x(i, l) + \Delta_{mix} G_i\} \qquad (3)$$

For example, for the compound $A_{x(A,s)}B_{x(B,s)}$, $i = $ A or B and G_{form} is defined by

$$G_{form} = G(A_{x(A,s)}B_{x(B,s)}, s, T) - x(A, s) G^{\ominus}(A, s, T) - x(B, s) G^{\ominus}(B, s, T)$$

where G_{form} is the Gibbs free energy of the compound and $G^{\ominus}(i, s, T)$ those of the pure salts. $S^*_{fus}(i)$ is an "apparent" entropy of fusion and has been defined in a previous publication [25]. In relation (3), we used the analytical equation provided by the Hoch-Arpshofen model and $\Delta_{mix} G_i$ is deduced from relation (2). For each binary system, Eq. (3) can be applied to several points of the equilibrium phase diagram (eutectic, peritectic, etc.). A system with N equations (N is the number of points) is obtained in this way with the unknown quantities $S^*_{fus(i)}$, G_{form} and ΔW. As we point out in a previous paper, the solution is reached through a least-squares minimization method which treats the three binary systems simultaneously in order to obtain single values for S^* (A), S^* (B) and S^* (C).

When the solution is obtained, Eq. (3) can be used to calculate the temperature of equilibrium in the ternary system between the liquid phase and each solid compound.

3. Results and discussion

3.1. Modeling

3.1.1. Binary

The parameters W_H, n and the choice of composition for the binary systems, BaF_2–ZrF_4 and KF–ZrF_4, were those found in previous research, respectively Refs. [15] and [24]. These parameters are given in Table 1. For the BaF_2–KF system, experimental enthalpy of mixing data published previously by Hong and Kleppa [26] was used. Calculated parameter values (w_H, n and x) are reported in Table 1.

Table 1
Parameters obtained from binary or ternary least-squares analysis

Compounds	Binary		Ternary	
	n	w/kJ mol^{-1}	n	w/kJ mol^{-1}
$x\mathrm{BaF_2} + (1-x)\,\mathrm{KF}$	2	-7.94 ± 0.39	2	1.47 ± 2.2
$x\mathrm{BaF_2} + (1-x)\mathrm{ZrF_4}$	3	-47.9 ± 3.9	3	-47.5 ± 2.7
$x\mathrm{KF} + (1-x)\mathrm{ZrF_4}$	4	-25.1 ± 2.0	4	-27.4 ± 0.5

3.1.2. Ternary system

Some sections of this ternary system were investigated, corresponding to different $x_{\mathrm{BaF_2}}/x_{\mathrm{KF}}$ and $x_{\mathrm{ZrF_4}}/x_{\mathrm{NaF}}$ ratio values. The experimental enthalpies of formation have been published recently [21].

As in an earlier paper [24], the model was used in the two following ways: the n and W_{H} values obtained for each binary mixture are introduced into Eq. (2) which gives the ternary enthalpy in terms of binary contributions; the second is to optimize the six (n, W_{H}) binary parameters from the experimental ternary enthalpies of formation and Eq. (2). The values obtained are reported in Table 2. The corresponding enthalpies of formation are also plotted in Figs. 1 and 2.

Except for the $\mathrm{BaF_2}$–KF system, the following remarks can be made: (i) good agreement is obtained between enthalpies deduced from either binary or ternary optimization; (ii) the maximum deviation between experimental and calculated enthalpy of mixing values does not exceed 15% for all ternary sections. This deviation leads to a variation in the calculated equilibria temperature of no more than 5 K.

The heat of mixing of the $\mathrm{BaF_2}$–KF binary system deduced from the ternary optimization is close to zero. This result is in contradiction with Hong and Kleppa's measurements [26]. This point will be discussed in the next section.

We conclude that the Hoch–Arpshofen model is suitable to describe the thermodynamics of the $\mathrm{BaF_2}$–KF–$\mathrm{ZrF_4}$ ternary mixture. It is likely that the binary interactions are not changed in the ternary mixing and that no new species formation occurs in the ternary melt.

3.2. Phase diagram

3.2.1. BaF_2–KF

The phase diagram of this system has been investigated by three authors. It has a single eutectic located at $x(\mathrm{BaF_2}) = 0.265$, $T = 1002$ K [27, 28]; or $x(\mathrm{BaF_2}) = 0.56$; $T = 1025$ K [29]. Our thermal analysis confirms the results given in Refs. [27] and [28].

