Thermodynamic analysis of LiF–BeF$_2$ and KF–BeF$_2$ melts by a structural model

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ABSTRACT

An earlier structural model for binary silicate melts and glasses is extended to MF–BeF$_2$ (M = Li, K) systems. The evaluation of the thermodynamic properties as well as the phase diagrams for the binary LiF–BeF$_2$ system and the integral enthalpy of mixing of the KF–BeF$_2$ system are carried out with this model. This thermodynamic model is based on the assumption that each alkali fluoride produces the depolymerization of BeF$_2$ network with a characteristic free energy change. A least squares optimization program permits all available thermodynamic and phase diagram data to be optimized simultaneously. In this manner, data for these binary systems have been analysed and represented with a small number of parameters. The model predicts the chain-length distribution of polymeric ions, even though these are not explicitly treated as structural units of the model. The calculated fluoride polyanion chain-length distribution for the LiF–BeF$_2$ system is in quantitative agreement with the predictions reported in the literature.

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1. Introduction

Molten fluorides constitute an important group of solutions, both from a theoretical point of view and because of their technological applications. These often involve extreme temperatures and dangerous or corrosive materials so that the ability to predict physical and thermodynamic properties over a wide range of conditions is valuable. Among the fluoride systems, the LiF–BeF$_2$ mixtures is of importance because of its potential applications as a solvent for actinide ions in molten-salt reactor and as a heat exchanger [1].

The thermodynamics of the binary systems MF–BeF$_2$ (M = Li, K) is of more than usual interest since the component salts are quite dissimilar in character. For example, LiF is a normal ionic salt while BeF$_2$ is evidently associated since it forms a very viscous liquid which is obviously polymeric [2]. Solid BeF$_2$ has a structure analogous to SiO$_2$, in which the Be^{2+} ions are surrounded tetrahedrally by four fluoride ions and each fluoride ion is bonded to two beryllium ions. The BeF$_4{}^{2-}$ tetrahedral shares corners to form a three-dimensional network. The liquid might be expected to have a similar polymeric structure. As LiF or another alkali

fluoride is added to molten BeF$_2$, the viscosity drops sharply presumably because bridging fluoride linkages are broken and the degree of polymerization decreases in a similar way that that of SiO$_2$ is broken up by the addition of alkali or alkaline earth oxides. Fukuda et al. [3] used a molecular-thermodynamic model for the LiF–NaF–BeF$_2$ based on the similar glass-forming tendencies of SiO$_2$ and BeF$_2$.

Three types of F$^-$ anions sharing between two tetrahedral can exist: two BeF$_4{}^{2-}$ tetrahedral can share a corner, an edge, or a face; that is, two cations share 1, 2 or 3 common F$^-$ ions. Salanne et al. [4] developed a geometrical criterion to distinguish the nature of the linkages and found that for all the LiF–BeF$_2$ mixtures, even those richer in BeF$_2$, less than 1% of edge sharing tetrahedral was obtained. Then they concluded that the network was formed almost exclusively of corner-sharing tetrahedral. The existence of a BeF$_4{}^{2-}$ ion in the liquid phase is supported by X-ray diffraction data [5], where each beryllium atom is connected to four fluorine atoms.

Lin and Pelton [6] developed a structural model for binary silicate systems AO–SiO$_2$ (A = Ca, Mn, Mg, Fe, etc.). In this model, one single formalism applies over the entire composition range and accounts for two- and three-dimensional silicate network structures. Later, the model was examined in more depth for binary systems [7] and a more general empirical expression for enthalpy was written, and an empirical nonconfigurational excess entropy was added.

The purpose of the present article is to use the structural model, formerly developed for silicate melts, to represent the thermodynamic properties of MF–BeF$_2$ (M = Li, K) melts. One important

aspect of the present model is the fact that one can calculate a polyanionic chain length distribution.

2. Thermodynamic model

The model is based on the depolymerization reaction of BeF_2:

$$M^+F^- + Be-F-Be = Be-F^{\overset{M^+}{}}F-Be, \quad M = Li, \ K \tag{1}$$
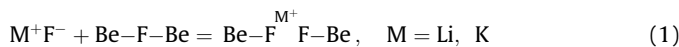
or, in shorthand notation:

$$F^- + F^0 = 2F^{-1/2} \tag{2}$$

where F^- is a free fluoride ion, F^0 is a fluoride ion bonded to two beryllium atoms, and $F^{-1/2}$ is a fluoride ion singly bonded to one beryllium atom.

