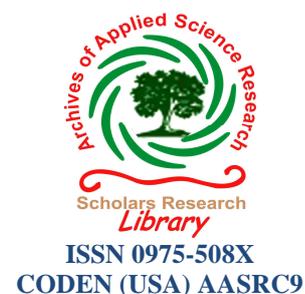




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## Debye-Waller factors and Debye temperatures of $KCl_xBr_{1-x}$ mixed crystals grown from aqueous solution

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### ABSTRACT

Mixed crystals of alkali halides find their applications in optical, opto electronics and electronic devices. In the present study the pure and ZnO added mixed crystals  $KCl_xBr_{1-x}$  were grown from the aqueous solution. The grown crystals were characterized by taking XRD, TG/DTA and Vickers microhardness measurement. The Debye temperature is an important parameter of a solid. Several methods of evaluating Debye temperature are available. In the present study Debye temperatures were calculated from the Debye-Waller factor, melting point and microhardness. The results were compared with the Kopp-Neumann relation.

**Keywords:** Mixed crystals, Alkali halides, Debye temperature, Debye frequency.

### INTRODUCTION

Single crystals of pure and mixed alkali halides have been grown for a very long time. The mixed crystals of alkali halides are found to be harder than the end members and so they are more useful in several applications in optical, opto electronic and electronic devices. Sirdeshmukh et al [1] have reported that impurity hardening is more effective than solid solution hardening. So in the present study we grown the pure mixed crystals of KCl-KBr and also ZnO added mixed crystals of KCl-KBr.

Since 1910 Einstein proposed a simple relation between the characteristic frequency of a solid and its compressibility and numerous relations have been proposed for calculating the Debye temperatures from elastic constants, melting point, micro hardness, force constant, Debye-Waller factor etc.

In the present study we have calculated the Debye temperatures for all the grown crystals experimentally from the melting point, micro hardness and Debye-Waller factor and they have been compared with the calculated Debye temperature from Kopp-Neumann relation.

### MATERIALS AND METHODS

#### 2.1 Growth of sample crystals

Analytical Reagent (AR) grade KCl and KBr along with doubly distilled water were used for the growth of single crystals. An aqueous solution of the salt with desired molecular ratio was prepared at super saturated concentration and seed crystals were used to grow the sample crystals. The temperature and volume were kept constant respectively at 32°C and 25 ml for all the crystals. 1N solution of 2.5 ml ZnO was added to the 25 ml supersaturated solution. In the present study total of fourteen crystals (two pure end members, two doped end members, five pure mixed crystals, and five doped mixed crystals) for various values of x viz. 0.2, 0.4, 0.5, 0.6 and 0.8 were grown in identical conditions.

## 2.2 Estimation of Bulk composition

The composition of pure and ZnO added crystals were accurately calculated from the EDAX spectrum taken by SUTW-SAPPIRE DETECTOR OF 139.91 RESOLUTION. The concentration of Zn and O atom also calculated for the doped systems.

## 2.3 Debye temperature calculation

Debye temperature of the crystals can be determined from various experimental measurements like melting point, Debye –Waller factor, hardness number, Kopp-Neumann relation etc.

### 2.3.1 Melting point

Debye temperature can be estimated from the melting point ( $T_m$ ) of the crystal using the formula [2]

$$\theta_m = C [ T_m / MV^{2/3} ]^{1/2}$$

Where C is a constant depending on the structure. The unit volume was estimated from the lattice constant. A value of 450 has been used for C as the structure is of NaCl type. This value evaluated from the known values of Debye temperature for the end member crystals. The melting point of all the grown crystals were determined from TG/DTA curve recorded on SEIKO TG/DTA 6200 system at heating ramp of 10<sup>0</sup> C/min. Nitrogen was used as purge gas at a flow rate of 500 ml/min.

### 2.3.2 Debye-Waller factor

The mean Debye-Waller factor was determined from the XRD data taken by using PAN analytical diffractometer with scintillation counter and monochromated CuK<sub>α</sub> (=1.5406Å<sup>0</sup>) radiation. The reflections were indexed following the procedures of Lipson and Steeple [3]. Analysis of the X-ray diffraction peaks by the available methods [4] shows that for the mixed crystals, all the X-ray diffraction peaks can be indexed with single fcc phase.

