Miscibility Gaps in Fused Salts

Note IX. Systems of Lithium Fluoride with Zinc, Lead and Cadmium Bromides

Chiara Margheritis, Giorgio Flor, and Cesare Sinistri

Centro di studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi del CNR
and Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforsch. **30 a**, 896–899 [1975]; received June 2, 1975)

An analysis was made of the demixing phenomena in the reciprocal ternaries Li, Me/Br, F (Me = Zn, Pb, Cd). It was found that the system Li, Zn/Br, F shows only a "tendency" to demix; the system Li, Pb/Br, F exhibits a miscibility gap (MG) which could be completely detected in the whole composition square; finally the system Cd, Li/Br, F shows a MG which was only partially measured along the stable diagonal.

The trend in demixing of these systems agrees with the values of the standard enthalpy variations of the metathetical reactions.

To increase the knowledge of the molten systems containing LiF, which show demixing phenomena, in the present work the stable diagonals of the ternaries Li, Zn/Br, F; Li, Pb/Br, F and Cd, Li/Br, F were studied. For the system containing lead, since the MG could be completely detected, it was found convenient to extend the study to the whole composition square.

To our knowledge, there are no experimental data available in literature on these systems.

The apparatus, the experimental technique and the characteristics of the employed salts were described in previous papers of this series [1].

Results and Discussion

Figure 1 reports the SL and LL equilibria for the pseudo-binaries $LiF + ZnBr_2$; $LiF + PbBr_2$ and $CdBr_2 + LiF$. As it can be observed, the first one shows no demixing: the liquidus curve is clearly "S" shaped, thus indicating only a tendency to demix. In the composition range close to pure $ZnBr_2$, measurements could not be carried out because of gel formation.

For the system $PbBr_2 + LiF$, the demixing area (shaded) was completely detected: the interpolated compositions, in molecular fractions, at which, by

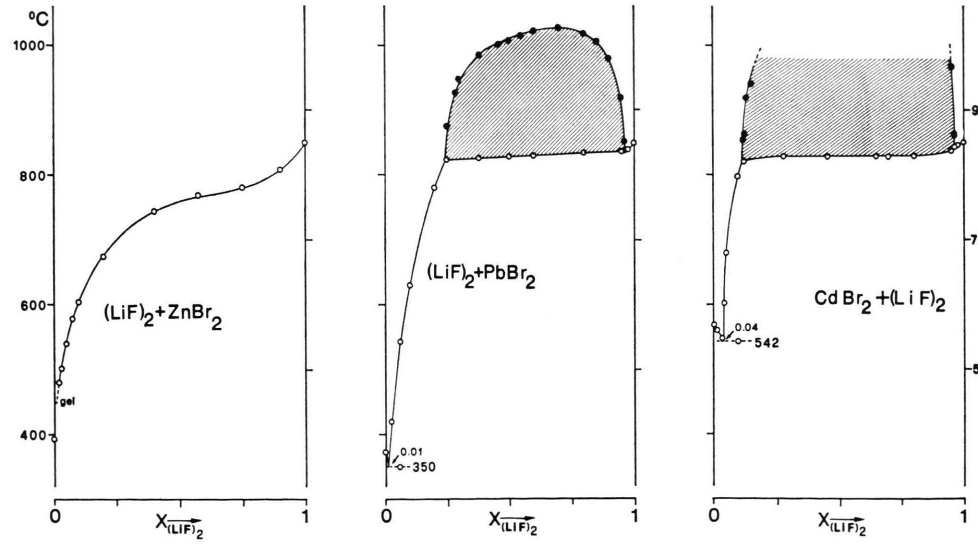

Fig. 1. SL and LL equilibria for the systems $LiF+ZnBr_2$, $LiF+PbBr_2$ and $CdBr_2+LiF$. The demixing areas are shaded.

