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Thermal expansion and Debye temperatures of KCl–KBr mixed crystals by an X-ray method

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The precision lattice parameters and the coefficients of thermal expansion of KCl, KBr, and their solid solutions have been determined as a function of temperature by an X-ray method using a high-temperature powder camera. From the X-ray diffractograms obtained at room temperature the Debye–Waller factors, Debye temperatures and the root mean square amplitudes of vibration of these mixed crystals have been evaluated. A linear relationship is obtained between the lattice parameter and the composition of the solid solution in accordance with Vegard's law. Both of the thermal parameters, the thermal expansion coefficient and the root mean square amplitude of thermal vibration, vary non-linearly with increasing mole percentage of KBr, the deviation from linearity being maximum around equimolar concentration. The composition dependence of these parameters is discussed in relation to a number of physical properties of these mixed crystals available in the literature.

1. Introduction

KCl and KBr, which are miscible in each other in all proportions, form a homogeneous solid solution over the entire composition range. For the past two decades extensive work has been done on these mixed crystals. Properties like microhardness [1, 2], dislocation density [2, 3], dielectric constant [4], piezo-optic birefringence [5], ionic conductivity [6], elastic constants [7, 8] and melting points [8] have been studied. A perusal of the literature shows that there are no data on the thermal expansion of these mixed crystals. Though the thermal expansion of pure crystals, KCl and KBr, has been studied extensively both by X-ray and macroscopic methods [9–18], there are large discrepancies among the results of the various workers. Hence, studies on the thermal expansion and Debye temperatures of mixed crystals of KCl and KBr, along with the pure crystals, have been undertaken with a view to correlating the results obtained with the other available physical properties.

2. Experimental details

Powder samples were obtained from single crystals of KCl, KBr and their solid solutions provided by Drs V. Hari Babu and Ravindharan Ethiraj of the Department of Physics, Osmania University. The details of the growth and determination of the composition of the crystals have been described by them elsewhere [6, 19]. The samples annealed at 300° C gave well-resolved sharp lines in the high-angle region. Specimens were prepared by putting the powders in 0.5 mm diameter thin-walled quartz capillaries. Using a Unicam 19 cm high-temperature powder camera, powder photographs were taken at different temperatures ranging from room temperature (30° C) up to temperatures close to the melting points of KCl and KBr, and from 30° to 635° C in the case of the mixed crystals. Seven photographs were obtained in each case. Cu$K\alpha$ radiation for pure crystals and Fe$K\alpha$ for mixed crystals were used. Temperature control was facilitated by the use of a voltage stabilizer and a Variac, and the temperature could be held constant to within about 2° C. The details of the experimental set-up and the construction of the camera have been described in an earlier paper [20]. Spectroscopically pure silver was used for the temperature calibration.

Reflections from (600) α_1, α_2; (622) α_1, α_2; (640) α_1, α_2 and (642) α_1, α_2 planes were recorded in the Bragg angle region 45° to 61° in the case of pure KCl and KBr, and reflections from (440) α_1, α_2; (600) α_1, α_2 and (622) α_1, α_2 planes in the Bragg angle region 57° to 81° in the case of the mixed crystals were used in determining the lattice parameters by Cohen's analytical method [21]. Above 300° C, since the intensities of some of the high-angle reflections were considerably diminished, a few of the low-angle reflections were also included in the lattice parameter determination at higher temperatures. In evaluating the lattice parameters, independent measurements and calculations were made on several films and the average of the deviations of the individual values from the mean was taken as the error in the lattice parameters. The mean

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TABLE I Lattice parameters of KCl, KBr and their solid solutions at room temperature (30° C)

Composition (mol %)	Source	Lattice parameter (nm)
KCl	Ravindharan Ethiraj [19]	0.628 77 ± 0.000 04
	Present study	0.628 68 ± 0.000 015
KCl–14 KBr	Ravindharan Ethiraj [19]	0.634 14 ± 0.000 04
	Present study	0.633 09 ± 0.000 015
KCl–31 KBr	Ravindharan Ethiraj [19]	0.639 67 ± 0.000 04
	Present study	0.637 46 ± 0.000 015
KCl–38.5 KBr	Subba Rao [36]	0.640 96 ± 0.000 04
	Present study	0.640 89 ± 0.000 015
KCl–57 KBr	Ravindharan Ethiraj [19]	0.645 83 ± 0.000 04
	Present study	0.644 30 ± 0.000 015
KCl–79 KBr	Ravindharan Ethiraj [19]	0.652 26 ± 0.000 04
	Present study	0.651 21 ± 0.000 015
KBr	Hanawalt *et al.* [27]	0.658 8
	Present study	0.658 58 ± 0.000 015