The mean Debye-Waller factor for all the fourteen grown crystals was determined by a method similar to that followed by Mahadevan and his Co-workers [2, 5-11]. As the number of reflections are limited, only a common Debye-Waller factor was determined for all the atoms in every system by using Wilson theory [12].

The structure factors were calculated using the relations

$$F(hkl) = 4(f_{K^+} \pm f_{Cl^-}) \quad \text{for KCl}$$

$$F(hkl) = 4(f_{K^+} \pm f_{Br^-}) \quad \text{for KBr}$$

$$F(hkl) = 4[x (f_{K^+} \pm f_{Cl^-}) + (1-x) (f_{K^+} \pm f_{Br^-})] \quad \text{for mixed systems.}$$

Here  $f_{K^+}$ ,  $f_{Cl^-}$  and  $f_{Br^-}$  are the respective scattering factors for K<sup>+</sup>, Cl<sup>-</sup> and Br<sup>-</sup> ions, calculated from the nine parameters taken from the literature [13]. x and (1-x) are the compositions of KCl and KBr present in the mixed system. The plus sign for the reflections with even values of h+k+l and minus sign for those with odd values of h+k+l.

The Bragg-intensity equation may be written as

$$(I_e/I_c) = K \exp(-2B \sin^2 \theta / \lambda^2)$$

The mean Debye–Waller factor ( $B_{obs}$ ) was obtained by taking a least squares approximation of  $\ln(I_e/I_c)$  against  $\sin^2 \theta / \lambda^2$ .  $I_e$  is experimentally observed (integrated) intensity,  $I_c$  is the calculated intensity, K is the scale factor,  $\theta$  is the Bragg angle and  $\lambda$  is the wave length of radiation used.

The presence of mixing of ions creates a static contribution in the case of mixed crystals. In the present study among the three ions viz K<sup>+</sup>, Cl<sup>-</sup> and Br<sup>-</sup>, replacement is possible between Cl<sup>-</sup> and Br<sup>-</sup>.

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

Where x and (1-x) are respective mole fractions of KCl and KBr in the mixed crystals and  $r_A$  and  $r_B$  are the respective ionic radii of KCl and KBr.

Observed Debye - Waller factors for the mixed crystals is given by

$$B_{\text{observed}} = B_{\text{static}} + B_{\text{thermal}}$$

$B_{\text{thermal}}$  was calculated from the above relation and the Debye temperature, mean square amplitude of vibration and Debye frequency were determined from the methods followed by Neelakanda Pillai and Mahadevan [2].

The Debye temperature ( $\theta_D$ ) was obtained from the Debye-Waller theory expressions.

For pure crystals

$$B_{\text{obs}} = (6h^2/mKT) W(x)$$

For mixed crystals

$$B_{\text{thermal}} = (6h^2/mKT) W(x)$$

Where  $m$  is the mean atomic mass,  $T$  is the absolute temperature (298K) at which the X-ray diffraction intensities were measured,  $h$  is the Planck's constant and  $k$  is the Boltzmann's constant The function  $W(x)$  is given by

$$W(x) = (\varphi(x)/x^2) + (1/4) x$$

Where  $x = \theta_D/T$  and  $\varphi(x)$  is an integral

$$\varphi(x) = \int_0^x (e^y/1-e^y) dy$$

The value of  $W(x)$  for a wide range of  $x$  are tabulated by Benson and Gill[14],  $\theta_D$  the Debye temperature was evaluated by using the above expression.

The mean square amplitude of vibration ( $\langle u^2 \rangle$ ) was obtained from [2]

$$B = 8\pi^2 \langle u^2 \rangle$$

The Debye frequency was obtained from the Debye temperature using the relation [2]

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

### 2.3.3 Microhardness value

Debye temperature can also be estimated from the micro hardness value calculated from Vicker's microhardness measurement reported else where [15] using the relation.

$$\theta_H = BH^{1/2} V^{1/6} M^{-1/2}$$

Where  $B$  is a constant and its value is 348, which is calculated from the known KCl data.

