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# Studies on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions: 1. Lattice and thermal parameters

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**Abstract** Solid solutions of NaCl, KBr and KI were prepared by the melt method for the first time. Densities and refractive indices of all the prepared solid solutions were determined and also used for the estimation of the bulk composition in the crystal. Lattice parameters and thermal parameters like Debye–Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency were determined from the X-ray powder diffraction data. The observed lattice parameters showed the existence of three phases in solid solutions each nearly corresponds to NaCl, KBr and KI. The thermal parameters show a highly non-linear bulk composition dependence.

## Introduction

A solid solution or mixed crystal is obtained by crystallizing together two isomorphous crystals like KCl and KBr with comparable lattice constants. For ionic crystals like alkali halides complete miscibility is possible only above a temperature $T$ (K) given by $T = 4.5\ S^2$, $S$ being the percentage difference in lattice constants [1]. $S$ takes a value of 8% for alkali halides at room temperature. Sixteen pairs of alkali halides are completely miscible at room temperature and several got limited miscibility [2].

Like the alkali halides their mixed crystals are also equally important. Alkali halide mixed crystals are of the completely disordered substitutional type. Haribabu and Subbarao [3] have reviewed the aspects of the growth and characterization of alkali halide mixed crystals. Sirdeshmukh and Srinivas [2] have reviewed the physical properties.

A study of literature has shown that there are broad miscibility gaps in several binary systems of alkali halides. NaCl–KCl [4] is an example. Barrett and Wallace [5] determined the lattice parameters of $Na_xK_{1-x}Cl$ crystals and found that this system does not form a continuous series. Nair and Walker [6] observed that for the extreme concentration ranges $x < 0.3$ and $x > 0.7$ the $KBr_{1-x}I_x$ crystals could be characterized by a single f.c.c. lattice parameter, while in the intermediate region three f.c.c. phases characterized by three lattice parameters.

Alkali halide crystals are widely used as neutron monochromaters, infrared prisms, infrared transmitters, laser window materials, etc. However, the uses are limited by their mechanical properties and hence there exists the need to strengthen these. The mixed and impurity added (doped) crystals of alkali halides are found to be harder than the end members and so they are more useful in these applications. Also, it is a known fact that alloys are more useful than the pure simple metals in device fabrications. In addition, mixed alkali halides find their applications in optical, optoelectronic and electronic devices. In view of this, it becomes necessary and useful to prepare binary and ternary solid solutions regardless of miscibility

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problem and characterize them by measuring their physical properties.

Mahadevan and his co-workers [7] obtained larger and more stable crystals from $(NaCl)_x(KCl)_{0.9-x}(KBr)_{0.1}$ solutions than from $Na_xK_{1-x}Cl$ solutions. They grew the crystals from aqueous solutions only. Though the miscibility problem was there, their study has illustrated that a KBr addition to NaCl–KCl system may yield a new class of stable materials.

The research program was planned and a series of investigations on $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions were undertaken: (1) Preparation of solid solutions, density and refractive index measurements and determination of lattice and thermal parameters like Debye–Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency; (2) D.C. and A.C. electrical measurements; etc. Results of the first part of our series of investigation are reported here in this paper.

## Experimental

### Growth of crystals

$(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ solid solutions (mixed crystals) were grown from the melt, for the first time, by a method similar to that followed by Kumaraswamy et al. [8]. AnalaR grade samples of NaCl, KBr and KI were used as the starting material for the growth of the crystals.

Hundred grams of the substances, weighed according to the molecular ratio by weight, was thoroughly mixed and was taken in a silica crucible. The amount of substance in grams for preparing the required samples of composition given by $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ may be obtained by using the following formula.

$$P[x \times \text{molecular weight of NaCl} + (y-x) \times \text{molecular weight of KBr} + (1-y) \times \text{molecular weight of KI}] = 100$$

$$P = \frac{100}{x \times \text{mol. wt. of NaCl} + (y-x) \times \text{mol. wt. of KBr} + (1-y) \times \text{mol. wt. of KI}}$$

Weight of NaCl to be taken $= P \times x \times$ mol. wt. of NaCl

Weight of KBr to be taken $= P \times (y-x) \times$ mol. wt. of KBr

Weight of KI to be taken $= P \times (1-y) \times$ mol. wt. of KI.

