The phase diagram of the RbF–RbI system

Ding Yimin *, Wu Ping, Liu Xu, Zhang Tingting

College of Science, Shanghai University, No. 99 Shangda Road, Shanghai 200444, China

ARTICLE INFO

ABSTRACT

In this paper, the phase diagram of the RbF–RbI system is studied by means of differential thermal analysis (DTA) firstly. The experimental data have been analysis and evaluation by using the thermodynamic calculation and the support vector machine (SVM)–atomic parameter method for the system. The results show that the phase diagram of the RbF–RbI system is of the simple eutectic type, where the eutectic is found to have the composition $X(RbF) = 35$ mol% (melting point $\approx 495\,^\circ$C), and it is suggested that no solid solution form in the system.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Molten salt phase diagrams are of central importance in metallurgy and materials science. Due to the interesting thermodynamic properties, the phase diagrams of the alkali halides have been investigated comprehensively. A large number of measurements on binary alkali halide systems have been performed in earlier investigations. However the phase diagram of the RbF–RbI system had not been determined before. Sangster and Pelton had calculated a tentative phase diagram of this system [1]. They supposed that the system was a simple eutectic with zero solid solubility. They assumed that the mixed enthalpy was $H^E = -3700 X_A X_B$ J mol^{-1} and eutectic was at 485 °C with 43 mol% RbF. However the enthalpy they assumed was not consistent with that of experimental data measured by Kleppa and Melnichak [2]. In order to resolve the uncertainties in this binary system, the support vector machine (SVM)–atomic parameter method has been applied to predict the formability of solid solution. A detailed experimental investigation has been undertaken employing differential thermal analysis (DTA).

2. Computation

Chen et al. has made successful computerized predictions on compound or solid solution formation in molten salt systems by using the SVM–atomic parameter method [3]. This method is utilized to find the regularity of the solid solution formability of the common-cation binary alkali halide MX_1–MX_2 systems. (M is alkali metals element; X_1 and X_2 are halogen element.)

In addition to the atomic parameters, Pauling's ionic radii and Batsanov's electronegativities are used in this work. X is the electronegativities of cation. R_1 and R_2 are ionic radii of X_1 and X_2, respectively. Here the element with the smaller anion is defined as X_1 and the larger one as X_2 in each system. The data from 24 known phase diagrams are used as a training set [4,5]. In computation, the systems that are simple eutectic with zero solid solubility are classified as "class 1", there are 10 systems: CsBr–CsF, CsF–CsI, KBr–KF, KF–KI, LiCl–LiF, LiF–LiI, NaBr–NaF, NaCl–NaF, NaI–NaF, RbBr–RbF. On the other hand, the systems with solid solution are classified as "class 2", there are 14 systems: CsBr–CsI, CsBr–CsCl, CsCl–CsI, KCl–KBr, KI–KBr, KI–KCl, LiBr–LiI, LiCl–LiBr, NaBr–NaCl, NaI–NaCl, NaI–NaBr, RbBr–RbCl, RbBr–RbI, RbCl–RbI. Using the SVM–atomic parameter method, we build a classification model. The criterion of formation for a solid solution in MX_1–MX_2 systems can be roughly expressed as follows:

$$y = 3.92X - 15.69 \left(\frac{R_1}{R_2} \right) + 10.04$$

If $y > 0$, there will be solid solution forms in MX_1–MX_2 systems. While if $y < 0$, there is no solid solution forms in MX_1–MX_2 systems.

According to this criterion, it is reasonable to suppose that the RbF–RbI system is a simple eutectic with zero solid solubility.

* Corresponding author. Tel.: +86 21 66134725.
E-mail address: ymding@shu.edu.cn (D. Yimin).

3. Experimental

The chemicals used in the studies were A.R. Grade RbF and RbI (Acros Organics, New Jersey, USA), their melting point are $795 \pm 5\,°C$ and $656 \pm 5\,°C$ [6,7], respectively. The preparations of samples were performed in a nitrogen-filled dry glove box. The chemicals of RbF and RbI were first dried at $500\,°C$ in vacuum. Mixtures of salts of desired composition were prepared by weighing appropriate quantities RbF and RbI on a AB104-N balance (± 0.1 mg), then mixing and homogenizing them in an agate mortar. About 15 mg of each mixture was packed into a platinum crucible and hermetically covered by a crucible cap for the DTA measurements.