Reprint requests to Prof. Cesare Sinistri, Ist. Chimica Fisica, Università di *I-27100 Pavia* (Italy).

cooling and shaking, demixing takes place, are reported in Table 1 as a function of temperature. The coordinates of the point of maximum (PM) are: $x_{(\mathrm{LiF})_2} = 0.70$, $t = 1027$ °C. Along the stable diagonal, the primary crystallization temperature (PCT) increases from 823 to 835 °C while $x_{(\mathrm{LiF})_2}$ varies from 0.24 to 0.95_5.

Table 1. LL equilibrium points for the pseudo-binary $(\mathrm{LiF})_2 + \mathrm{PbBr}_2$.

First phase	Second phase	Temperature (°C)
$x_{(\mathrm{LiF})_2} = 0.243$	$x_{(\mathrm{LiF})_2} = 0.955$	840
0.252	0.953	880
0.277	0.942	920
0.325	0.918	960
0.440	0.865	1000
0.580	0.790	1020
0.700	0.700	1027 (PM)

To fully describe the topology of the mixture Li, Pb/Br, F, the four binaries which are the sides of the composition square and 10 cuts were studied.

Figures 2, 3 show the SL equilibria and the coordinates of the eutectics of the four binaries. The system $\mathrm{PbBr}_2 + \mathrm{PbF}_2$ shows a compound 1:1 which melts congruently at 576 °C, and a 1:4 compound which decomposes at 579 °C. These results are in agreement with those reported by Sandonnini[2]. In the stability field of solid PbF_2 ($1 \geqq x_{\mathrm{PbF}_2} > 0.8$), two different thermal effects at about 360 and 410 °C were observed by DTA measurements. These effects were not satisfactorily reproducible, their presence being dependent on the thermal history of the sample. X-ray diffraction patterns taken on pure PbF_2 at different temperatures yielded the following information. On samples slowly heated, first an orthorombic phase[3] stable up to about 350 °C, then a cubic phase[3] stable up to about 400 °C was observed. According to Ssauka[4] the orthorombic-cubic transition starts at 316 °C. On cooling, these transitions were no longer present: the phase stable at high temperature persists down to room temperature for a long time.

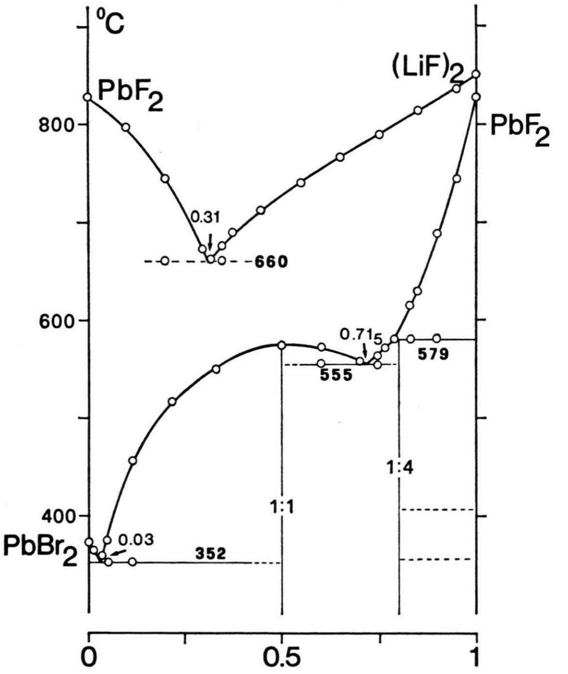

Fig. 2. Phase diagrams for the binaries $\mathrm{LiF} + \mathrm{PbF}_2$ and $\mathrm{PbBr}_2 + \mathrm{PbF}_2$.