The structural model assumes that every beryllium atom is bonded to four fluorine atoms. Thus, mass balance considerations require that:

$$N_{F^0} = 2X_{BeF_2} - \frac{N_{F^{-1/2}}}{2} \tag{3}$$

$$N_{F^-} = X_{MF} - \frac{N_{F^{-1/2}}}{2} \tag{4}$$

where X_{MF} and X_{BeF_2} are the mole fractions of the components and N_{F^0}, N_{F^-} and $N_{F^{-1/2}}$ are the numbers of moles of the various fluorine species per mole of solution. The configurational entropy is calculated by assuming a tetrahedral quasi lattice in which the sites are occupied by F^- ions and Be atoms (each associated with four fluorine atoms bonded to it):

$$\Delta S^c = -R\left[X_{BeF_2}\ln\left(\frac{X_{BeF_2}}{X_{BeF_2}+N_{F^-}}\right) + N_{F^-}\ln\left(\frac{N_{F^-}}{X_{BeF_2}+N_{F^-}}\right)\right]$$
$$-R\left[N_{F^0}\ln\left(\frac{N_{F^0}}{N_{Be-Be}}\right) + (N_{Be-Be}-N_{F^0})\ln\left(\frac{N_{Be-Be}-N_{F^0}}{N_{Be-Be}}\right)\right]$$

where N_{Be-Be} is the number of moles of neighboring Be–Be pairs per mole of solution:

$$N_{Be-Be} = \frac{4X_{BeF_2}}{2}\left(\frac{X_{BeF_2}}{X_{BeF_2}+N_{F^-}}\right) \tag{6}$$

The structural model assumes that reaction (1) is associated with a Gibbs energy change containing an enthalpic (ω) and entropic (η) term:

$$\Delta H = \left(\frac{N_{F^{-1/2}}}{2}\right)\omega \tag{7}$$

$$S^{nc} = \left(\frac{N_{F^{-1/2}}}{2}\right)\eta \tag{8}$$

Finally, ω and η are expanded as polynomials:

$$\omega = \omega_0 + \omega_1 X_{BeF_2} + \omega_2 X_{BeF_2}^2 + \cdots \tag{9}$$

$$\eta = \eta_0 + \eta_1 X_{BeF_2} + \eta_2 X_{BeF_2}^2 + \ldots \tag{10}$$

The coefficients ω_i and η_i are the parameters of the model which are obtained by optimization of the data. Given a composition, X_{BeF_2}, and values of the parameters ω_i and η_i, the actual value of $N_{F^{-1/2}}$ can be calculated by minimizing the Gibbs energy at constant X_{BeF_2}, ω and η:

$$\Delta G = \Delta H - T(\Delta S^c + S^{nc}) \tag{11}$$

$$2\left[\frac{\partial \Delta G}{\partial N_{F^{-1/2}}}\right]_{X_{BeF_2},\omega,\eta} = (\omega - \eta T) - RT\left[\ln\left(\frac{N_{F^-}}{1-X_{MF}+N_{F^-}}\right)\right.$$
$$\left. + \ln\left(\frac{N_{F^0}}{N_{Be-Be}}\right) - \left(1+\frac{N_{Be-Be}}{1-X_{MF}+N_{F^-}}\right)\ln\left(\frac{N_{Be-Be}-N_{F^0}}{N_{Be-Be}}\right)\right] = 0 \tag{12}$$

Substitution of Eqs. (3), (4) and (6) into (12) gives an equation in terms of X_{MF} (or X_{BeF_2}) and $N_{F^{-1/2}}$, which can be solved numerically at a fixed composition, X_{BeF_2}, and for given values of the parameters ω_i and η_i to give $N_{F^{-1/2}}$. This value can then be substituted back into Eqs. (3)–(5), (7) and (8) to give ΔS and ΔH.