DTA measurements were performed with a DTA–TG type microcomputer differential thermal analysis balance (WCT-1A, Beijing Optical Apparatus Co., China) under a nitrogen atmosphere. The heating rate was $5\,°C\,min^{-1}$. Initially a temperature calibration was performed with In ($154\,°C$), SiO$_2$ ($571\,°C$) and SrCO$_3$ ($928\,°C$) at the same heating rate. Alumina powder was used as the reference material. The measuring range of DTA and the sampling interval were $\pm 25\,\mu V$ and 1000 ms, respectively. The DTA curves were automatically shown on the computer.

4. Results and discussion

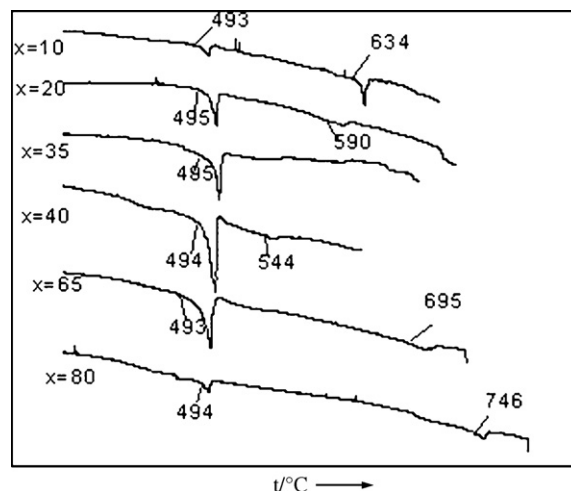The melting points of RbF and RbI measured under the same condition were $790\,°C$ and $650\,°C$, coinciding with the thermochemical data for the pure substance in accuracy $\pm 5\,°C$ in two reports [6,7]. TG analysis showed that it was reasonable to neglect the mass change for all samples. Due to the large degree of undercooling of the system, the transition and liquidus temperature were taken only from the heating curves. The transition temperatures were derived from extrapolated peak onsets for the eutectic reactions and offsets for the liquidus. The compositions (RbF, mol%) of samples are as follows: 0, 10, 20, 30, 35, 40, 55, 65, 70, 80, 90, 100. The results from DTA are given in Table 1. Some typical DTA heating curves are shown in Fig. 1.

From the DTA data, we can see that in the range of 10–90 mol% RbF (excluding the component of 35 mol% RbF), there are apparently two endothermic peaks for each composition of the sample in the heating curve. The first sharp endothermic peak is round $495\,°C$, which corresponds to the eutectic reaction temperature. The second tailed endothermic peak corresponds to the liquidus, which varies with the RbF content of the samples. The only one endothermic peak at $495\,°C$ of the 35 mol% RbF sample indicate the eutectic point, as was confirmed by extrapolation of liquidus curves and Tamman triangle methods. On the basis of the data from the DTA analysis, the phase diagram of the RbF–RbI system is plotted, and shown in Fig. 2.

Table 1
The transition temperature data obtained by DTA

RbF (mol%)	Peak 1 (°C)	Peak 2 (°C)
0		650
10	493	634
20	495	590
30	494	551
35	495	–
40	494	544
55	493	608
65	493	695
70	495	722
80	494	746
90	491	766
100	–	790

Fig. 1. Some DTA curves for the system.

According to the enthalpy of experimental data measured by Kleppa [2], we also calculate the phase diagram. The liquid is a regular solution with an excess enthalpy given by

$$H^E = x_{RbF}x_{RbI}(-3912 + 5977x_{RbF})\,J\,mol^{-1} \tag{1}$$

For a binary regular or sub-regular solution, the relation between activity and the concentration is as follows:

$$RT \ln \gamma_{RbF} = \lambda(x_{RbI})^2 \tag{2}$$

$$RT \ln \gamma_{RbI} = \lambda(x_{RbF})^2 \tag{3}$$

and

$$G^E = H^E = \lambda x_{RbF}x_{RbI} \tag{4}$$

so

$$\lambda = -3912 + 5977x_{RbF} \tag{5}$$

λ is the interactional parameter of binary system. According to the Clausius–Clapyron equation, the temperature of liquidus can be calculated by

$$\ln a = \ln x + \ln \gamma = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) \tag{5}$$