TABLE II Lattice parameters of KCl and KBr at different temperatures

Temperature (°C)	Lattice parameter (nm)	
	KCl	KBr
30	0.628 68	0.658 58
112	0.630 33	0.660 73
220	0.632 96	0.663 85
365	0.637 09	0.668 08
490	0.640 67	0.672 12
590	0.643 86	0.675 38
715	–	0.679 82
760	0.649 38	–

standard error in the lattice parameters was found to be about 1.5×10^{-5} nm. The error was found to be of the same order at higher temperatures. From the lattice parameter against temperature data the coefficients of thermal expansion at various temperatures were evaluated by a graphical method described by Krishna Rao *et al.* [22].

For determining the Debye–Waller factors of KCl, KBr and their solid solutions at room temperature, the X-ray diffractograms were obtained on a Philips diffractometer. Filtered copper radiation was used together with a proportional detector. The profiles of the (2 0 0), (2 2 0), (2 2 2), (4 0 0), (4 2 0), (4 2 2), (6 2 0) and (6 2 2) reflections were recorded. Before the integrated intensity data were analysed, each peak was corrected for thermal diffuse scattering following the method of Chipman and Paskin [23]. Scattering factors (corrected for anomalous dispersion), Lorentz polarization factors and multiplicity factors were taken from the International Tables for X-ray crystallography [24–26]. A plot of log I_0/I_c against $\sin^2\theta/\lambda^2$ for all reflections was drawn for each crystal and the slopes of the straight lines obtained by least-squares treatment to give the Debye–Waller factors. From these factors the values of the Debye temperatures and the root mean square amplitudes of vibration were evaluated.

3. Results

3.1. Lattice parameters

The lattice parameters of KCl, KBr and their solid solutions, obtained at room temperature in the present study, are given along with the available data in the literature in Table I. In addition to these, a large number of workers have determined the lattice parameters of pure KCl [9, 16, 18, 19, 27–36] and of pure KBr [17–19, 27, 28, 31, 33, 36–40] at room temperature. These values vary from 0.6277 to 0.6307 nm for KCl and from 0.6577 to 0.6616 nm for KBr. The present values are in agreement with those obtained by Ravindharan Ethiraj [19] for KCl and Hanawalt *et al.* [27] for KBr. In the case of the mixed crystals, all the reported values are higher than those obtained in the present investigation.

The lattice parameters obtained at different temperatures are given in Tables II for KCl and KBr and in Table III for mixed crystals, and are shown graphically for all the crystals in Fig. 1. It can be seen that the lattice parameter for all the compositions increases non-linearly with increasing temperature.

3.2. Coefficients of thermal expansion

The coefficients of thermal expansion evaluated at various temperatures for all the crystals are given in Table IV. The temperature dependence of the coefficients of thermal expansion can be represented by an equation of the type

$$\alpha_T = A + BT + CT^2 \qquad (1)$$

where α and T are expressed in reciprocal degrees

TABLE III Lattice parameters (nm) of KCl–KBr mixed crystals at different temperatures

Temperature (°C)	KCL–14 mol % KBr	KCl–31 mol % KBr	KCl–38.5 mol % KBr	KCl–57 mol % KBr	KCl–79 mol % KBr
30	0.633 09	0.637 46	0.640 89	0.644 30	0.651 21
120	0.635 11	0.640 11	0.642 89	0.646 53	0.653 39
214	0.637 57	0.642 66	0.645 69	0.649 79	0.655 78
325	0.640 97	0.646 32	0.648 98	0.653 05	0.659 68
435	0.644 36	0.649 48	0.652 30	0.656 38	0.663 52
550	0.648 08	0.653 16	0.656 12	0.660 02	0.667 69
635	0.651 08	0.656 08	0.658 71	0.663 28	0.670 82