The phase diagram calculation was made using the thermodynamic data relative to the pure salts reported in Table 2 and the value for the interaction parameter w_{H} was deduced either from Kleppa's data (-7.98 kJ mol^{-1}) or from the above-mentioned

Table 2
Thermodynamics quantities used or calculated

	S^* or	S_{fus}	$G_{form(s+s \to s)}$	$W_G = W_H + \Delta WT$	
	($J k^{-1} mol^{-1}$)		($kJ mol^{-1}$)	($kJ mol^{-1}$) W_H	($J K^{-1} mol^{-1}$)ΔW
	Values used in the calculation				
BaF_2		18.2			
KF		24.02			
ZrF_4	19.8 ± 0.26				
$xBaF_2 + (1-x)KF$				0	
$xBaF_2 + (1-x)ZrF_4$				-47.5 ± 2.7	
$xKF + (1-x)ZrF_4$				-27.4 ± 0.5	
	Values calculated from the binary phase diagram systems				
$xKF + (1-x)ZrF_4$					12.5 ± 0.6
$1/4(3KF \cdot ZrF_4)$			-24.0 ± 0.8		
$1/3(2KF \cdot ZrF_4)$			-24.8 ± 0.8		
$1/5(3KF \cdot 2ZrF_4)$			-24.1 ± 0.6		
$1/2(KF \cdot ZrF_4)$			-22.6 ± 0.6		
$1/4(3BaF_2 \cdot ZrF_4)$			-49.5 ± 1.3		
$1/3(2BaF_2 \cdot ZrF_4)$			-56.6 ± 1.0		
$1/5(3BaF_2 \cdot 2ZrF_4)$			-55.0 ± 1.0		
$1/2(BaF_2 \cdot ZrF_4)$			-49.3 ± 1.0		
$1/3(BaF_2 \cdot 2ZrF_4)$			-37.8 ± 1.0		

calculation ($w_H = 1.47$ kJ mol^{-1}). The position of the eutectic is, of course, different and the best result was obtained in the second way, $x(BaF_2) = 0.3$, $T = 1005$ K. It appears that the heat of mixing given by Kleppa is not suitable for use with the phase diagram.

3.2.2. $KF–ZrF_4$

Several authors [30–32] have performed an experimental investigation of this phase diagram. The solid compounds formed upon mixing were identified by spectroscopic methods and/or thermal analysis. We assessed the previous results and selected the phase diagram proposed by Barton et al. [30].

As in the $NaF–ZrF_4$ system, we took into account the temperature dependence of the interaction parameter W_G. The apparent entropy of fusion of ZrF_4 is the same as that deduced for the $NaF–ZrF_4–BaF_2$ system [15]. The calculated phase diagram was in good agreement with the experimental phase diagram except for the coordinates of the eutectic between liquid phase, KF(s) and $3KF \cdot ZrF_4$(s). Indeed the calculated melting temperature is 200 K lower than the experimental data. The composition is correct. If the experimental data are correct we conclude that the calculation failed (in this part of the phase diagram). Taking into consideration only the apparent entropy of fusion of KF,S^*(KF), in this calculation is not sufficient, whereas the introduction in this part of the diagram of a solid–solid solution is consistent with increasing the liquidus temperature. However, we recently performed DTA experiments in this part of