The crucible was placed in a 1,200 °C capable muffle furnace having a temperature controller (accuracy is ±2 °C) and heated till the whole substance was melted. The temperature was then increased to 900 °C where it was held for 1 h to homogenize by convection-assisted mixing. The molten liquid was then gradually cooled. A total of 13 crystals [10 ternary mixed crystals, viz. $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ with $x$ varying from 0.1 in steps of 0.2 and $y$ = 0.3, 0.5. 0.7 and 0.9; three end member crystals, viz. NaCl, KBr and KI] were grown by the above method and under identical conditions. The end member crystals were grown for comparison purposes.

### Density measurement

Densities of all the grown crystals were determined to an accuracy of ±0.008 g/cc by using the flotation method. Carbon tetrachloride of density 1.594 g/cc and bromoform of density 2.890 g/cc were used as the lower and higher density liquids, respectively. For the crystals having density values higher than that of bromoform [KI and $(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$], the density was measured by finding the mass/volume for a large size (shaped) crystal.

### Refractive index measurement

Refractive index of an under saturated solution of the crystal in distilled water was measured using an Abbe refractometer. Refractive index of the crystal was determined (to an accuracy of ±0.006) by using the Gladstone's rule [9]:

$$[(n-1)/d]P = [(n_1-1)/d_1]P_1 + [(n_2-1)/d_2]P_2$$

where $n$, $n_1$ and $n_2$ represent the refractive indices of solution, solvent and solute (crystal), respectively. $d$, $d_1$ and $d_2$ are the densities of solution, solvent and solute, respectively. $P$, $P_1$ and $P_2$ are the percentage weights of solution, solvent and solute, respectively.

## Estimation of bulk composition

It has been found that the density and refractive index values form linear relationship with composition for the binary mixed crystals [2]. Assuming that these values have a linear relationship with composition for the ternary mixed crystals also, the following relations may be written:

$$d = xd_1 + (y - x)d_2 + (1 - y)d_3$$
$$n = xn_1 + (y - x)n_2 + (1 - y)n_3$$

Here, $d$, $d_1$, $d_2$ and $d_3$ represent the densities of mixed crystal, NaCl, KBr and KI, respectively; $n$, $n_1$, $n_2$ and $n_3$ represent the refractive indices of mixed crystal, NaCl, KBr and KI, respectively. Composition of the grown mixed crystals were estimated by solving the above two equations for $x$ and $y$ values.

## Determination of lattice parameters

X-ray diffraction data were collected from powdered samples using an automated X-ray powder diffractometer with scintillation counter and monochromated $CuK_\alpha$ ($\lambda$ = 1.5418 Å) radiation available in the Central Electrochemical Research Institute (CSIR), Karaikudi, India. The reflections were indexed following the procedures of Lipson and Steeple [10].

Analysis of the X-ray diffraction peaks was done by the available methods [11]. Lattice parameters were also calculated by extending to ternary solid solutions the Retger's rule [3]:

$$a^3 = xa_1^3 + (y - x)a_2^3 + (1 - y)a_3^3$$

where $a$ is the lattice parameter of the solid solution and $a_1$, $a_2$ and $a_3$ are, respectively the lattice parameters of the NaCl, KBr and KI crystals.

## Determination of thermal parameters

The mean Debye–Waller factor ($B$) for all the grown crystals were determined using the X-ray intensity data by the Wilson plot method [12].