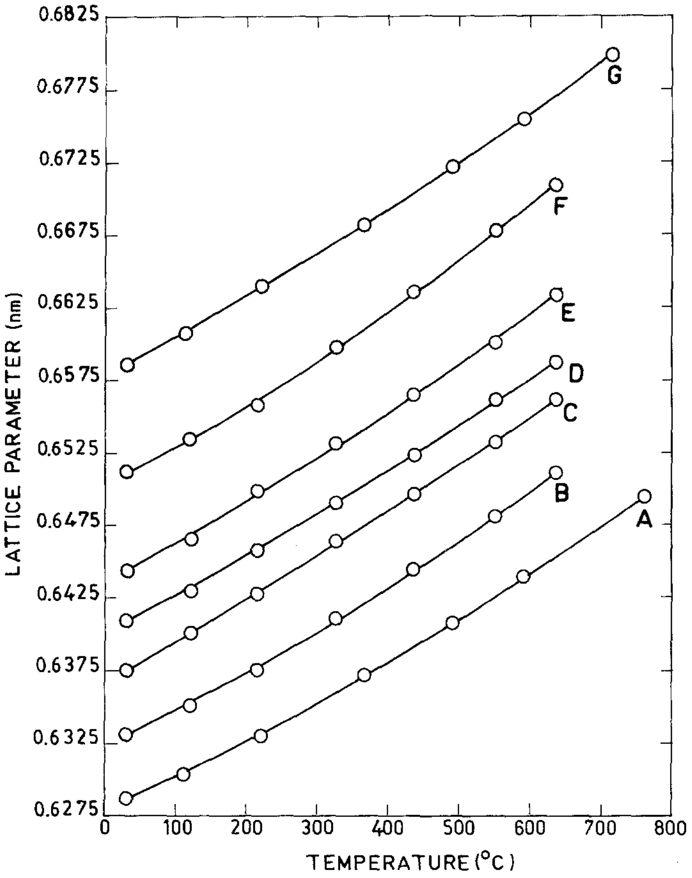

Figure 1 Variation of lattice parameters of KCl, KBr and their solid solutions with temperature: (A) KCl, (B) KCl–14 mol % KBr, (C) KCl–31 mol % KBr, (D) KCl–38.5 mol % KBr, (E) KCl–57 mol % KBr, (F) KCl–79 mol % KBr, (G) KBr.

Celsius and degrees Celsius respectively, and the values of A, B and C for the various crystal compositions are presented in Table V. The maximum difference between the observed values and the values calculated from this equation is found to be less than 2%.

It is observed that the coefficient of expansion for all the compositions, except for pure KBr, increases non-linearly with increasing temperature. The KCl–31 mol % KBr mixed crystal has the highest value of the coefficient of thermal expansion at room temperature, and the lowest value at maximum temperature when compared with all the other crystals.

Figs. 2 and 3 show the values of the coefficients of thermal expansion of KCl and KBr respectively obtained at various temperatures by various workers. From these it can be seen that there are wide discrepancies among the various values at higher temperatures, though the results agree to some extent at lower temperatures (below 300° C). Up to 300° C the present values are in very good agreement with those obtained by Eucken and Dannohl [10] in the case of KCl and with those obtained by Pathak *et al.* [17] in the case of KBr, a linear relationship between the coefficient of expansion and temperature is obtained by Pathak and Pandya [14] as in the present study.

TABLE IV Coefficients of thermal expansion of KCl–KBr system at various temperatures