### 2.3.4 Kopp-Neumann relation

Sirdeshmukh and Srinivas [16] reviewed the data on fourteen alkali halide mixed crystals and conducted that, by and large, the composition dependence of  $\theta_D$  (i.e.  $\theta$ ) of alkali halide mixed crystals is well described by the Kopp-Neumann relation given by

$$\theta^{-3} = x \theta_A^{-3} + (1-x)\theta_B^{-3}$$

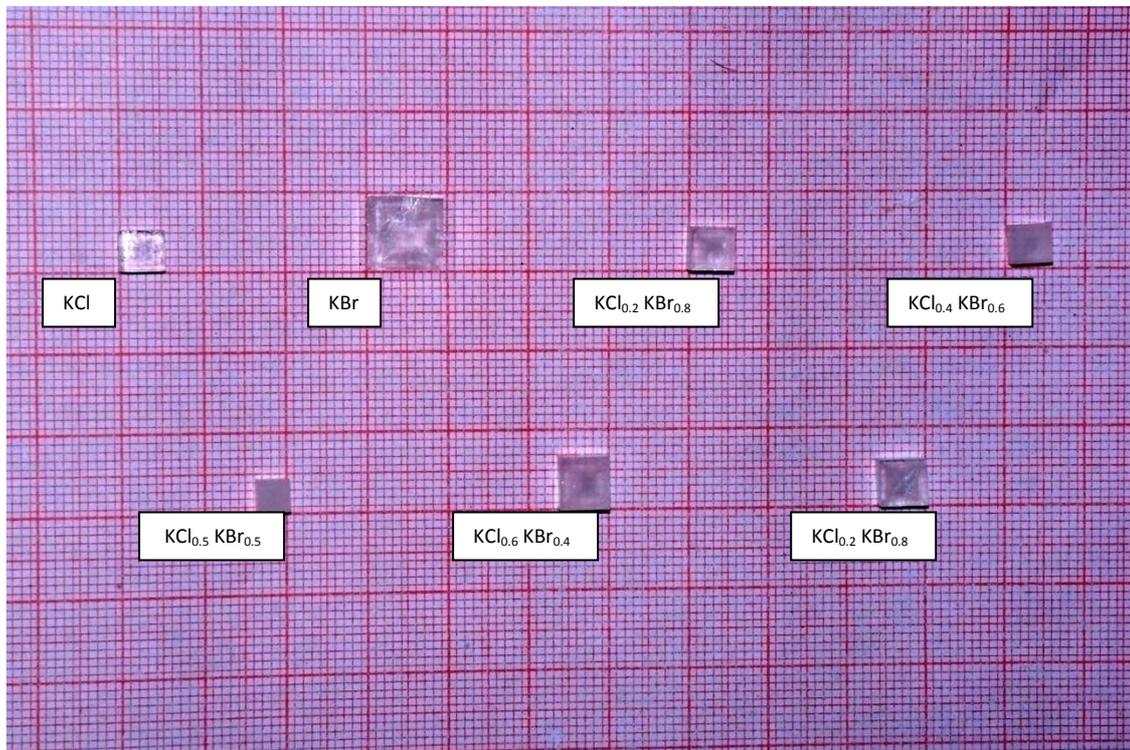
Where  $\theta_A$  and  $\theta_B$  are the Debye temperatures of the end member crystals.