The structure factors for the end member crystals were calculated using the relations:

$$F_{NaCl} = 4(f_{Na^+} \pm f_{Cl^-})$$
$$F_{KBr} = 4(f_{K^+} \pm f_{Br^-})$$
$$F_{KI} = 4(f_{K^+} \pm f_{I^-})$$

The structure factors for the ternary solid solutions were calculated using the relation:

$$F_{hkl} = 4[x(f_{Na^+} \pm f_{Cl^-}) + y(f_{K^+} \pm f_{Br^-}) + z(f_{K^+} \pm f_{I^-})]$$

here, $f_{Na^+}$, $f_{K^+}$, $f_{Cl^-}$, $f_{Br^-}$ and $f_I^-$ are the respective scattering factors for $Na^+$, $K^+$, $Cl^-$, $Br^-$ and $I^-$ ions taken from the literature [13]. $x$, $y$ and $z$ are the respective fractional contents of NaCl, KBr and KI present in the solid solution. The plus sign applies to reflections with even values of h + k + l and minus sign to those with the odd values of h + k + l.

The equation for Bragg intensity may be written in logarithmic scale as

$$\ln(I_E/I_C) = \ln K - 2B(\sin\theta/\lambda)^2.$$

The mean Debye–Waller factor ($B$) was obtained from a least squares treatment of $\ln(I_E/I_C)$ against $(\sin\theta/\lambda)^2$. This is called $B_{obs}$. $I_E$ is the experimentally observed intensity, $I_C$ is the calculated intensity, $K$ is the scale factor, $\theta$ is the Bragg angle and $\lambda$ is the wavelength of the radiation.

In the case of solid solutions, the presence of mixing of ions creates a static contribution ($B_{static}$). According to Dernier et al. [quoted in 14] $B_{static}$ for binary solid solutions of the form $A_xB_{1-x}C$ is given by

$$B_{static} = x(1 - x)(r_A - r_B)^2$$

where $r_A$ and $r_B$ are ionic radii of A and B ions, respectively. $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ crystals contain $Na^+$, $K^+$, $Cl^-$, $Br^-$ and $I^-$ ions. Replacement of ions is possible only between $Na^+$ and $K^+$ ions and $Cl^-$, $Br^-$ and $I^-$ ions. Hence, $B_{static}$ for the present system can be estimated by using the relation

$$B_{static} = x(1 - x)[(r_A - r_B)^2] + x[(y - x)(r_C - r_D)^2 + (1 - y)(r_C - r_E)^2]$$

where $x$, ($y$–$x$) and (1–$y$) are the mole fractions of NaCl, KBr and KI and $r_A$, $r_B$, $r_C$, $r_D$ and $r_E$ are the ionic radii of $Na^+$, $K^+$, $Cl^-$, $Br^-$ and $I^-$. For solid solutions,

$$B_{obs} = B_{thermal} + B_{static}.$$

The Debye temperature ($\theta_D$) was obtained from the Debye–Waller theory expression (for end member crystals, $B_{obs} = B_{thermal}$):

$$B_{thermal} = \frac{6h^2}{mkT} W(x)$$

where $m$ is the mean atomic mass, $T$ is the absolute temperature at which the X-ray intensities were

measured, $h$ is the Planck's constant and $k$ is the Boltzmann's constant. The function $W(x)$ is given by

$$W(x) = \frac{\varphi(x)}{x^2} \times 1/4x$$

where $x = \theta_D/T$ and $\phi$ $(x)$ is an integral. The values of $W(x)$ for a wide range of $x$ have been tabulated by Benson and Gill [15]. $\theta_D$, the Debye temperature, was evaluated by using the above expression.

The mean square amplitude of vibration ($< u^2 >$) was obtained from [16].

$$B = 8\pi^2 < u^2 > .$$

The Debye frequency ($f_D$) was obtained from [17]

$$f_D = \theta_D(k/h).$$

## Results and discussion

### Nature of crystals

The ternary solid solutions are found to be harder, more stable and less transparent when compared to the end members. The transparency of the crystals is found to be reduced and becoming white when the crystals are cooled from high temperature to the room temperature which may be due to the introduction of thermal defects. Also, the crystals obtained are found to be polycrystalline.