Temperature (° C)	$10^6 \times \alpha$ (° C^{-1})						
	KCl	KCl–14 mol % KBr	KCl–31 mol % KBr	KCl–38.5 mol % KBr	KCl–57 mol % KBr	KCl–79 mol % KBr	KBr
50	33.40	38.30	44.32	38.23	41.52	35.70	39.48
90	34.99	39.02	44.71	39.40	41.52	38.39	41.00
130	36.98	39.88	45.10	40.18	43.07	40.31	42.14
170	37.78	40.28	45.89	41.61	44.23	42.65	42.14
210	39.37	41.87	46.28	42.58	45.40	45.30	43.28
250	41.36	43.35	47.06	43.94	46.56	47.22	44.03
290	43.34	44.65	47.85	44.80	47.34	49.52	45.55
330	44.21	45.81	48.63	45.91	48.11	51.44	46.31
370	45.63	48.18	49.02	46.59	49.60	52.98	47.07
410	46.82	49.35	49.81	47.51	50.44	54.90	48.21
450	46.98	51.12	50.20	48.73	51.22	56.82	48.59
490	47.82	53.01	50.59	50.01	51.99	58.44	49.73
530	49.22	54.57	50.98	51.60	53.00	59.51	49.73
570	49.98	55.78	51.38	52.58	53.93	60.44	50.87
610	51.30	57.87	51.77	54.26	55.87	61.42	52.39
650	52.09	–	–	–	–	–	53.15
690	52.89	–	–	–	–	–	54.28
730	54.08	–	–	–	–	–	–

TABLE V Values of the constants *A*, *B* and *C* in Equation 1

Composition (mol %)	$10^6 \times A$	$10^8 \times B$	$10^{11} \times C$
KCl	31.470	4.370	−1.832
KCl–14 KBr	36.483	2.293	+2.044
KCl–31 KBr	43.065	1.830	−0.624
KCl–38.5 KBr	37.242	2.360	+0.574
KCl–57 KBr	39.819	2.613	−0.143
KCl–79 KBr	32.042	7.047	−3.560
KBr	38.787	2.203	0

TABLE VI Thermal vibration data for KCl–KBr mixed crystals at room temperature (300 K)

Composition (mol %)	Debye–Waller factor B (nm^2)	Debye temperature θ (K)	R.m.s. amplitude of vibration $(\bar{u}^2)^{1/2}$ (nm)
KCl	0.020 13	215	0.0277
KCl–14 KBr	0.021 06	202	0.0283
KCl–31 KBr	0.021 74	190	0.0287
KCl–38.5 KBr	0.021 82	186	0.0288
KCl–57 KBr	0.021 37	180	0.0285
KCl–79 KBr	0.019 27	181	0.0271
KBr	0.016 97	185	0.0254

3.3. Debye–Waller factors, Debye temperatures and root mean square amplitudes of thermal vibration

The values of the Debye–Waller factors, Debye temperatures and the root mean square amplitudes of vibration obtained at room temperature for KCl, KBr and their solid solutions are listed in Table VI. It is found that these values vary non-linearly with increasing mole percentage of KBr, the deviation from linearity being maximum around equimolar concentration.

The values of the Debye temperatures of KCl and KBr at room temperature have also been found by various workers by various methods. The range of variation of the values is from 210 to 230 K for KCl [41–47] and from 157 to 170 K for KBr [41, 46–51]. For KCl–KBr mixed crystals, no experimental values of θ are available. Some theoretical calculations from elastic constants have been made [47, 52], but it is not possible to make a direct comparison with the present study as the compositions of the mixed crystals were different in both cases.

4. Discussion

4.1. The lattice parameter and the expansion coefficient

The variation of the lattice parameter with mole percentage of KBr for KCl–KBr mixed crystals, at room temperature, is shown in Fig. 4. A linear relationship is obtained between the lattice parameter and the composition of the solid solution in accordance with Vegard's law [53].

The coefficients of thermal expansion of these solid solutions at room temperature calculated using Equation 1 are plotted against mole percentage of KBr in Fig. 5. The coefficient of thermal expansion is found to be greater in a mixed crystal than in its constituents. It increases with increasing mole percentage of KBr, attaining a maximum value around equimolar concentration, and then falls to the value of pure KBr. Thus no gradation is observed between the lattice parameter and the coefficient of thermal expansion of these mixed crystals.

