

## Melting temperatures of some alkali halide mixed crystal systems

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**Abstract.** The melting points in the KCl–KBr, RbCl–RbBr and KBr–RbBr mixed crystal systems have been measured using the microscopic method. In all the three systems, melting points vary nonlinearly with composition, with negative deviations from linearity and maximum deviation at about the equimolar concentration. The observed composition dependence of the melting points is explained qualitatively in terms of the enhanced concentration of point defects and dislocations in mixed crystals.

**Keywords.** Mixed crystals; alkali halides; melting points.

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### 1. Introduction

Several physical properties of mixed crystals of the alkali halides have been studied in recent times. While growth and characterisation aspects of alkali halide mixed crystals have been reviewed by Hari Babu and Subba Rao (1974), Sirdeshmukh and Srinivas (1986) reviewed the physical properties of these mixed crystals. However, data on the melting temperatures of mixed crystals are very scanty. The melting of a crystal takes place at a temperature lower than that predicted from any lattice theory. Weyl (1961) suggested that the presence of a large number of vacancies at temperatures close to the melting point is responsible for the lowering of melting point. Since a mixed crystal has, by its very nature, a defect structure, it would be interesting to study the composition dependence of melting temperatures of mixed crystals.

Slagle and McKinstry (1967) quoted the melting temperatures for KCl–KBr mixed crystals from the work of Lifshitz (1955). Cholokov *et al* (1970) referred to the liquidus curve of KCl–RbCl system, but did not give the actual values of the melting point. Srinivas (1984) calculated the melting temperatures of some alkali halide mixed crystal systems from Debye temperature values using Lindemann's formula.

The composition dependence of melting points of the KCl–KBr, RbCl–RbBr and KBr–RbBr systems has been determined in the present study by hot stage microscopy.

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## 2. Experimental

Mixed crystals of KCl–KBr, RbCl–RbBr and KBr–RbBr with different compositions were prepared by melt growth technique. The starting materials were 99.99% pure AR grade KCl and KBr (supplied by BDH) and RbCl and RbBr (supplied by Fluka). The materials were used in the as supplied form without further purification. The preparation of the mixed crystals was similar to that described by Srinivas and Sirdeshmukh (1985).

In KCl–KBr and RbCl–RbBr mixed crystals, the relative concentrations of chloride and bromide were determined by the potentiometric titration method. The composition of the mixed crystals in the KBr–RbBr system was determined from lattice constants using Vegard's law.

The melting temperatures may be determined by several methods. Pistorius (1966) used the differential thermal analysis (DTA) technique for determining the melting points of alkali halides. Bruton (1974) used a thermobalance and also the DTA technique for the  $\text{Bi}_2\text{O}_3$ – $\text{Ti}_2\text{O}_3$  system. In the present work, melting was observed under a microscope. A simple microscope was modified for the purpose by incorporating on the specimen stage a small heater designed to give temperatures up to  $1000^\circ\text{C}$ . The salient feature of the heater is good thermal insulation so that the microscope parts are unaffected by the presence of the heater even at  $1000^\circ\text{C}$ . A quartz crucible designed so as to just fit into the central region of the heater was inserted into the heater and was used as the sample holder. The change of state of the sample from solid to liquid was visually observed under transmitted light. A chromel-alumel thermocouple could be simultaneously viewed under the microscope. This ensured that the thermocouple was in contact with the sample. The thermo-emf was measured with a  $4\frac{1}{2}$  digit millivoltmeter with 0.02% accuracy. The melting point of the crystals studied was determined as the temperature at which the solid is completely converted into liquid. For each sample at least six measurements were made and the average taken. The standard deviation in the melting temperature varied slightly from crystal to crystal, but was always close to  $\pm 2^\circ\text{C}$ .

For standardizing the procedure adopted, the melting temperatures of several standard substances having values between  $100^\circ\text{C}$  and  $800^\circ\text{C}$  were measured. The results for some of these substances are given in table 1. It is seen that the present results agree reasonably with earlier values.

Table 1. Melting points of some standards.

Substance	$t_m$ $^\circ\text{C}$	
	present	from CRC Hand Book*
Acetanilide	109	113
$\text{NaClO}_3$	262	248–261
RbBr	693	682
RbCl	718	715
KBr	734	730
KCl	770	776

CRC Handbook of Physics and Chemistry  
(Chemical Rubber Co., Cleveland, Ohio), 1971.