### Density, refractive index and composition

The observed specific refractive energy, density and refractive index of all the solid solutions and pure (end member) crystals are given in Table 1. Observed density and refractive index of the end members compare well with those reported in the literature (reported values are given in brackets). Composition of the starting material and estimated bulk composition of the grown crystals are also provided in Table 1. The bulk composition dependence of density and refractive index (for $x = 0.1$ only) are shown (as an illustration) in Figs. 1 and 2, respectively.

### Lattice parameters

The lattice parameters obtained in the present study are provided in Table 2. Lattice parameters of the end member crystal compositions are in reasonable agreement with those reported in the literature [2] (literature values are given in brackets). No reported values are available to compare the lattice parameters of the solid solutions.

It has been found that, for the ternary solid solutions, all the X-ray diffraction peaks can be indexed with three f.c.c. lattices instead of one which shows the existence of three f.c.c. phases. The calculated lattice parameters show that each phase corresponds nearly to pure NaCl, KBr and KI. A similar result was reported for the intermediate compositions of KBr–KI mixed crystals [6]. Lattice parameters calculated by extending to ternary solid solutions the Retger's rule along with the estimated total average values are also presented in Table 2. The former values are found to be less than the latter values.

In effect, it is clear that the ternary solid solutions prepared in the present study are of multiphased systems. Occurrence of this may be due to the large percentage deviation in lattice parameters between NaCl and KBr (14.54%), NaCl and KI (20.17%) and KBr and KI (6.59%).

**Table 1** Specific refractive energy, density and refractive index values together with the initial and final compositions

| System (with composition taken for crystallization) | Specific refractive energy, $[(n-1)/d]$ | Density, $d$ (g/cc) | Refractive index, $n$ | Estimated composition in the crystals |
|---|---|---|---|---|
| NaCl | 0.2512 | 2.198 (2.168) | 1.5522 (1.5443) | NaCl |
| KBr | 0.2110 | 2.690 (2.750) | 1.5677 (1.5594) | KBr |
| KI | 0.2183 | 3.084 (3.129) | 1.6732 (1.6678) | KI |
| $(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$ | 0.2159 | 2.682 | 1.5790 | $(NaCl)_{0.115}(KBr)_{0.760}(KI)_{0.124}$ |
| $(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$ | 0.2218 | 2.603 | 1.5774 | $(NaCl)_{0.283}(KBr)_{0.583}(KI)_{0.134}$ |
| $(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$ | 0.2283 | 2.526 | 1.5767 | $(NaCl)_{0.455}(KBr)_{0.393}(KI)_{0.153}$ |
| $(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$ | 0.2380 | 2.372 | 1.5646 | $(NaCl)_{0.705}(KBr)_{0.220}(KI)_{0.075}$ |
| $(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$ | 0.2168 | 2.780 | 1.6026 | $(NaCl)_{0.093}(KBr)_{0.561}(KI)_{0.344}$ |
| $(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$ | 0.2241 | 2.663 | 1.5969 | $(NaCl)_{0.313}(KBr)_{0.364}(KI)_{0.323}$ |
| $(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$ | 0.2329 | 2.500 | 1.5822 | $(NaCl)_{0.562}(KBr)_{0.218}(KI)_{0.220}$ |
| $(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$ | 0.2182 | 2.831 | 1.6177 | $(NaCl)_{0.105}(KBr)_{0.405}(KI)_{0.489}$ |
| $(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$ | 0.2250 | 2.722 | 1.6125 | $(NaCl)_{0.312}(KBr)_{0.218}(KI)_{0.471}$ |
| $(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$ | 0.2190 | 2.917 | 1.6389 | $(NaCl)_{0.089}(KBr)_{0.223}(KI)_{0.688}$ |