3. Chain-length distribution of polymeric anions

It is generally accepted [8] that MF–BeF_2 (M = Li, K) melts contain BeF_4^{2-} in the MF rich region which, at higher BeF_2 concentration, can polymerize to form dimers $Be_2F_7^{3-}$, trimers $Be_3F_{10}^{4-}$, tetramers $Be_4F_{13}^{5-}$, etc. An important feature of the present model is that the concentrations of these polymers can be calculated, even though they are not explicitly considered in the formulation of the model. At any composition, the model permits the calculation of N_{Be-Be}, the number of moles of neighboring Be–Be pairs, as well as N_{F^0}, the number of bridges between neighboring berylliums. From these two quantities, the number of monomers BeF_4^{2-} can be estimated by calculating the probability that a Be is bridged to no other berylliums. The number of dimers $Be_2F_7^{3-}$ is given by calculating the probability that two berylliums are bridged only to each other. The concentrations of trimers and linear tetramers can be calculated similarly. The statistical treatment is as follows.

The number of fluorine "bridges" is N_{F^0}. There are X_{BeF_2} beryllium atoms in one mole of solution. Therefore, the average number of bridges per beryllium atoms is $m = 2N_{F^0}/X_{BeF_2}$ since each bridge joins two beryllium atoms. Each Be is bonded to four fluorine atoms. Consider a Be atom, and choose one of the F atoms bonded to it. The probability, p, that this F atom is a bridging fluorine is equal to the average number of bridges per Be atom divided by 4. That is:

$$p = \frac{N_{F^0}}{2X_{BeF_2}} = \frac{m}{4} \tag{13}$$

Let α_n ($n = 0$–4) be the probability that a given Be is bridged to exactly n other berylliums. α_n is given by the binomial distribution:

$$\alpha_n = \frac{4!}{(4-n)!n!}p^n(1-p)^{4-n} \tag{14}$$

The average number of bridges on a Be atom, m, can now be written as:

$$m = \frac{2N_{F^0}}{X_{BeF_2}} = \sum_{n=1}^{4}n\alpha_n \tag{15}$$

A variable P_n ($n = 1$–4) is now introduced. P_n is the probability that, given a bridge, a given end of this bridge will be joined to a beryllium which has exactly n bridges. It can be seen that:

$$P_n = \frac{n\alpha_n}{\alpha_1 + 2\alpha_2 + 3\alpha_3 + 4\alpha_4} = \frac{n\alpha_n}{m} \tag{16}$$

The factors n multiplying α_n in both the numerator and denominator of Eq. (16) arise because a given bridge has n times the chance of finding itself bonded to a Be with n bridges as to a Be with one bridge.

Let us now introduce the symbols N_1, N_2, N_3 and N_4 for the numbers of monomers, dimers, trimers and linear tetramers per

mole of solution. Clearly,

$$N_1 = X_{BeF_2}\alpha_0 \tag{17}$$

The number of dimers, N_2, is given by the number of bridges times the probability that each end of a bridge is bonded to a beryllium atom which possesses only one bridge. That is:

$$N_2 = N_{F^0}P_1^2 \tag{18}$$

The number of trimers, N_3, is equal to the number of bridges times the probability that one end of a bridge is bonded to a Be possessing exactly one bridge, times the probability that the Be at the other end possesses exactly two bridges, times the probability that this Be is, in turn, bonded to a Be with only one bridge:

$$N_3 = N_{F^0}P_1P_2P_1 \tag{19}$$

Similarly, the number of linear tetramer can be shown to be given by:

$$N_4 = N_{F^0}P_1P_2P_2P_1 \tag{20}$$

Since N_{F^0} is determined from the model for the binary systems MF–BeF$_2$ the polymeric anion distribution can easily be calculated from Eqs. (13)–(20).

4. Results and discussion

The coefficients ω_i and η_i are obtained by optimization of experimental data for a given binary system. Since all integral and partial properties are expressed in terms of the same parameters, all available data (phase diagram, activities, enthalpies, etc.) can be considered in one simultaneous least-squares optimization. For the present model, a nonlinear least-squares optimization program was written [9].