**Table 2.** Accuracy obtained in the experiments on melting point determinations by different workers.

Author	Method	Accuracy
Clark Jr (1959)	DTA	$\pm 5$ C & $\pm 10$ C
Pistorius (1965)	DTA	$\pm 5$ C to $\pm 8$ C
Kruger and Moser (1967)	V shaped tungsten filament in conjunction with a pyrometer	$\pm 30$ C
Akella <i>et al</i> (1973)	DTA	$\pm 7$ C to $\pm 10$ C
Bruton (1974)	thermobalance and DTA	$\pm 3$ C
Present work	hot stage microscopy	$\pm 5$ C

As a further check on the accuracy of the results obtained, the melting points of KCl and KBr crystals were also measured by DTA technique. Heating was done in air at the rate of  $10^{\circ}\text{C}/\text{min}$ . Melting temperature of  $768^{\circ}\text{C}$  and  $740^{\circ}\text{C}$  were obtained for KCl and KBr respectively by DTA measurements. These are in good agreement with the values obtained in this study by hot stage microscopy ( $770^{\circ}\text{C}$  and  $734^{\circ}\text{C}$ ).

Different workers have reported different accuracies of measurement (table 2). When the accuracy of the present method was compared with that of other methods, the present procedure seems to be satisfactory as an overall accuracy of  $\pm 5^{\circ}\text{C}$  is obtained in the melting temperatures.

### 3. Results

The melting points of the mixed crystals in the systems KCl–KBr, RbCl–RbBr and KBr–RbBr have been measured over the whole composition range. These results are given in table 3. These values are also plotted in figure 1. For the KCl–KBr system, the melting points given by Slagle and McKinstry (1967) are also included in the figure. For the other two systems there is no earlier work. The present results for KCl–KBr are in good agreement with those of Slagle and McKinstry within experimental errors. Further, it can be seen from the figure that the variation of melting points with composition is non-linear for all the three systems. The deviations from linearity are negative, i.e. the measured values are below the straight line joining the values of the end members. Further, the maximum deviation occurs at about the equimolar composition. The maximum deviations from linearity are  $19^{\circ}\text{C}$ ,  $19^{\circ}\text{C}$  and  $16^{\circ}\text{C}$  in the KCl–KBr, RbCl–RbBr and KBr–RbBr systems respectively. These deviations are much larger than the experimental uncertainty of  $\pm 5^{\circ}\text{C}$  discussed earlier.

### 4. Discussion

As mentioned in the preceding section, the composition dependence of the melting points ( $t_m$ ) for the three mixed crystal systems studied viz. KCl–KBr, RbCl–RbBr and KBr–RbBr is nonlinear with negative deviations from linearity. This is similar to the observations by Slagle and McKinstry (1967) in KCl–KBr system and by Singh

Table 3. Melting points ( $t_m$  in °C) of alkali halide mixed crystals.

$KCl_xBr_{1-x}$				$RbCl_xBr_{1-x}$		$K_xRb_{1-x}Br$	
Mole fraction (x)	$t_m$ present	Mole fraction (x)	$t_m$ Slagle & McKinstry	Mole fraction (x)	$t_m$ present	Mole fraction (x)	$t_m$ present
0.00	734 (730)*	0.00	740	0.00	693 (682)*	0.00	693
0.15	734	0.30	736	0.25	684	0.13	693
0.28	733	0.40	734	0.40	682	0.37	698
0.41	733	0.62	738	0.50	688	0.53	699
0.51	732	0.83	752	0.75	698	0.58	696
0.61	732	1.00	775	0.80	704	0.67	700
0.66	738			1.00	718	0.76	713
0.79	754				(715)*	0.93	726
0.86	759					1.00	734
0.93	765						
1.00	770 (776)*						

\*Values from CRC Handbook of Physics and Chemistry (Chemical Rubber Co., Cleveland, Ohio), 1971.

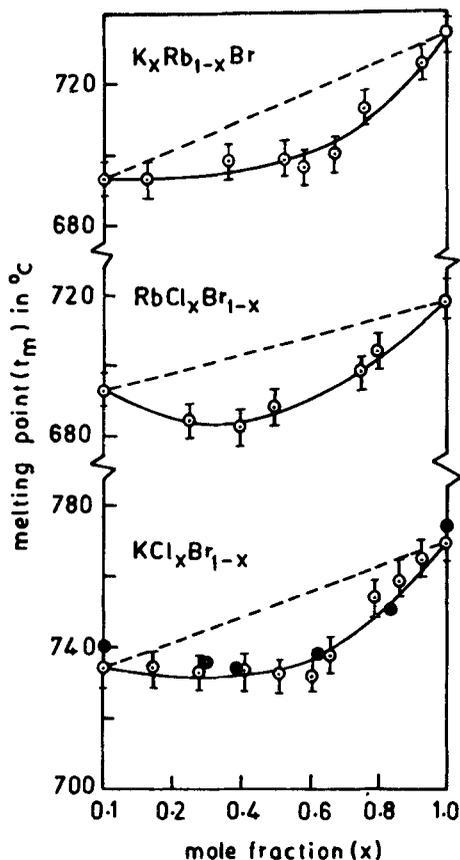


Figure 1. Variation of melting point ( $t_m$ ) with composition ( $x$ ) for the KCl-KBr; RbCl-RbBr and KBr-RbBr mixed crystal systems. Dashed lines represent variation expected from additivity rule. ● Slagle and McKinstry (1967); ○ Present work.