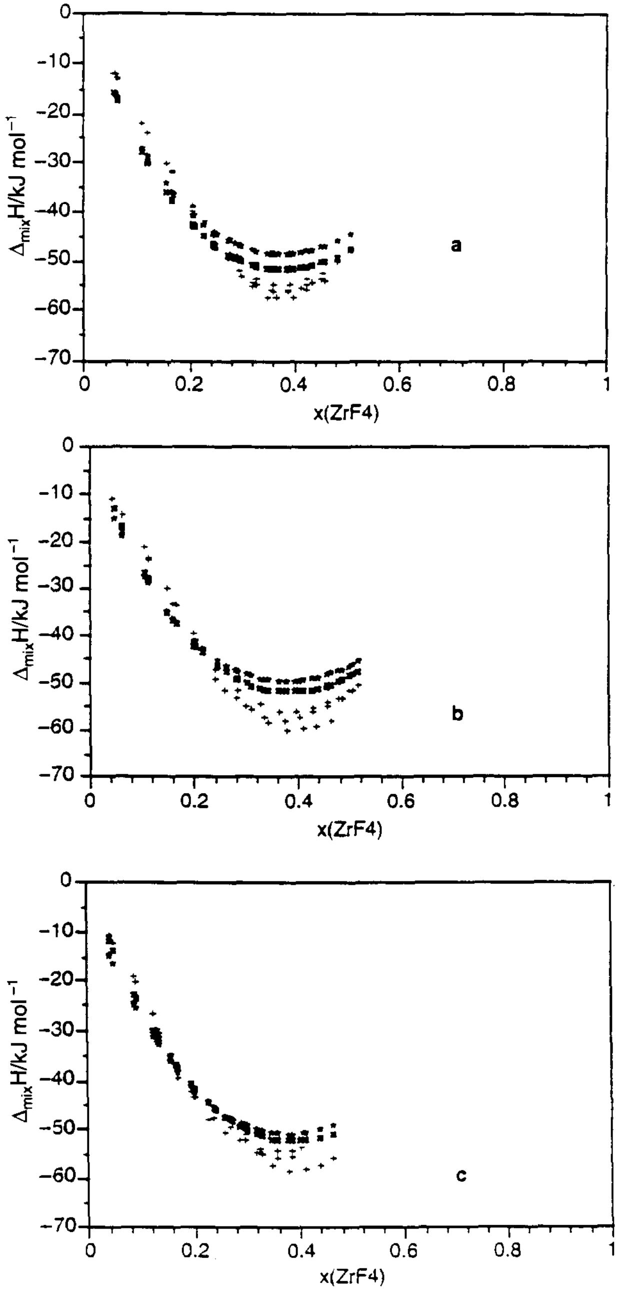

Fig. 1. Enthalpies of formation of the ternary mixtures along the sections $x(\mathrm{BaF_2})/x(\mathrm{KF}) = 1/9$ (a); 2/8 (b); 3/7 (c): +, experimental values; $*$, binary Hoch–Arpshofen model; ×, ternary Hoch–Arpshofen model.