4.1. The LiF–BeF$_2$ system

The assessed phase diagram is shown in Fig. 1. The optimization of this system is based on the phase diagram reported by Romberger et al. [10] who used emf measurements of cell with transference which permited equilibrium determination of the phase boundaries. They reported that Li$_2$BeF$_4$ melts congruently at 459.1 °C and forms two eutectics, one with LiF at 458.9 °C at 32.80 mol% BeF$_2$ and other eutectic with BeF$_2$ at 363.5 °C at 53.10 mol% BeF$_2$. They also reported that the compound LiBeF$_3$ is stable below 280 °C. Fig. 1 shows that the calculated LiF–BeF$_2$
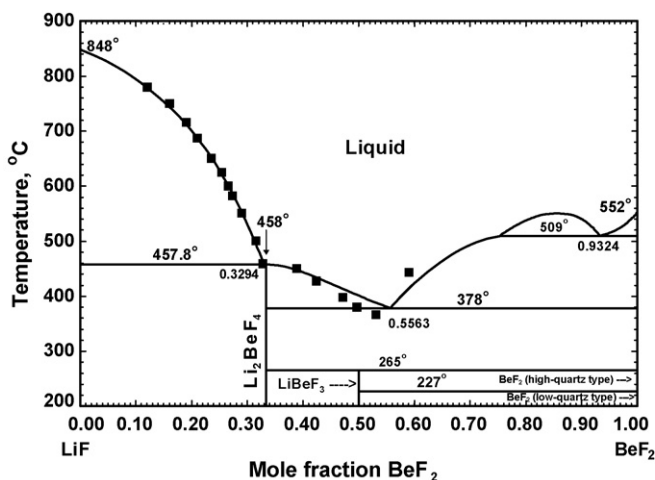

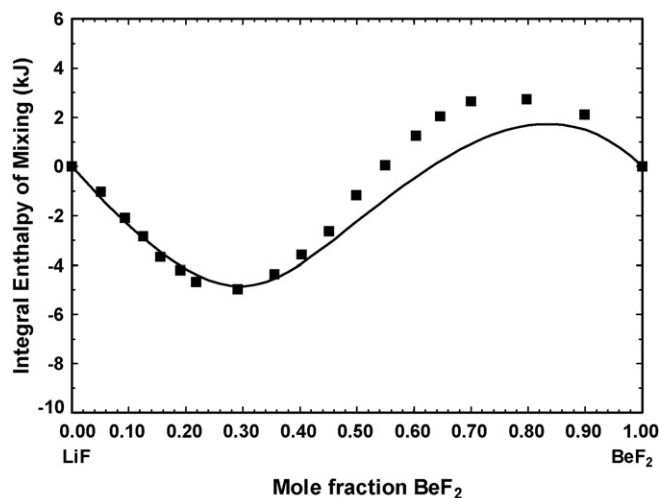Fig. 1. Calculated optimized LiF–BeF$_2$ phase diagram. Experimental points: (■) Ref. [10].

Fig. 2. Calculated optimized integral enthalpy of mixing of the liquid LiF–BeF$_2$ system at 1135 K. Experimental points: (■) Ref. [11].

phase diagram is in good agreement with the experimental values reported by Romberger et al. [10], even though small deviations appear on the eutectic between Li$_2$BeF$_4$ and BeF$_2$.

The integral enthalpies of mixing of the liquid LiF–BeF$_2$ system were determined calorimetrically at 1135 K by Holm and Kleppa [11]. They found that this system has an S-shaped enthalpy curve with positive values in the high BeF$_2$ range. Calculated enthalpies of mixing are plotted in Fig. 2, where they may be compared with the data of Holm and Kleppa [11].

ΔH°_{298} and S°_{298} as well as Cp for LiF, BeF$_2$, Li$_2$BeF$_4$ and LiBeF$_3$ were taken from Barin [12]. The value of S°_{298} of Li$_2$BeF$_4$ was subsequently changed by 0.502 J/mol K. This change was made by trial and error to fit the experimental phase diagram and is well within the stated error limits. The thermodynamic properties of the pure fluorides as well as those of the intermediate compounds are given in Table 1. Activities of BeF$_2$ in melts of the LiF–BeF$_2$ system were estimated by Hitch and Baes [13] using the electromotive force technique within the temperature range 773–1173 K. Their results show a significant positive deviation from the ideal behavior in the BeF$_2$ rich region. The experimental and the calculated activities of BeF$_2$ at 898 K are shown in Fig. 3.

There is not experimental evidence of a miscibility gap on the BeF$_2$-rich side, however, Vallet and Braunstein [14] and Van der Meer et al. [15] calculated the LiF–BeF$_2$ phase diagram with a miscibility gap in the liquid phase. Our calculated diagram also contains a miscibility gap in the liquid phase in order to let the calculated activities of BeF$_2$ and the integral enthalpy of mixing be in concordance with the experimental data.