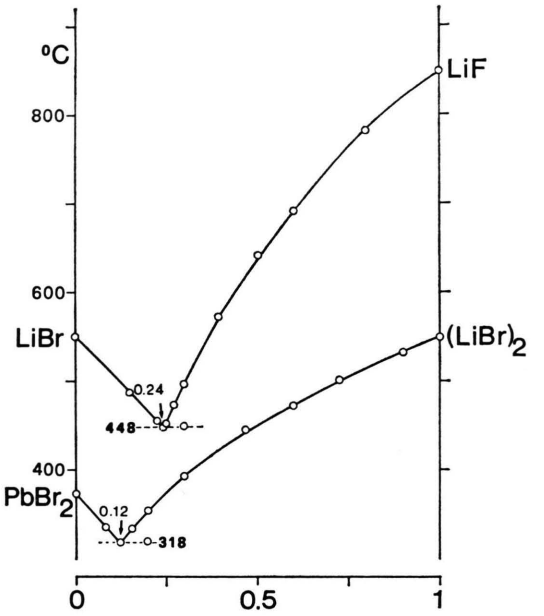

Fig. 3. Phase diagrams for the binaries $\mathrm{LiBr} + \mathrm{LiF}$ and $\mathrm{LiBr} + \mathrm{PbBr}_2$.

As regards the binary $\mathrm{LiF} + \mathrm{PbF}_2$, no data are available in literature. For the binaries containing LiBr (see Fig. 3) Bergman et al.[5] reported data in agreement with those of the figure.

Figure 4 reports the unstable diagonal $\mathrm{LiBr} + \mathrm{PbF}_2$: the PCT varies from 766 °C ($x_{(\mathrm{LiBr})_2} = 0.64_5$) to 785 °C ($x_{(\mathrm{LiBr})_2} = 0.35$) through a maximum at 835 °C ($x_{(\mathrm{LiBr})_2} = 0.48_5$). The PM of the MG is at 1020 °C ($x_{(\mathrm{LiBr})_2} = 0.48_5$).

The general topology of the system Li, Pb/Br, F is shown in Figures 5 and 6. Figure 5 reports the

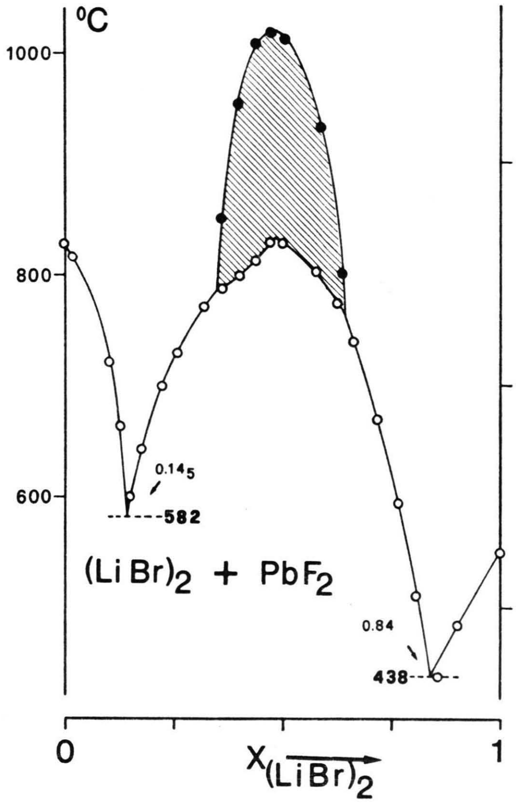

Fig. 4. SL and LL equilibria for the unstable diagonal LiBr+PbF$_2$.