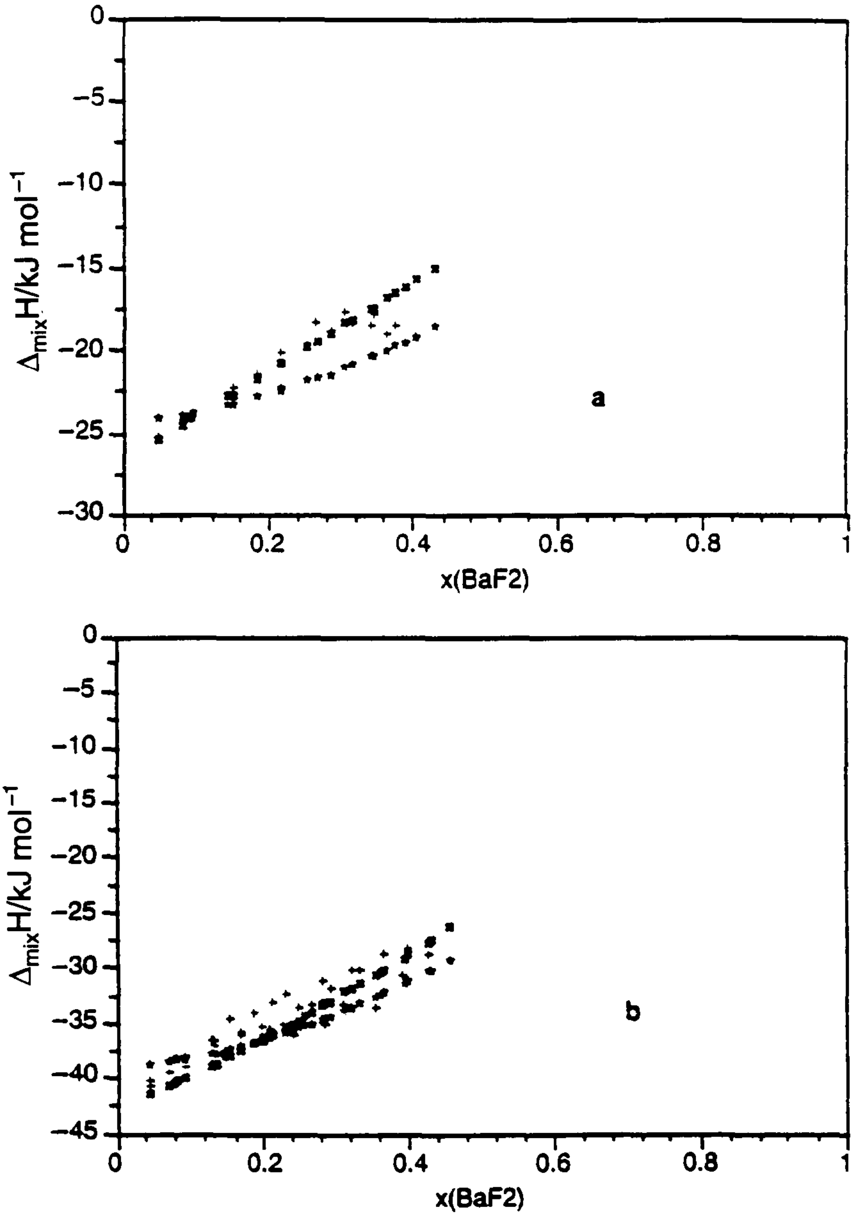

Fig. 2. Enthalpies of formation of the ternary mixtures along the sections $x(\mathrm{ZrF_4})/x(\mathrm{KF}) = 1/9$ (a); 2/8 (b): +, experimental values; *, binary Hoch–Arpshofen model; x, ternary Hoch–Arpshofen model.

the diagram and it appears that the eutectic temperature is correct: the DTA curves do not suggest the existence of a solid solution.

The calculated phase diagram is illustrated at Fig. 3. Table 2 reports the calculated values with associated uncertainties of the Gibbs free energies for each compound.

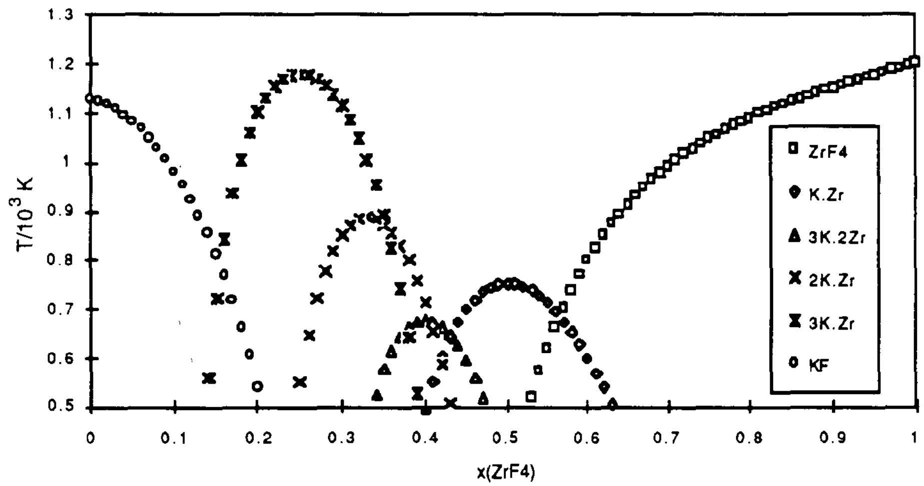

Fig. 3. Calculated phase diagram of the KF–ZrF_4 system.

A comparison of the Gibbs free energy of formation of the two compounds obtained, either K or Na ($3MF \cdot ZrF_4$ and $2MF \cdot ZrF_4$) seems to indicate that the compounds formed with potassium are most stable.

	$3NaF \cdot ZrF_4$	$3KF \cdot ZrF_4$	$2NaF \cdot ZrF_4$	$2KF \cdot ZrF_4$
$G_{\mathrm{form}(s+s \to s)}$ (kJ mol^{-1})	−43	−96	−34	−74

Some years ago Kaufman [16] made the first attempt to calculate this binary phase diagram. The calculated phase diagram was in good agreement with the experimental data but the calculated heat of formation of $KF \cdot ZrF_4$ is not in accordance with the measured values [33]. Indeed for $x(KF) = 0.25$, $\Delta_{\mathrm{mix}}H$(calculated) $= -36$ kJ mol^{-1} and the measured value is -47 kJ mol^{-1}.

3.2.3. BaF_2–ZrF_4

This phase diagram has been calculated previously [15]. Table 2 gives the Gibbs free energies of formation for the different compounds.