Values reported in the literature are given in brackets

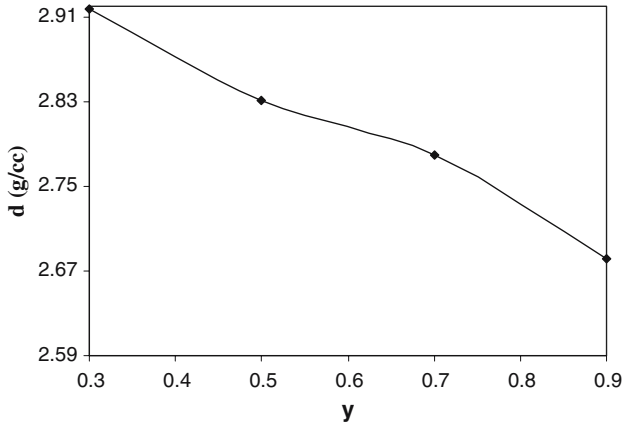


**Fig. 1** Composition (taken for crystallization) dependence of density, $d$, for $x = 0.1$

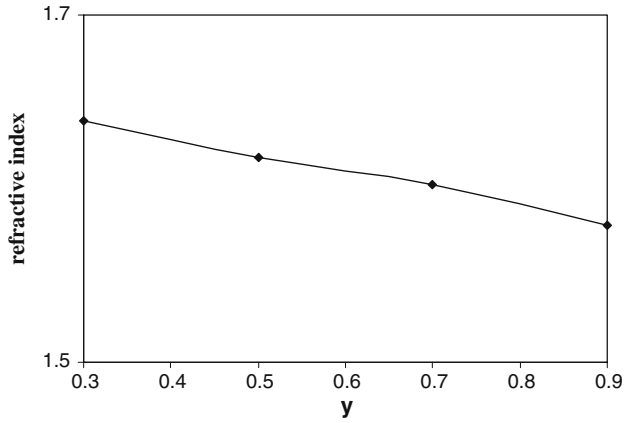


**Fig. 2** Composition (taken for crystallization) dependence of refractive index for $x = 0.1$

Very recently, Sirdeshmukh et al. [18] have reported that impurity hardening is more effective than solid solution hardening. In our studies also we have found that (though not studied systematically) the multiphased systems are harder than the other ones. Hence, these multiphased systems may be treated in par with the impurity added systems in gaining more mechanical strength.

## Thermal parameters

The thermal parameters obtained in the present study, viz. Debye Waller factors ($B_{obs}$, $B_{static}$ and $B_{thermal}$), mean square amplitude of vibration, Debye temperature and Debye frequency are given in Table 3. In order to compare the present values with the literature ones, the Debye temperatures for the end members quoted by Sirdeshmukh et al. obtained by the same X-ray diffraction method [19] are given in brackets. The differences observed in these values may be attributed to the difference in the preparation of crystals. Also, the samples prepared and used in the present study are polycrystalline.

The bulk composition dependence of the Debye–Waller factor for the systems with $x = 0.1$ (as an illustration) is shown in Fig. 3. The composition dependence of Debye–Waller factor in the case of solid solutions is highly non-linear and in some cases it even exceeds that for the end members.

Even after making correction for the static component, the Debye–Waller factors for some mixed crystals are found to be larger. Kumaraswamy et al. [8] made similar observations in the case of RbBr–RbI mixed crystals and attributed the enhancement of the Debye–Waller factor to an increase in the vibrational entropy due to mixing. Similar reasons may be responsible for the enhancement of $B_{thermal}$ observed in the present system.