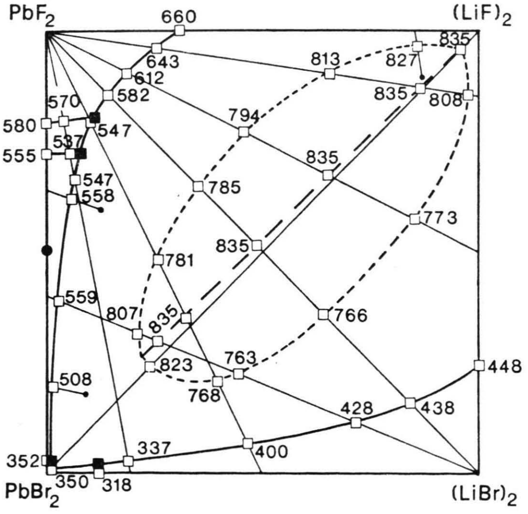

Fig. 5. Diagonal and offdiagonal cuts in the reciprocal ternary Li, Pb/Br, F with some significant temperatures.

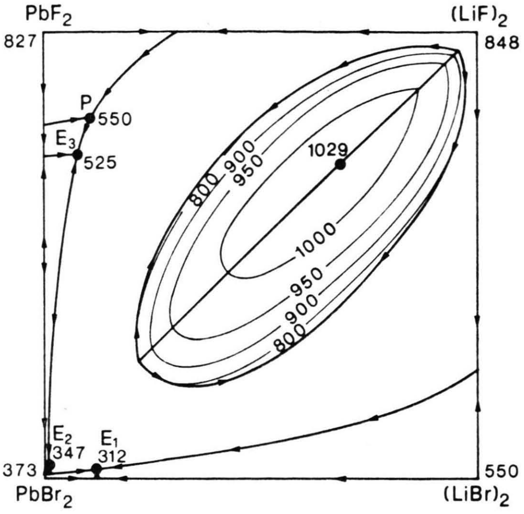

Fig. 6. General topology of the ternary Li, Pb/Br, F with the projections of some LL isotherms.

projections of the studied cuts along with various significant temperatures. The stratification lens (dashed) impinges on the LiF crystallization field and occupies 33.0% of the square. The main axis of the lens is shifted from the principal diagonal towards the PbF$_2$ corner. Along this axis, PCT is constant at 835 °C. Figure 6 reports the projections of some LL isotherms: the upper critical point of the system can be evaluated at $t = 1029$ °C and $x_{(\text{LiF})_2} = 0.38$; $x_{(\text{LiBr})_2} = 0.30$ and $x_{\text{PbF}_2} = 0.32$.

The system presents four invariant points three of which are eutectics. The coordinates of these characteristic points are:

E$_1$:	$t=312$ °C;	$x_{(\text{LiF})_2}=0.02$;	$x_{(\text{LiBr})_2}=0.10$;	$x_{\text{PbBr}_2}=0.88$.
E$_2$:	$t=347$ °C;	$x_{(\text{LiF})_2}=0.01$;	$x_{\text{PbBr}_2}=0.97$;	$x_{\text{PbF}_2}=0.02$.
E$_3$:	$t=525$ °C;	$x_{(\text{LiF})_2}=0.08$;	$x_{\text{PbBr}_2}=0.28$;	$x_{\text{PbF}_2}=0.64$.
P:	$t=550$ °C;	$x_{(\text{LiF})_2}=0.11$;	$x_{\text{PbBr}_2}=0.19$;	$x_{\text{PbF}_2}=0.70$.

The general topology of the system agrees with the triangulation rules.

Finally, the system CdBr$_2$ + LiF shows a large demixing area which has been shaded in the Figure 1. The PCT of this MG increases from 821 to 842 °C while $x_{(\text{LiF})_2}$ varies from 0.11 to 0.96. The upper portion of the gap could not be measured.

On the basis of Fig. 1 it is evident that in the three studied systems the trend in demixing is:

$$\text{Cd-system} > \text{Pb-system} > \text{Zn-system} \qquad (1)$$

this is analogous to what was found for the reciprocal ternaries Li, Me/Br, SO$_4$ (Me = Cd, Pb, Zn) [1].