3.2.4. BaF_2–KF–ZrF_4

The following calculations were performed assuming that the solid phases in equilibrium were the same in the ternary and binary systems (no ternary compound was formed on mixing). The n and W values obtained for each binary system are introduced into Eq. (3) which gives the ternary enthalpy in terms of binary contributions.

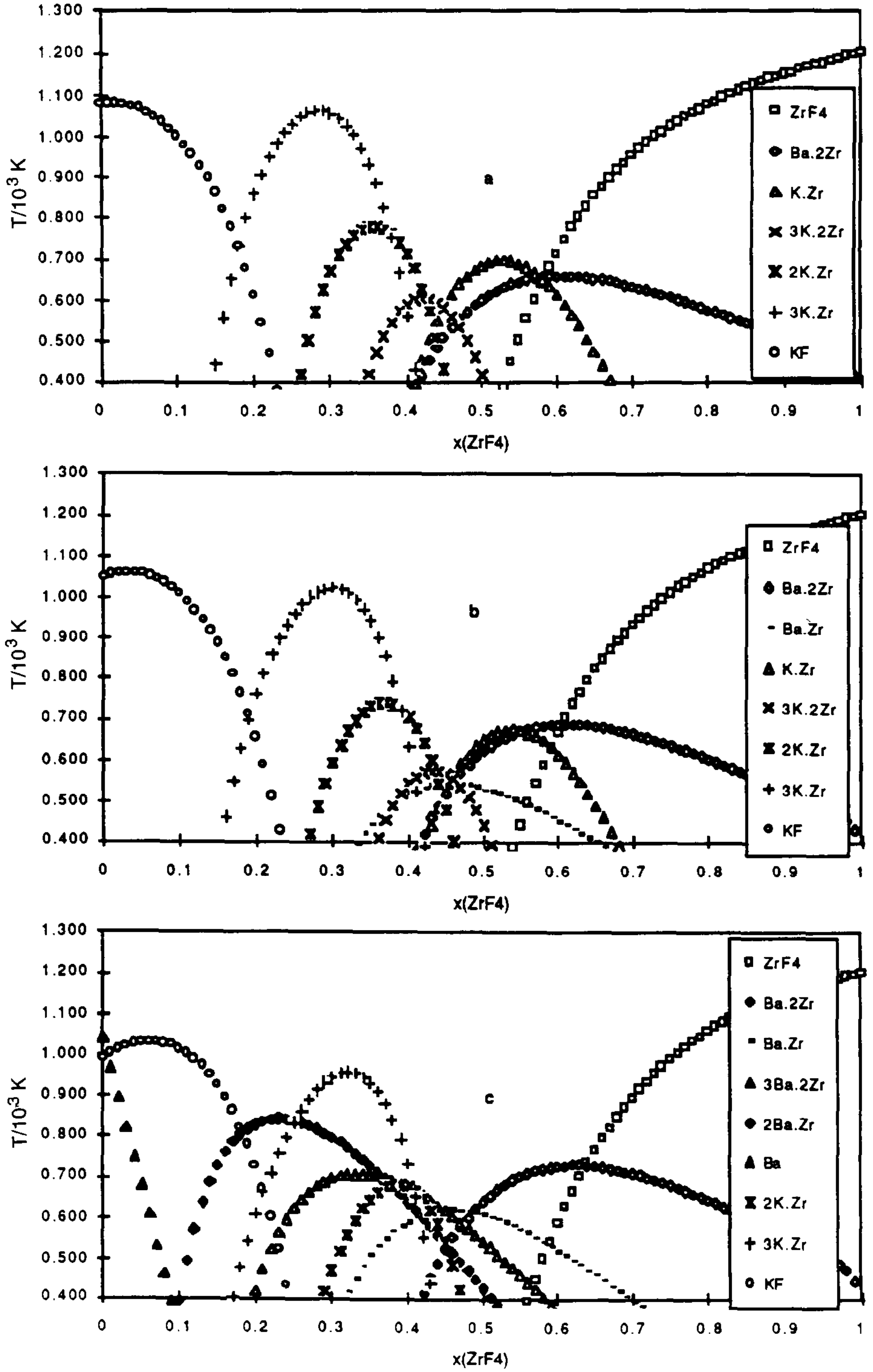

Fig. 4. Calculated liquidus of the BaF_2–NaF–ZrF_4 system; $x(BaF_2)/x(KF) = 0.15$ (a); 0.15 (a); 0.25 (b); 0.5 (c).