**Table 2** Lattice constants (e.s.d's are given in parenthesis). Also the literature value for the end members are given in parenthesis

| System (with composition taken for crystallization) | Lattice constants (Å) | | | | |
|---|---|---|---|---|---|
| | Phase I[a] | Phase II[a] | Phase III[a] | Total average | As per Retger's rule |
| NaCl | – | – | – | 5.5940(25) (5.6402) | |
| KBr | – | – | – | 6.5524(03) (6.6000) | |
| KI | – | – | – | 7.0080(30) (7.0655) | |
| $(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$ | 5.6700 | 6.5210(55) | 6.9810 | 6.474 | 6.5183 |
| $(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$ | 5.5985 | 6.5453(02) | 6.9450(43) | 6.521 | 6.3470 |
| $(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$ | 5.5690(35) | 6.4970(50) | 6.8590(56) | 6.427 | 6.1660 |
| $(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$ | 5.5960(15) | 6.4860(27) | 6.9150(36) | 6.478 | 5.9730 |
| $(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$ | 5.5630(17) | 6.5720(58) | 6.9380(33) | 6.511 | 6.6152 |
| $(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$ | 5.5880(27) | 6.5260(33) | 6.8820(33) | 6.602 | 6.4490 |
| $(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$ | 5.5910(41) | 6.5280(17) | 6.9502(19) | 6.561 | 6.2740 |
| $(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$ | 5.6530(35) | 6.4910(76) | 6.9080(41) | 6.602 | 6.7094 |
| $(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$ | 5.5260(17) | 6.5090(49) | 6.9090(50) | 6.636 | 6.5480 |
| $(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$ | 5.9810 | 6.5100 | 6.9500(29) | 6.396 | 6.8100 |

[a] Phase I nearly corresponds to NaCl; Phase II nearly corresponds to KBr; Phase III nearly corresponds to KI

**Table 3** Thermal parameters [Values of mean Debye–Waller factors ($B_{obs}$, $B_{static}$ and $B_{thermal}$ Å$^2$), mean square amplitude of vibration ($< u^2 >$ Å$^2$), Debye temperature ($\theta_D$ K) and Debye frequency ($f_D \times 10^{12}$ Hz)]

| System (with composition taken for crystallization) | $B_{obs}$ | $B_{static}$ | $B_{thermal}$ | $< u^2 >$ | $\theta_D$ | $f_D$ |
|---|---|---|---|---|---|---|
| NaCl | 1.853 | | 1.853 | 0.023 | 253.3 (278.0) | 5.272 |
| KBr | 5.234 | | 5.234 | 0.066 | 148.49 (155.0) | 3.091 |
| KI | 3.016 | | 3.016 | 0.038 | 116.82 (117.0) | 2.432 |
| $(NaCl)_{0.1}(KBr)_{0.8}(KI)_{0.1}$ | 13.375 | 0.120 | 13.255 | 0.170 | 66.15 | 1.377 |
| $(NaCl)_{0.3}(KBr)_{0.6}(KI)_{0.1}$ | 6.668 | 0.242 | 6.426 | 0.085 | 99.21 | 2.065 |
| $(NaCl)_{0.5}(KBr)_{0.4}(KI)_{0.1}$ | 6.282 | 0.302 | 5.980 | 0.080 | 107.66 | 2.241 |
| $(NaCl)_{0.7}(KBr)_{0.2}(KI)_{0.1}$ | 3.736 | 0.252 | 3.484 | 0.047 | 157.05 | 3.269 |
| $(NaCl)_{0.1}(KBr)_{0.6}(KI)_{0.3}$ | 5.076 | 0.105 | 4.971 | 0.064 | 104.29 | 2.171 |
| $(NaCl)_{0.3}(KBr)_{0.4}(KI)_{0.3}$ | 5.746 | 0.274 | 5.472 | 0.073 | 104.18 | 2.168 |
| $(NaCl)_{0.5}(KBr)_{0.2}(KI)_{0.3}$ | 6.894 | 0.316 | 6.578 | 0.087 | 104.48 | 2.175 |
| $(NaCl)_{0.1}(KBr)_{0.4}(KI)_{0.5}$ | 8.120 | 0.122 | 7.998 | 0.103 | 79.41 | 1.653 |
| $(NaCl)_{0.3}(KBr)_{0.2}(KI)_{0.5}$ | 7.637 | 0.287 | 7.350 | 0.097 | 87.19 | 1.815 |
| $(NaCl)_{0.1}(KBr)_{0.2}(KI)_{0.7}$ | 3.568 | 0.110 | 3.458 | 0.045 | 116.50 | 2.425 |