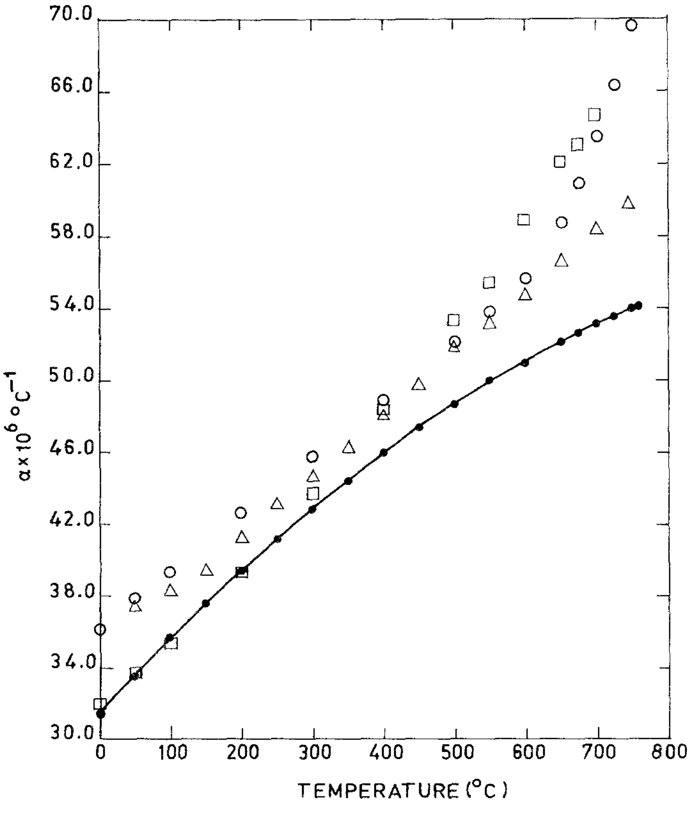

Figure 2 Comparison of the coefficients of thermal expansion of KCl at various temperatures. (□) Eucken and Donnohl [10], (△) Enck *et al.* [15], (○) Pathak and Vasavada [16], (●) present study.

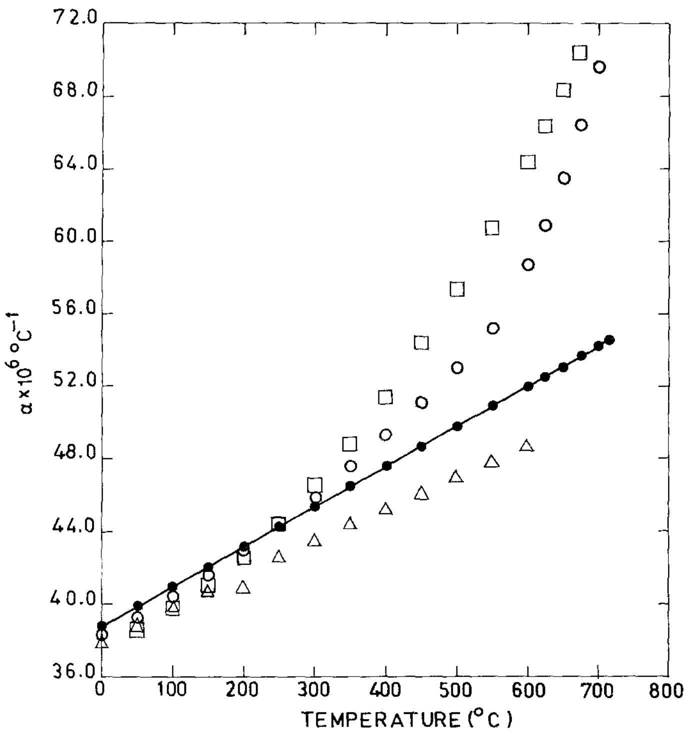

Figure 3 Comparison of the coefficients of thermal expansion of KBr at various temperatures. (□) Eucken and Donnohl [10], (△) Pathak and Pandya [14], (○) Pathak *et al.* [17], (●) present study.

4.2. Mass of the ions and the expansion coefficient

An observation was made by Henglein [54] regarding the effect of the mass of the ions upon the thermal expansion coefficients of the alkali halides. She showed that the mean expansion coefficient increases as the mass of the halogen ion increases. In the present study, however, it is observed that the mean expansion coefficient (Table VII) varies non-linearly, having a maximum value around equimolar concentration as the mass of the solid solution increases by increasing the percentage of Br^- ions.

4.3. Grain size and the expansion coefficient

The grain size of a solid affects many of its physical properties. The effect of grain size on the lattice parameter has been studied by Boswell [34] for some alkali halides using the X-ray method. He found that the lattice parameter decreases as the grain size decreases. This concentration has been attributed to the presence of surface forces. No study seems to have been made to find out whether this contraction is temperature-dependent. The results of such a study have an important bearing on the X-ray method of determining thermal expansion.

