

# Phase diagram of the CsCl–RbCl system

Q. ZHANG\*, S. HARADA†, H. TAKAHASHI, M. SAITO, SHIGERU TAMAKI  
*Department of Physics, Faculty of Science and †Faculty of Engineering, Niigata University,  
 Niigata 950-21, Japan*

As part of the systematic research on the phase stability of alkali halides, the phase diagram of the CsCl–RbCl system was determined by using differential scanning calorimetry (DSC) with the help of high-temperature X-ray diffractometry. It is indicated from the phase diagram that the CsCl-enriched solid solution which possesses rocksalt structure and the RbCl-enriched solid solution which also possesses rocksalt structure separate into two phases below 803 K. It is stressed that the elimination of the thermal hysteresis by annealing is important in the precise determination of phase diagram of this system.

## 1. Introduction

It is well known that the alkali halides are representative ionic crystals. The structural properties of alkali halides have been studied over many years. Although their cohesive energy is largely dominated by the Madelung energy, the structural properties of alkali halides depend strongly on the small energy correction, such as van der Waals energy terms. Most of the alkali halides have NaCl structure (B1), while CsCl, CsBr and CsI have CsCl structure (B2) at room temperature. Several models have been proposed [1–3] to evaluate the cohesive energy in order to explain the relative stability of B1- or B2-type structure. In addition to this, the temperature- and pressure-induced phase transitions are understandably based on the empirical rigid ion model [1].

As part of the experimental research on the phase stability of alkali halides, we are interested in the thermodynamic properties of the CsCl–RbCl system. RbCl has B1-type structure at room temperature and does not have any phase transitions to the other structures. On the other hand, CsCl has B2-type structure and transforms into B1-type structure at about 700 K. From their structural properties, mixtures of these halides should offer useful information about the phase stability of alkali halides. It is expected that mixtures of RbCl and CsCl will form solid solutions of B1-type structure in the higher temperature region.

The phase diagram of this system has been reported [4] but is incomplete. This prompted us to report the phase diagram of the CsCl–RbCl system obtained by differential scanning calorimetry with the help of high-temperature X-ray diffractometry.

## 2. Experimental details

The specimens were prepared by the co-melting of CsCl (99.9%) and RbCl (99.9%). In order to desiccate the samples, they were dried at 100°C for 20 h before measurements were made.

The phase diagram was determined by differential scanning calorimetry (DSC) measurements. Thermal analysis was performed at heating rates of 5 and 10 K min, respectively. The calibration of temperature was carried out using standard samples such as indium, tin and zinc metals.

X-ray diffraction patterns at high temperatures were obtained with a diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation.

## 3. Results and discussion

Fig. 1a shows experimental results of the thermal analysis of the specimen  $(\text{Cs}_{0.8}\text{Rb}_{0.2})\text{Cl}$ . The highest peak of absorption of heat appears at about 700 K. This may correspond to B2 and B1 phase transition of the CsCl crystal. However, in this case the peaks would disappear after the sample was annealed in air atmosphere at 533 K for 60 h. The DSC curves became flatter as shown in Fig. 1b. This means that the higher temperature phase (B1-type structure) is more stable below 700 K. This thermal history trend is a common feature of samples of composition  $x = 0.8$  to 0.3, where  $x$  is the mole fraction of CsCl. Therefore, all the samples were annealed before DSC measurements were made. The characteristic features of this flattened peak (Fig. 1b) are as follows; the peak appears at about 593 K and disappears at about 773 K. The flattened peaks observed in the composition range  $x = 0.7$  to 0.3 are shown in Fig. 2. The temperatures at which the flattened peaks appear seem to be unaltered (593 K) with composition, whereas the temperatures at which they disappear change with composition. On the basis of the DSC measurements, the whole phase diagram of the CsCl–RbCl system is outlined in Fig. 3. In order to verify the crystal structures in each phase, high-temperature X-ray diffractometry was performed. The X-ray diffraction patterns of  $x = 0.8$  at room temperature and at 723 K are shown in Fig. 4. In Fig. 4a, the diffraction peaks at 26.8° and 30.7°

\* Present address: Department of Physics, Harbin Normal University, Harbin, Heilongjiang, China.