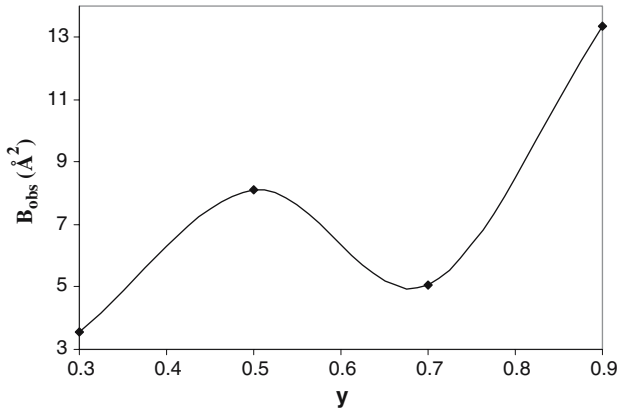


**Fig. 3** Composition (taken for crystallization) dependence of Debye–Waller factor, $B_{obs}$, for $x = 0.1$

The bulk composition dependence of the Debye temperature for the systems with $x = 0.1$ (as an illustration) is shown in Fig. 4. Debye temperatures

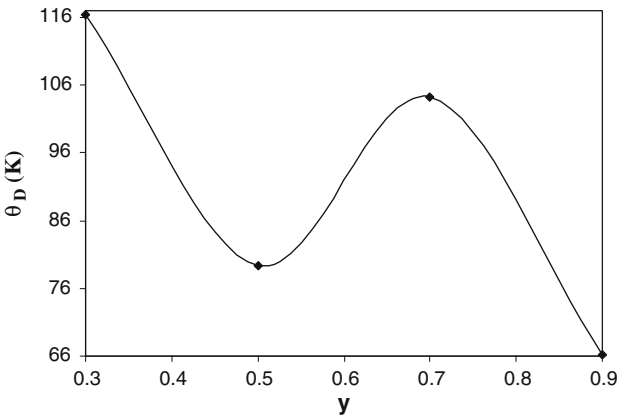


**Fig. 4** Composition (taken for crystallization) dependence of Debye temperature, $\theta_D$, for $x = 0.1$

of the solid solutions show a non-linear variation with the composition and, in some cases, it is even less than that of the end members. This happens because of the enhancement of the Debye–Waller factor which may be related to the increase in vibrational entropy due to mixing.

Debye frequencies obtained for all the grown crystals lie in the infrared range. Variation of the Debye frequency with composition is not in any order similar to that for the Debye temperature.

## Conclusions

Ternary solid solutions of NaCl, KBr and KI were prepared by the melt method. Composition of the grown crystals were determined using the measured density and refractive index values by assuming the additive rule satisfying for them. Lattice parameters were estimated by the X-ray diffraction method. The present study shows that the ternary solid solutions exhibit three f.c.c phases instead of a single f.c.c. phase each nearly corresponds to NaCl, KBr and KI. Thermal parameters, viz. Debye–Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency were determined for $(NaCl)_x(KBr)_{y-x}(KI)_{1-y}$ crystals from the X-ray powder diffraction data. The thermal parameters are found to vary non-linearly with bulk composition. Values for some solid solutions even exceed those for the end members which may be attributed to the increase in vibrational entropy due to mixing. The present study indicates that the ternary solid solutions are expected to be more useful than the end member crystals though their internal structures contain three (multiple) phases.

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