The wide discrepancies in the values of the lattice parameters (Table I) and the coefficients of thermal expansion (Figs. 2 and 3) reported by various workers may be due to the grain size of the samples. More definite information will be available when experiments are performed over a wide range of grain size and a wider range of temperature.

TABLE VII $\bar{\alpha}T_m$ values for the KCl–KBr system

Composition (mol %)	Melting point T_m(K) [8]	$10^6 \times \bar{\alpha}$(0 to T_m)	$10^6 \times \bar{\alpha}T_m$
KCl	1047	41.30	43 241
KCl–14 KBr	1028	43.20	44 410
KCl–31 KBr	1014	47.00	47 658
KCl–38.5 KBr	1011	43.04	43 513
KCl–57 KBr	1007	45.77	46 090
KCl–79 KBr	1009	46.45	46 868
KBr	1013	43.93	44 501

4.4. The melting point and the expansion coefficient

Tarasoff [55] has shown that the product $\bar{\alpha}T_m$ is a constant for NaCl-type crystals, T_m being the melting point and $\bar{\alpha}$ being the mean expansion coefficient over the range 0 to T_m. Table VII gives the mean expansion coefficients for the KCl–KBr system over the temperature range 0 to T_m, evaluated using Equation 1, and also the product $\bar{\alpha}T_m$. This product is found to be a constant for the mixed-crystal system as well. The mean expansion coefficient varies non-linearly with increasing mole percentage of KBr, the deviation from linearity being maximum around equimolar concentration.

4.5. Reduced temperature (T/T_m) and expansion ($\alpha/\alpha_{m/2}$)

From a consideration of the temperature variation of thermal diffuse X-ray scattering, it has been shown by

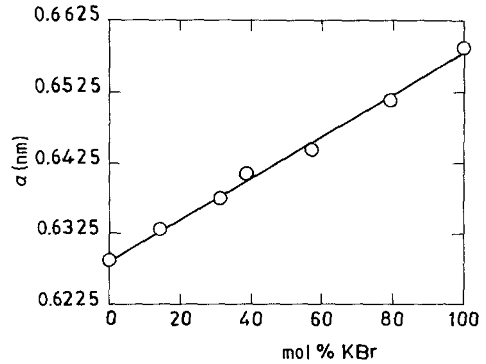

Figure 4 Lattice parameter at room temperature against mol % KBr for KCl–KBr mixed crystals.

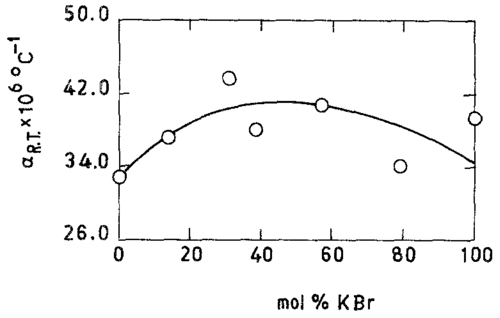

Figure 5 Coefficients of expansion at room temperature against mol % KBr for KCl–KBr mixed crystals.

Cartz [56] that for cubic crystals

$$\bar{u}^2/(\bar{u}^2)_m = T/T_m \qquad (2)$$

where $\bar{u}^2$ is the mean square amplitude of vibration at absolute temperature T, and $(\bar{u}^2)_m$ the value at the melting point T_m. T/T_m is termed the reduced temperature. The properties which depend on the atomic vibrations such as the elastic constants, electrical resistance, atomic diffusion, specific heat, thermal expansion and thermal conductivity are also expected to vary similarly with reduced temperature. In the case of the thermal expansion of cubic metals, Cartz [56] has shown that the following relation exists:

$$\alpha/\alpha_{m/2} = 0.74 + 0.52(T/T_m) \qquad (3)$$

over the temperature range $\sim 0.2 < T/T_m < \sim 0.7$ where $\alpha_{m/2}$ is the coefficient of thermal expansion at $T = \frac{1}{2}T_m$. In the present investigation also, the same relation (Equation 3) has been found to hold good for KCl–KBr solid solutions, over the temperature range $\sim 0.039 < T/T_m < \sim 0.943$. This has been graphically shown in Fig. 6. Thus the "law of corresponding states" is found to exist in these mixed crystals.