The calculated liquidus temperatures of the system corresponding to the experiment composition are given in Table 2. The phase diagram of the RbF–RbI system according to the calculated value is
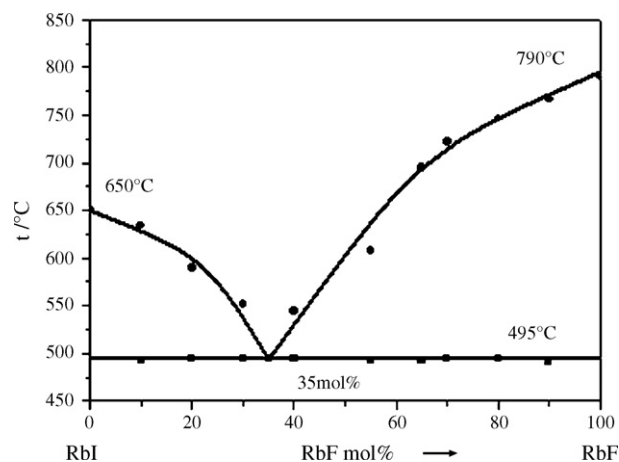
Fig. 2. Phase diagram obtained from experiment.

Table 2
The calculated temperature of liquidus of the RbF–RbI system

X_{Rbf} (%)	t (°C)
0	656
10	623
20	589
30	553
35	508
40	537
55	611
65	661
70	676
80	717
90	756
100	795
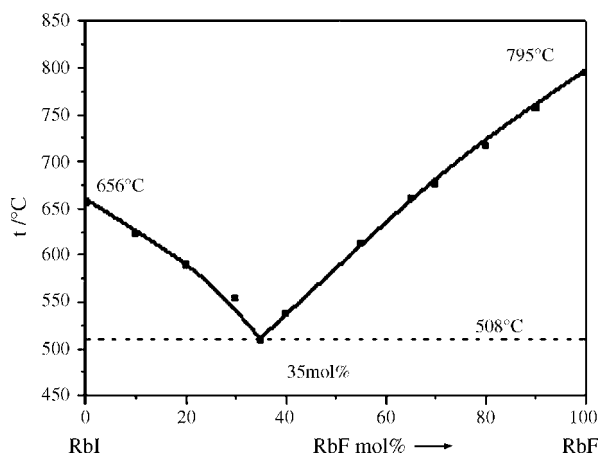
Fig. 3. Phase diagram obtained from calculation.

plotted and shown in Fig. 3, which are identical to the experimental result.

Pelton and Sangster had calculated the eutectic, which is 485 °C, 43 mol% RbF. The difference of the result probably is caused by the different mixed enthalpy. Because the value of enthalpy of RbF–RbI system calculated by Sangster is not consistent with that of the experimental data measured by Kleppa, it is reasonable to explain his calculated phase diagram is different with our experimental results.

5. Conclusion

We have used the SVM–atomic parameter method to find the regularity of the solid solution formability of the common-cation binary alkali halide MX_1–MX_2 systems. On the basis of a criterion found in the paper, it is predicted successfully that the RbF–RbI system is a simple eutectic with zero solid solubility. The result is in good agreement with the measured phase diagram. Furthermore in the measured phase diagram of RbF–RbI system we can see the eutectic is at 495 °C with 35 mol% RbF.

References

[1] J. Sangster, A.D. Pelton, J. Phys. Chem. Ref. Data (1987).
[2] O.J. Kleppa, M.E. Melnichak, Thermochemistry of anion mixtures in binary fused salt systems, in: Proceedings of the 4th International Conference on Chemical Thermodynamics, Montpellier, France, August, 1975.
[3] N.Y. Chen, W.C. Lu, J. Yang, G.Z. Li, Support Vector Machine in Chemistry, World Scientific Publishing Co., Singapore, 2004.
[4] N.K. Voskresinskaya, Handbook for Fusibility of Anhydrous Inorganic Salt Systems, Publisher of Sciences of Soviet Union, Moscow, 1961.
[5] F.E. Pasipaiko, E.A. Alexivoi, Phase Diagrams of Salt Systems, Metallurgy, Moscow, 1977.
[6] I. Barin, Thermochemical Data of Pure Substances, Science Press, Beijing, 2003.
[7] J.A. Dean, Lange's Handbook of Chemistry, 15th ed., Science Press, Beijing, 2003.