All the above experimental data were used as input to a least squares optimization program in order to find the coefficients of Eqs. (9) and (10) which best reproduce all the data. The following parameters were found for the liquid:

$$\omega = -13360.7 + 11,302X_{BeF_2} + 24721.6X_{BeF_2}^3 \text{ J/mol} \tag{21}$$

$$\eta = 8.4924 + 16.378X_{BeF_2}^2 \text{ J/mol K} \tag{22}$$

Calculated concentrations of free fluoride ions (N_{F^-}), coordinated only to Li, monomers, dimers, trimers and tetramers for the LiF–BeF$_2$ system at 1073 K are presented in Fig. 4. Also shown in this figure are chain-length distribution calculated by Salanne et al. [4] using a polarizable ionic interaction potential, constructed from first-principles calculations. They reported the percentage of F

Table 1
Thermodynamic properties of the compounds in the LiF–BeF$_2$ system relative to elements at 298.15 K.

	A	B	a	b	c
LiF(l) (298–1121 K)	−589844.0	59.81700	42.68889	17.41843	−5.300714
LiF(l) (>1121 K)	−598660.0	42.91200	64.18300	–	–
LiF(s) (298–1121 K)	−616931.0	35.6600	42.68889	17.41843	−5.300714
BeF$_2$ (l) (> 825 K)	−1021620.0	61.0410	57.92259	29.65952	−19.39668
BeF$_2$ (l) (298–825 K)	−1021340.0	60.2950	47.36373	33.47047	–
BeF$_2$ (high-quartz type) (500–825 K)	−1026090.0	54.5290	47.36373	33.47047	–
BeF$_2$ (low-quartz type) (298–500 K)	−1026750.0	53.354	−9.045279	161.01792	11.45922
Li$_2$BeF$_4$(s) (298–732.2 K)	−2273586.0	131.085	90.08061	149.09586	–
LiBeF$_3$(s) (298–650 K)	−1651843.0	89.245	54.39380	125.51688	–

$H \ (\mathrm{J\,mol^{-1}}) = A + \int_{298.15}^{T} Cp \, dT; \quad S \ (\mathrm{J\,mol^{-1}\,K^{-1}}) = B + \int_{298.15}^{T} \left(\frac{Cp}{T}\right) dT; \quad Cp \ (\mathrm{J\,mol^{-1}\,K^{-1}}) = a + b(10^{-3})T + c(10^{5})T^{-2}.$