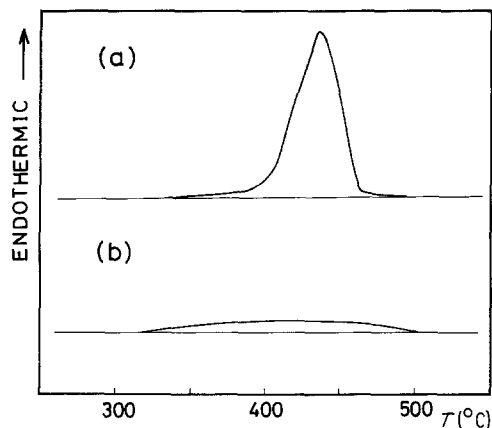


Figure 1 The DSC curves of  $(\text{Cs}_{0.8}\text{Rb}_{0.2})\text{Cl}$  (a) before annealing and (b) after annealing at 533 K for 60 h.

correspond to the Bragg reflections from B1- and B2-type structures, respectively. The reflection from B2-type structure disappears at 723 K and the diffraction peak appears at  $25.6^\circ$ . The Bragg reflections at  $25.6^\circ$  and  $26.4^\circ$  result from the co-existence of CsCl-enriched B1-type structure and RbCl-enriched B1-type structure at 723 K. With the help of high-temperature X-ray diffractometry, the horizontal line at 593 K was verified to be the eutectic line of the B1–B2 phase transition. The B1-type structure above the eutectic point separates into two phases up to 803 K, because of the large difference in the lattice spacing.

After heating to the melting point, the endothermic peaks of DSC from the specimen at  $x = 0.3$  to  $0.7$  were seen to be similar to that of Fig. 1a. This indicates that the solid solutions of B1-type structure are readily supercooled. It is important for precise determination of the phase diagram to anneal the specimen well, in order to remove the thermal history.

For most binary solution systems, the simple regular solution formulae give a good approximation to the thermodynamic properties [5]. In the framework of the regular solution approximation, an increase in the deviation from the ideal mixture leads to phase separation. In the present system, B1-type solid solution separates into two phases below 803 K at  $x = 0.57$ . An extended regular solution model, which includes the anharmonic term given below, was

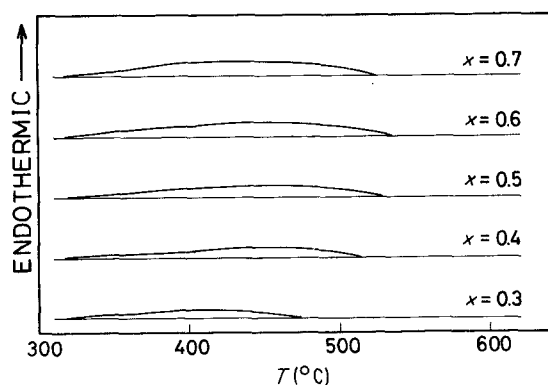


Figure 2 The DSC curves at various compositions, where  $x$  is the mole fraction of CsCl.

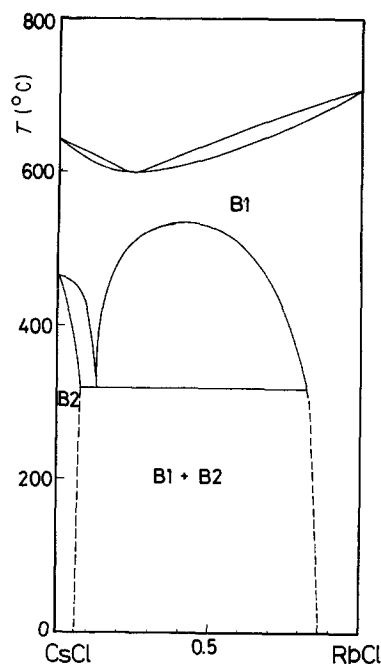


Figure 3 The phase diagram of the CsCl–RbCl system. The identification of the phase and the solubility curves represented by the broken line were determined by powder X-ray diffractometry.