The temperature of the thermodynamic equilibrium between the liquid phase and the different compounds was calculated for several sections $x(BaF_2)/x(KF)$. Some of them are plotted against the mole fraction to ZrF_4 in Fig. 4. Unfortunately no experimental temperature of fusion of these systems is available in the literature.

From the liquidus temperature obtained for different sections, it was possible to deduce the coordinates of some ternary eutectics. The temperatures of fusion of these eutectics are much lower than the melting temperatures of the pure salts (1131 K (KF), 1205 K (ZrF_4) and 1563 K (BaF_2)) and lower than those obtained with the ternary system BaF_2–NaF–ZrF_4. The lowest eutectic temperature is 548 K in this system and 750 K in the system containing NaF.

Fortunately these eutectics points are not located in the field where the KF–ZrF_4 phase diagram calculation failed.

If we accept once more the empirical statement that the glass-forming ability is best observed close to "deep" eutectics and by comparison with the ternary system BaF_2–NaF–ZrF_4, the region delimited by the glassy domain of the BaF_2–ZrF_4 system and the three ternary "deep eutectics" (Fig. 5) is a good glass formation range.

It will be interesting to perform some experiments to confirm (or not) this conclusion. A comparison with the glass formation range obtained in the BaF_2–CsF–ZrF_4 system

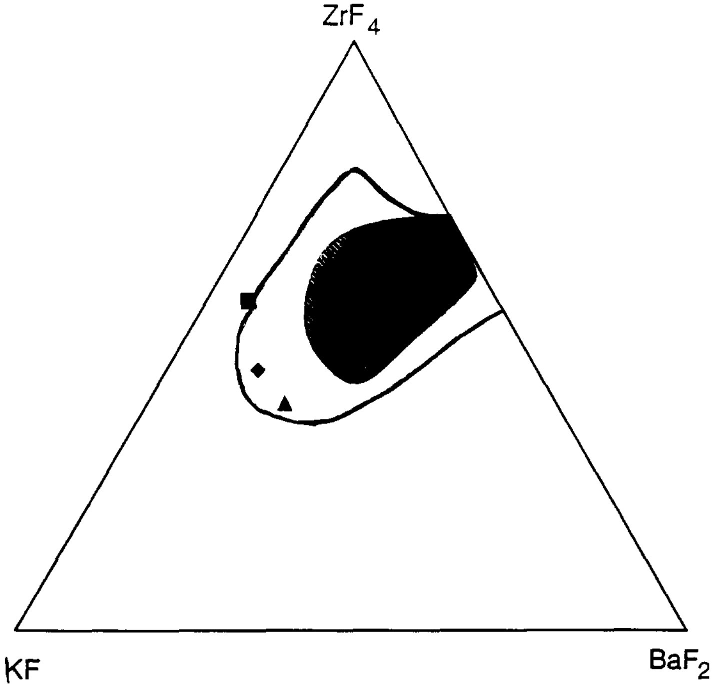

Fig. 5. Calculated ternary eutectic; ■, $x(BaF_2) = 0.05$, $x(KF) = 0.37$, $x(ZrF_4) = 0.58$, $T = 655$ K; ◆, $x(BaF_2) = 0.46$, $x(KF) = 0.43$, $x(ZrF_4) = 0.46$, $T = 548$ K; ▲, $x(BaF_2) = 0.20$, $x(KF) = 0.40$, $x(ZrF_4) = 0.40$, $T = 678$ K; hatched domain is the glass formation in the BaF_2–NaF–ZrF_4 system [17] and the full line is the limit of the glass formation in the BaF_2–CsF–ZrF_4 system [18].

[18] is presented in Fig. 5. We note that the calculated eutectic points are located around this field.

4. Conclusion

In this paper, we prove once more that it is possible to calculate the phase diagram of a ternary mixture from the thermodynamic quantities deduced from the three limiting binary systems. The success of this calculation depends on the thermodynamic model used for describing the liquid mixtures and calculating the excess functions. The Hoch–Arpshofen model is very suitable for systems containing ZrF_4.

These results illustrate how the development of a database for binary-based fluoride systems can be employed to predict the phase diagram of multicomponent systems containing three or more compounds. From this calculated phase diagram, the most appropriate compositions to investigate in the search for fluoride glasses can be deduced.

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