## RESULTS AND DISCUSSION

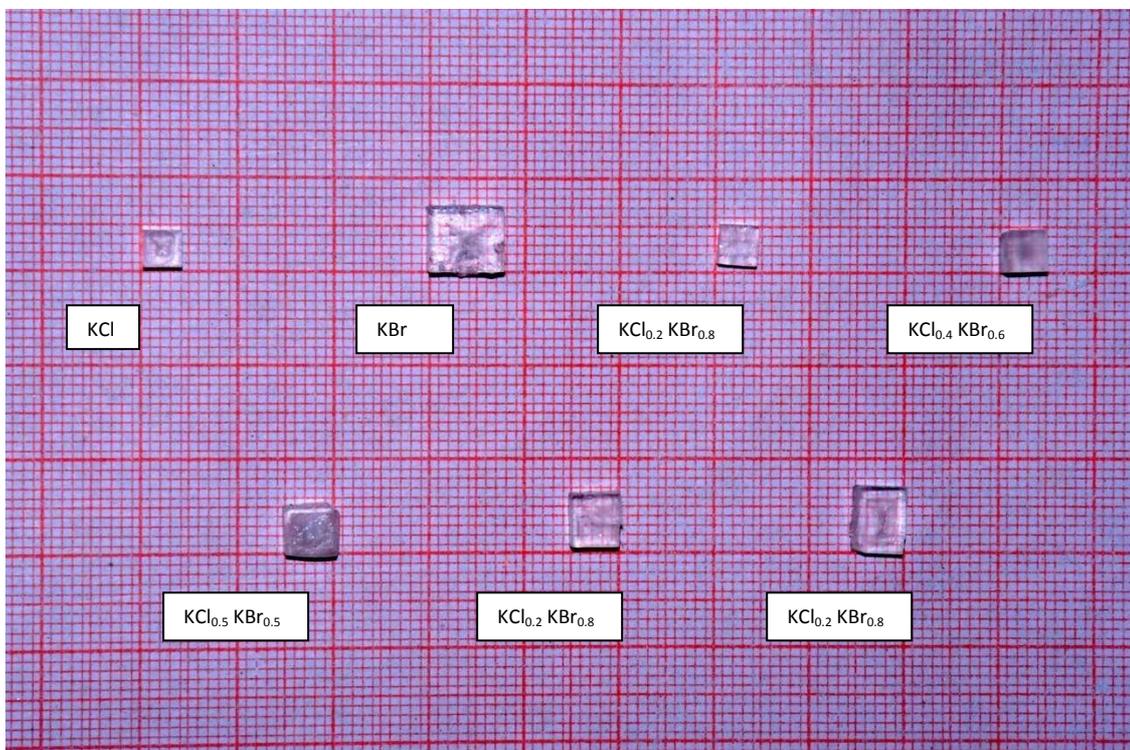
### 3.1 Growth of Sample Crystals

The grown mixed crystals of  $KCl_x Br_{1-x}$  are provided in photograph 1 along with end member crystals and ZnO added mixed crystals of  $KCl_x Br_{1-x}$  along with ZnO added end member crystals are provided in photograph 2. It is found that all the fourteen crystals grown in the present study were stable and transparent. The microhardness values show that the mixed crystals are found to be more harder than end member crystal KCl and also ZnO added crystals

were found to be more harder than the undoped mixed crystals. It shows that the dopant addition increases the hardness further.



Photograph 1 : Undoped mixed crystals of KCl-KBr



Photograph 2 : ZnO doped mixed crystals of KCl-KBr

### 3.2 Estimation of Bulk composition

The composition of all the crystals except the undoped and doped end member crystals were estimated from the EDAX data. The estimated composition along with the weight percentage of  $K^+$ ,  $Cl^-$ ,  $Br^-$  and  $Zn^{2+}$  (for doped crystals only) are provided in Table.1. It is found that the estimated composition of all the mixed crystals well agree with the composition taken. EDAX spectrum for the equimolar composition of KCl and KBr is provided in fig.1 for an illustration.