4.6. The Debye temperature and the lattice parameter

In the case of the alkali halides and the alkaline earth chalcogenides, it was shown by Baldwin and Thompson [57] that the Debye temperature varies linearly with the reciprocal of the lattice parameter; but in the case of mixed crystals of KCl–KBr it has been observed that the relation is non-linear, (Fig. 7) showing maximum deviation around equimolar concentration as observed in the case of other physcial properties.

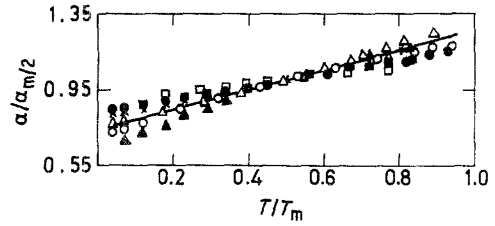

Figure 6 Plot of reduced expansion $\alpha/\alpha_{m/2}$ against reduced temperature T/T_m of the KCl–KBr system. T_m is the melting temperature and $\alpha_{m/2}$ is the value of α at $T = \frac{1}{2}T_m$. (○) KCl, (●) KBr, (△) KCl–14 mol % KBr, (□) KCl–31 mol % KBr, (×) KCl–38 5 mol % KBr, (■) KCl–57 mol % KBr, (▲) KCl–79 mol % KBr.

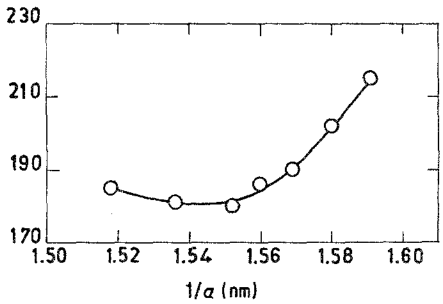

Figure 7 Debye temperature against reciprocal of the lattice parameter for the KCl–KBr system.

4.7. Thermal expansion and root mean squares amplitude of thermal vibration in relation to other physical properties

The behaviour of the coefficient of thermal expansion at room temperature (Fig. 5) and the mean coefficient of expansion over the range 0 to T_m (Table VII) is similar to that of the microhardness [1, 2], dislocation density [2, 3], dielectric constant [4], piezo-optic birefringence [5] and ionic conductivity [6], which increase with increase of mole percentage of KBr and finally fall to the value of pure KBr, the deviation from linearity being around equimolar concentration. The variation of microhardness and dislocation density has been explained as arising due to lattice distortions induced by the large size of the Br^- ions, the distortion being maximum around equimolar concentration.

According to Ahtee *et al.* [58], the differences in the sizes of the component atoms give rise to small random displacements from the sites of the average lattice in solid solutions. In addition to the existance of size effects, the vibrational states of the constituent atoms may change during solid solution formation as a result of new interatomic interactions. They observed that the amplitude of thermal vibration is slightly higher in the equimolar KCl–KBr solid solution than in the pure components. Similar results have been obtained in the present investigation. Fig. 8 shows that at the equimolar concentration the root mean square amplitude of thermal vibration is maximum. It was also found that the Gruniesen parameter which measures the anharmonicity has a large value for the KCl–KBr mixed system when compared with the pure alkali halide crystals [52]. These factors account for the thermal expansion behaviour in the KCl–KBr system.

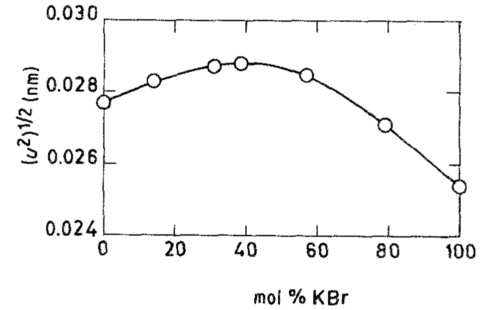

Figure 8 Plot of root mean square amplitude of thermal vibration against mol% KBr for the KCl–KBr system.

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