atoms in various polymeric species as function of composition and we transformed them into the concentrations per mole of solution of monomers (N_1), dimers (N_2), trimers (N_3) and linear tetramers (N_4) assuming that they contain 4, 7, 10 and 13 fluorine atoms, respectively. The agreement in both magnitude and shape between the chain-length distributions calculated by the two models is striking, in view of the fact that the models are formerly different.
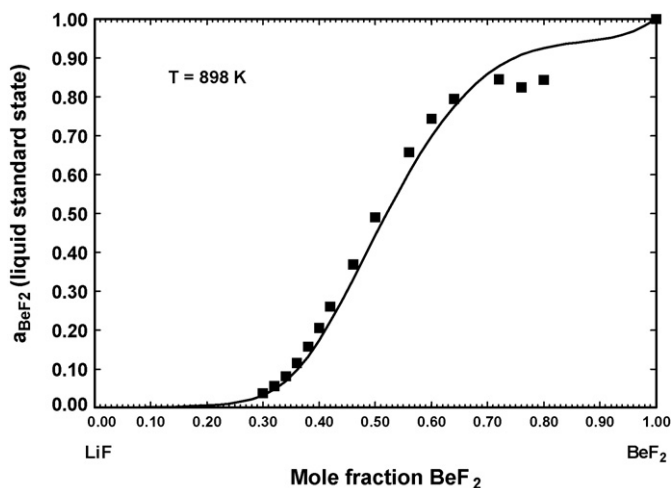
Fig. 3. Activity of BeF$_2$ in liquid LiF–BeF$_2$ system at 898 K. Experimental points: (■) Ref. [13].
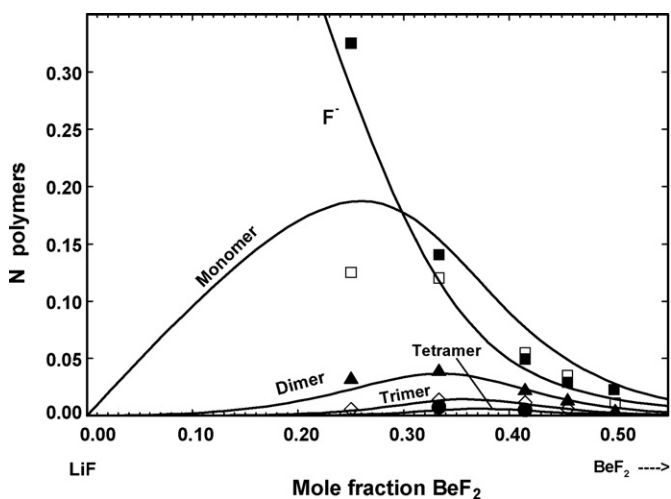
Fig. 4. Calculated fluoride polyanion chain-length distribution in the LiF–BeF$_2$ system at 1073 K. Molecular dynamics model results [4]: (■) F$^-$ is the ion coordinated only to Li; (□) monomers BeF$_4^{2-}$; (▲) dimers Be$_2$F$_7^{3-}$; (◇) trimers Be$_3$F$_{10}^{4-}$; (●) tetramers Be$_4$F$_{13}^{5-}$.
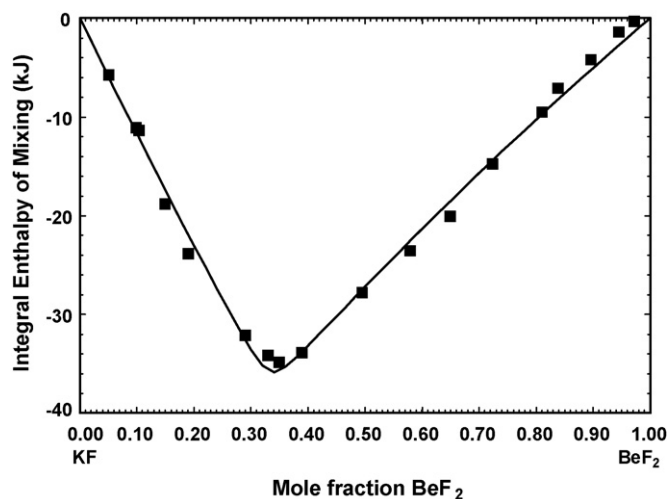
4.2. The KF–BeF$_2$ system

There is a significant uncertainty in the KF–BeF$_2$ phase diagram as well as the thermodynamic data of the intermediate compounds which are formed in this system. The only reliable data correspond to the integral enthalpy of mixing of the liquid determined calorimetrically at 1135 K by Holm and Kleppa [11]. The following parameters were found for the liquid KF–BeF$_2$ system:

$$\omega = -59242.52 + 9123.62X_{\mathrm{BeF_2}} + 1363.96X_{\mathrm{BeF_2}}^2 \ \mathrm{J/mol} \qquad (23)$$

Calculated enthalpies of mixing are plotted in Fig. 5, where they may be compared with the data of Holm and Kleppa [11]. This figure shows that there is a tendency of ΔH^{mix} to peak at $X_{\mathrm{BeF_2}} = 1/3$, which corresponds with the composition of the K$_2$BeF$_4$ compound. The KF–BeF$_2$ phase diagram has been reported by Hu and Novoselova [16], however there are not reliable thermodynamic data of the intermediate compounds of this system and many assumptions should be done in order to calculate this diagram.

Fig. 6 shows the calculated fluoride polyanion chain-length distribution in the KF–BeF$_2$ system at 1073 K. The potassium ion is known to be a better "network-breaker" than lithium and this figure shows that the monomers dominate over most of the composition range in the KF–BeF$_2$ system.