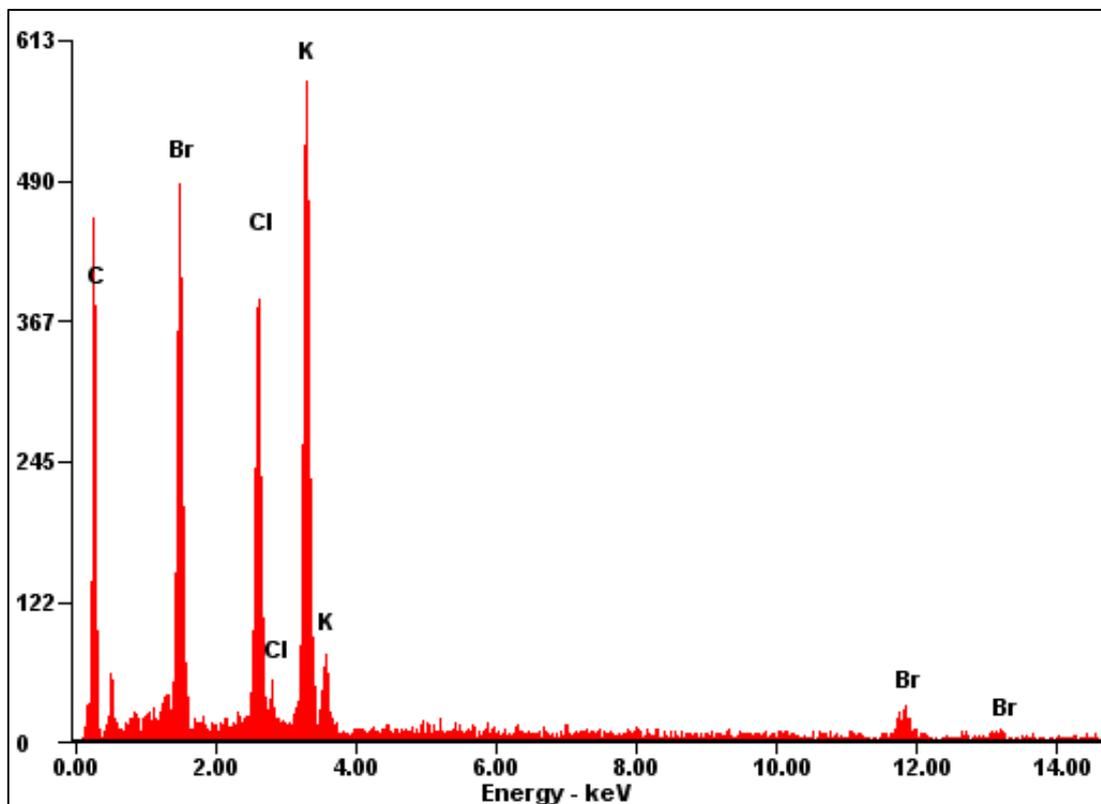


Fig.1 The EDAX spectrum of  $KCl_{0.5}KBr_{0.5}$  crystal

Table: 1 Weight percentage and estimated composition values together with the composition taken for pure and doped crystals

System	Weight percentage of				Estimated Composition
	K	Cl	Br	Zn	
Undoped mixed crystals KCl	25.05	28.77	-	-	KCl
KBr	15.68	-	60.71	-	KBr
$KCl_{0.2}KBr_{0.8}$	18.1	2.52	46.39	-	$KCl_{0.1467}KBr_{0.8533}$
$KCl_{0.4}KBr_{0.6}$	22.5	8.93	40.16	-	$KCl_{0.3625}KBr_{0.6375}$
$KCl_{0.5}KBr_{0.5}$	13.55	7.17	21.49	-	$KCl_{0.4594}KBr_{0.5406}$
$KCl_{0.6}KBr_{0.4}$	22.8	16.83	15.07	-	$KCl_{0.6620}KBr_{0.33799}$
$KCl_{0.8}KBr_{0.2}$	15.13	16.33	4.9	-	$KCl_{0.84769}KBr_{0.1523}$
ZnO doped mixed crystals KCl	21.65	22.08	-	0.51	KCl
KBr	16.62	-	49.17	0.81	KBr
$KCl_{0.2}KBr_{0.8}$	21.25	3.35	54.75	0.08	$KCl_{0.1535}KBr_{0.8465}$
$KCl_{0.4}KBr_{0.6}$	22.45	8.87	39.79	0.3	$KCl_{0.3629}KBr_{0.6371}$
$KCl_{0.5}KBr_{0.5}$	32.22	20.8	32.65	0.14	$KCl_{0.5494}KBr_{0.4506}$
$KCl_{0.6}KBr_{0.4}$	36.99	31.22	22.25	0.11	$KCl_{0.6885}KBr_{0.3115}$
$KCl_{0.8}KBr_{0.2}$	28.87	28.5	10.37	0.21	$KCl_{0.8343}KBr_{0.1656}$