(1970) for the AgCl–AgBr system. Thus, while the magnitude of the deviation from linearity differs from system to system, the sign of the deviation seems to be the same for all the mixed crystal systems studied.

Ubbelhode (1978) discusses two approaches to the problem of melting viz., the vibrational and the mechanical approach. The former approach is based on Lindemann's (1910) picture of melting. As the temperature increases, the amplitude of atomic vibrations increases and when its value as a fraction of the interatomic distance reaches a critical value, the crystal would become mechanically unstable. An exact verification of this picture has not been possible because of several difficulties. Firstly, the critical value of the amplitude of vibration varies from structure to structure (Shapiro 1970); secondly, the amplitudes of vibration are affected by anharmonicity (Gupta 1983) and thirdly, experimental data on the amplitudes of vibration near melting point are scarce.

An outcome of Lindemann's theory (Lindemann 1910) has been the so called Lindemann melting point formula,

$$\nu = C(T_m/MV^{2/3})^{1/2} \quad (1)$$

where  $\nu$  is the characteristic frequency,  $T_m$  the melting point in  $^{\circ}\text{K}$ ,  $M$  the atomic mass and  $V$  the molar volume. This formula can be used either to estimate the characteristic frequency from the melting temperature, or the melting temperature from the characteristic frequency. Adopting the former approach, Ubbelhode (1978) calculates the ratio of the characteristic frequency estimated from Lindemann's formula to that calculated from experimental data on specific heats. Ubbelhode finds that in most of the crystals for which the calculations were made, the ratio was less than unity. This implies that the observed melting temperatures are lower than that for the ideal lattice.

The mechanical approach is based on Born's stability conditions (Born 1939), according to which for a cubic crystal

$$C_{11} - C_{12} \geq 0 \quad (2)$$

and

$$C_{44} \geq 0. \quad (3)$$

Here  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  are the elastic constants. The melting temperature can be taken as the temperature at which the elastic constants reach this limiting value. Using experimental data on the temperature variation of elastic constants, melting temperatures were estimated in this way for NaCl and KCl by Slagle and McKinsty (1967), for NaI and KI by Barsch and Shull (1971) and for several alkali halides by Jackson and Liebermann (1974). In all these cases, it was observed that the estimated melting point was higher than the experimental melting point. Thus, both the vibrational and mechanical approaches lead us to the conclusion that the melting point of a real crystal is lower than that calculated for a perfect crystal.

According to Weyl (1961) crystals develop a large concentration of lattice vacancies as the temperature approaches the melting point. These vacancies in turn change the nature of binding forces in their vicinity producing fluctuating fissures which permit easy flow. Cahn (1978) has pointed out that melting occurs when the vacancy concentration attains a critical value of 0.37%. A linear correlation has been observed between melting temperature and vacancy formation energy for alkali halides (Barr and Lidiard 1970). According to another defect model of melting (Ubbelhode 1965), at high enough temperatures, there is a catastrophic increase in dislocation density

which leads to the loss of crystallinity. Cahn (1978) discusses a model where both types of defects play a role. The increase in population of dislocations 'cuts the crystal structure to pieces', large number of point defects are created and the combination of liquid-like disorder in dislocation cores and large point defect concentrations destroy crystalline order at an effective melting temperature. Thus, qualitatively at least, the lowering of the melting point from that of an ideal crystal to that of a real crystal seems to be due to the presence of point defects as well as dislocations.

There is considerable evidence to show that the concentration of point defects is greater in mixed crystals than in pure crystals. Evidence to this effect was obtained by Wallace and Flinn (1953) and Wollam and Wallace (1956) in their pycnometric studies on KCl–KBr and NaCl–NaBr systems. Further, Arends *et al* (1965) and Thyagarajan (1966) on the basis of their studies of colour centres in alkali halide mixed crystals observed that the concentration of vacancies is more in mixed crystals than in pure crystals, the concentration being maximum for mixed crystals with equimolar composition. There is also evidence to show that the concentration of dislocations is more in mixed crystals than in pure crystals (Arends *et al* 1965; Subba Rao and Hari Babu 1978 and Hussain *et al* 1988), the crystals with equimolar composition having the maximum dislocation density.

Thus, lattice vacancies and dislocations lower the melting points of pure crystals and because of the comparatively larger concentrations of vacancies and dislocations, the lowering is all the more in mixed crystals. If the defects in mixed crystals (vacancies, as well as, dislocations) were comparable in concentration to those in pure crystals, the composition dependence of melting point might have been additive (linear). The existence of these defects in higher concentration in the mixed crystals results in the depression of the melting point of the mixed crystal in comparison to the value predicted from additivity. This deviation from additivity increases as we approach the equimolar composition from either end resulting in a melting point versus composition curve which is non-linear with negative deviations from linearity. This picture should qualitatively explain the observed composition dependence of melting temperatures of mixed crystals.

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