applied in order to explain the asymmetric form of the two-phase region

$$RT \ln a = A(1 - x)^2 + B(1 - x)^3 + RT \ln x \quad (1)$$

The activity coefficients of molten salt,  $a$ , are calculated from the melting curves using Schroder–van Laar equation assuming that the enthalpy of melting is independent of temperature. Simple regular solution was also postulated for the molten CsCl–RbCl system

$$RT \ln a^{\text{liq}} = C(1 - x)^2 + RT \ln x \quad (2)$$

Parameters  $A$ ,  $B$  and  $C$  were determined so as to reproduce the observed phase separation and melting

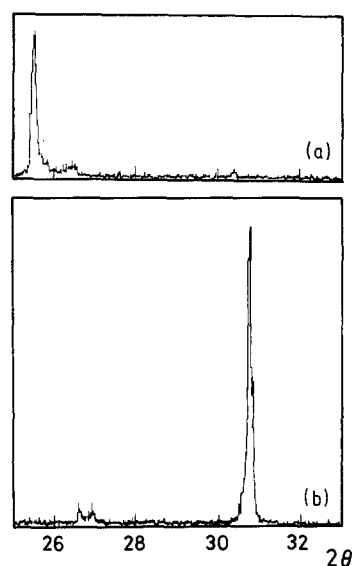


Figure 4 The characteristic X-ray diffraction patterns at the composition of  $x = 0.8$ , using  $\text{CuK}\alpha$  radiation: (a) at  $450^\circ\text{C}$ , (b) at room temperature.

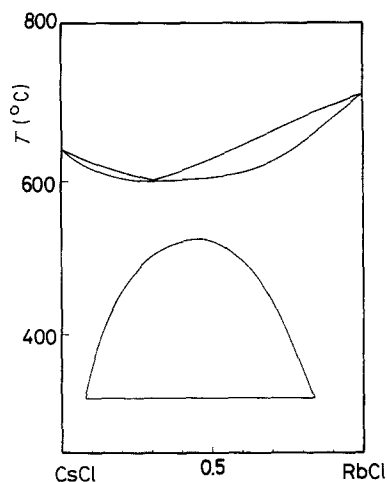


Figure 5 The calculated liquidus and the two-phase separation curve.

curves, and their values are 2187, 1235 and 2000 cal mol<sup>-1</sup>, respectively. The calculated and observed curves are shown in Fig. 5. A good agreement is obtained in both curves in spite of the use of a simple analytic function for the activity coefficient. This fact suggests that the thermodynamic properties of binary ionic solids can be approximately described by the regular solution model. The enthalpy of mixing in some binary liquid halide mixtures were investigated by Hersh and Kleppa [6]. They obtained the interaction parameter  $C$  from a direct measurement of the

enthalpy of mixing only for near the equiatomic composition of the present system and its value was 80 cal mol<sup>-1</sup>. However, the liquidus curve of the present results has a minimum temperature at the intermediate region, which indicates that the thermodynamic properties of the solution deviate considerably from that of ideal solution. Therefore, within the regular solution model, the present values seem to be not unreasonable.

### Acknowledgements

X-ray diffractions were carried out at the Analytical Instruments Laboratory, Niigata University. One of the authors (QZ) is grateful for the financial support of Niigata Prefecture for his stay at Niigata University.

### References

1. M. P. TOSI, *Solid State Phys.* **16** (1964) 1.
2. A. COHEN and R. G. GORDON, *Phys. Rev.* **B12** (1975) 3228.
3. B. G. DICK Jr and A. W. OVERHAUSER, *ibid.* **112** (1958) 90.
4. N. B. CHANH and B. DE LUZY DE PELISSAC, *Bull. Soc. Franc. Miner. Crist.* **91** (1968) 13.
5. I. PRIGOGINE and R. DEFAY, "Chemical Thermodynamics" (Longmans-Green, London, 1954).
6. L. S. HERSH and O. J. KLEPPA, *J. Chem. Phys.* **42** (1965) 1309.

Received 24 August

and accepted 1 December 1987