A guide to understand sequence (1) could be given by the ΔG values of the metathetical reactions at the demixing temperatures. Since data on the corresponding free energies are lacking, in a first rough approximation, one can use the ΔH^0_{298} values of the reaction. Through the data available in literature[6] and the standard heat of formation of ZnF_2 as estimated in the Appendix, the following values were calculated:

$$CdF_2 + 2\,LiBr \rightarrow CdBr_2 + 2\,LiF \quad \Delta H^0_{298} = -35.4 \text{ kcal/mole},$$

$$2\,LiBr + PbF_2 \rightarrow 2\,LiF + PbBr_2 \quad \Delta H^0_{298} = -32.9 \text{ kcal/mole},$$

$$2\,LiBr + ZnF_2 \rightarrow 2\,LiF + ZnBr_2 \quad \Delta H^0_{298} = -26.3 \text{ kcal/mole}.$$

The magnitude of these values follows sequence (1).

Appendix

In order to estimate the H^0_{298} value of solid ZnF_2 (not reported in literature), a search was made for some regularities in the heats of formation of analogous bivalent cation halides.

Among the various regularities observed, the simplest and most effectual one, when the halides of a particular cation are considered, is the linear dependence of $H^0_{29\infty}$ on $1/r_-$, where r_- is the ionic radius[7] of Cl^- (1.81 Å), Br^- (1.96 Å) and I^- (2.20 Å) respectively.

In order to include the fluorides in this behaviour, it was found sufficient to assume for F^- an "apparent" radius of 1.42 Å (crystal radius = 1.33 Å). By means of this assumption and using the experimental values of the heats of formation of the: Ca, Sr, Ba, Cd, Pb, Mg, Cu, Ni chlorides, bromides and iodides, it was possible to estimate the H^0_{298} of the corresponding fluorides with a mean difference (with respect to the experimental value) of ±1.9%. For example, in the case of lead and cadmium halides the following relations were found:

$$H^0_{PbX_2} = 164.47 - 453.07\,(1/r_-) \text{ kcal/mole} \quad (\underline{r}^2 = 0.9998),$$

$$H^0_{CdX_2} = 163.29 - 465.41\,(1/r_-) \text{ kcal/mole} \quad (\underline{r}^2 = 0.998)$$

($\underline{r}^2$ = coefficient of determination which gives a measure of the goodness of the regression line fit; note that if $\underline{r}^2 = 1$ the fit is perfect).
These equations, for $r_- = 1.42$, give: $H^0_{PbF_2} = -154.6$ (exp. value = -158.5; -2.5%) and $H^0_{CdF_2} = -164.5$ (exp. value = -164.9; -0.2%).

An analogous procedure, based on the experimental values of the heats of formation of $ZnCl_2$, $ZnBr_2$ and ZnI_2, gives: $H^0_{ZnF_2} = -177.0$ kcal/mole.

---

[1] a) G. Flor, C. Margheritis, and C. Sinistri, Z. Naturforsch. **26 a,** 1322 [1971]; — b) C. Margheritis, G. Flor, and C. Sinistri, ibid. **28 a,** 1329 [1973].

[2] C. Sandonnini, Gazz. Chim. Ital. **41** II, 144 [1911].

[3] H. E. Swanson, N. P. T. Gilfrich, and G. M. Ugrinic, NBS Circular 539, Vol. **V** (1955).

[4] E. J. Banashek, N. N. Patsukova, and I. S. Rassonskaya, Izv. Sektora Fiz. Khim. Analiza Inst. Obchch. Neorgan. Khim. Akad. Nauk SSSR **27,** 223 [1956].

[5] a) A. G. Bergman and Yu. I. Andryushchenko, Russ. J. Inorg. Chem. 362 [1963]; — b) A. G. Bergman and A. S. Arabadzhan, Russ. J. Inorg. Chem. 636 [1963].

[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, Circular NBS 500, Washington D.C. 1962.

[7] Handbook of Chemistry and Physics, 52th Ed. The Chemical Rubber, Ca., Cleveland, Ohio 1972.