Fig. 7 shows the mixing free energy of the LiF–BeF$_2$ and KF–BeF$_2$ systems at 873 K. This figure also shows that the energy of the KF–BeF$_2$ is much lower than that of the LiF–BeF$_2$ system. This means that K$^+$ and Li$^+$ must play a different role in the network. We can

Fig. 5. Calculated optimized integral enthalpy of mixing of the liquid KF–BeF$_2$ system at 1135 K. Experimental points: (■) Ref. [11].
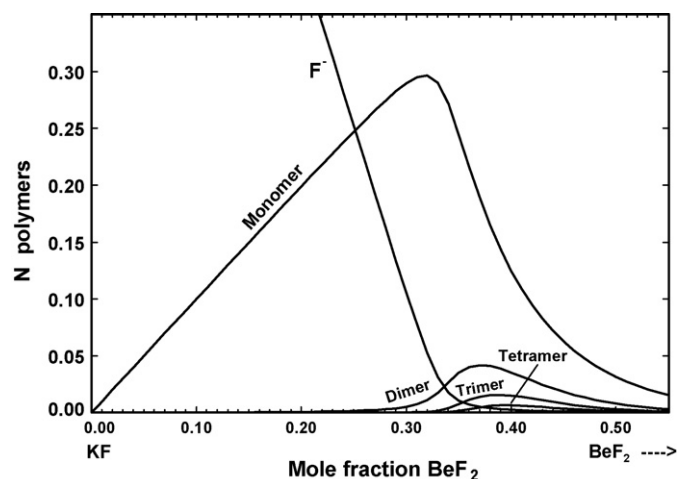
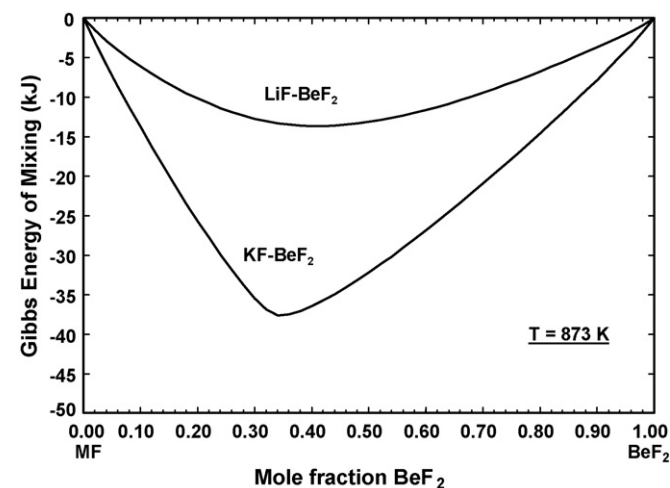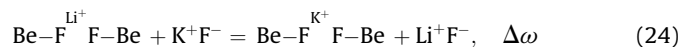**Fig. 6.** Calculated fluoride polyanion chain-length distribution in the KF–BeF$_2$ system at 1073 K.

Fig. 7. Calculated Gibbs free energy of mixing of the LiF–BeF$_2$ and KF–BeF$_2$ binary systems at 873 K.

explain this behavior according to the following reaction:

$$Be-\overset{Li^+}{F}\ F-Be + K^+F^- = Be-\overset{K^+}{F}\ F-Be + Li^+F^-, \quad \Delta\omega \quad (24)$$

where $\Delta\omega = (\omega - \eta T)_{KF-BeF_2} - (\omega - \eta T)_{LiF-BeF_2}$. At 873 K and $X_{BeF_2} = 1/3$ the value of $\Delta\omega$ for the BeF$_2$–LiF–KF system is around -39 kJ/mol and reaction (24) moves to the right, then the cations K$^+$ will be found associated to the Be–F network and the cations Li$^+$ will be close to the free fluoride ion F$^-$.

Some thermodynamic model have been developed to study the LiF–BeF$_2$ liquid system [3,15] with relatively mathematical simplicity. However, these models do not give the insight into the fluoride melt structure. The model that we propose permits all available thermodynamic and phase diagram data to be optimized simultaneously. From the model equations, all of the thermo-dynamic properties and the phase diagram can be back-calculated. The model also predicts the chain length distribution of the polymeric fluoride chains.

5. Conclusions

The evaluation of the available thermodynamic and phase diagrams data for the binary LiF–BeF$_2$ system have been carried out with a structural model for glasses. This model is based on the assumption that each alkali fluoride produces the depolymeriza-tion of the BeF$_2$ polymeric network with a characteristic free-energy change. The model parameters for the liquid phase were obtained through a least squares optimization method. This model was also used to calculate the integral enthalpy of mixing of the KF–BeF$_2$ system.

The model predicts the chain-length distribution of polymeric anions, even though these are not explicitly considered in the model. The results for LiF–BeF$_2$ are in quantitative agreement with the predictions obtained by Salanne et al. [4]

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