### 3.3 Lattice Parameter

Analysis of X-ray diffraction peaks by available methods show that all the diffraction peaks can be indexed with a single FCC lattice. The observed lattice parameter along with those calculated from Vegard's law and Retger's rule are provided in Table.2. According to Tobolski [17] two alkali halides AB and AC will form continuous solid solutions  $AB_xC_{1-x}$  provide the difference between their lattice parameters is less than 6%. Two compounds or elements are said to form a continuous solid solution if a single lattice parameter as measured by X-ray powder photographs can be assigned to the solid solution at all composition. In the present work, from the Table.2 it is found

that all the compositions are assigned single lattice parameter and it indicates that they form continuous solid solutions.

$$a_0 = x a_1 + (1-x) a_2 \quad (\text{Vegard's law})$$

$$a_0^3 = x a_1^3 + (1-x) a_2^3 \quad (\text{Retger's Rule})$$

Where  $a_0$  is the lattice parameter of the mixed crystals,  $a_1$  and  $a_2$  are the lattice parameters of two end member crystals. The estimated compositions were taken for calculation. Following O. D. Slagle and McKinstry [18] the difference between the lattice parameter value calculated from laws of Vegard and Retger were given in table.2. It is seen that the observed values show negative deviations from both Vegard's law and Retger's rule. But the deviation from Vegard's law are much less than those from Retger's rule. The XRD pattern of the sample  $\text{KCl}_{0.5}\text{Br}_{0.5}$  is provided in fig.2 for illustration.

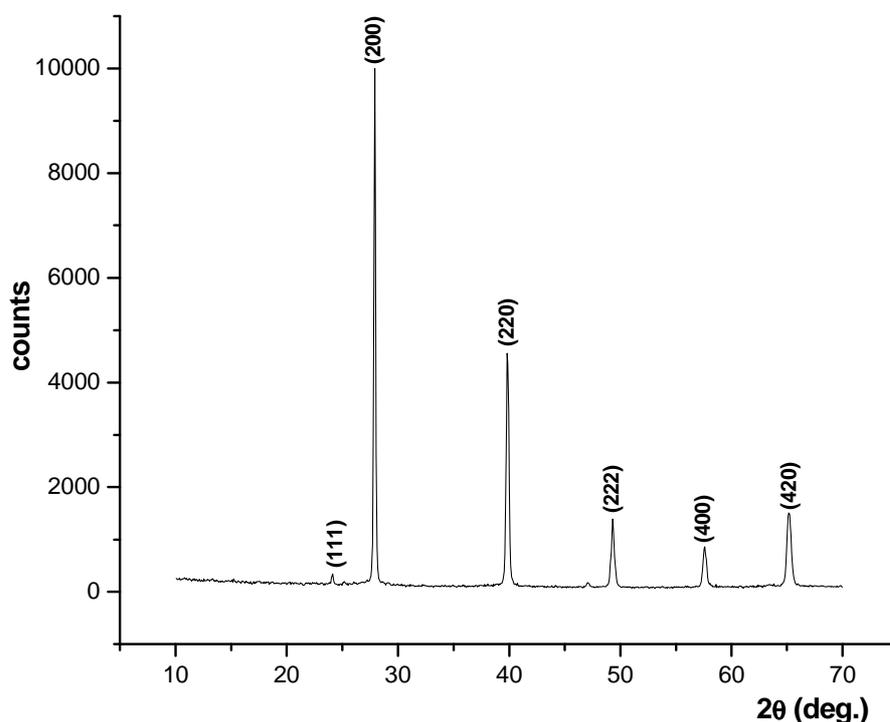


Figure 2 : XRD pattern of the sample  $\text{KCl}_{0.5}\text{Br}_{0.5}$

Table 2. The observed lattice parameter ,calculated lattice parameter and deviation from Vegard's law and Retger's rule together with the composition taken for pure and doped crystals.

System	Lattice parameter (Å)		Calculated lattice parameter (Å)		Deviation (Å)	
	Pure	Doped	From Vegard's law	From Retger's Rules	From Vegard's law	From Retger's Rules
KCl	6.3433	6.3199	-	-	-	-
KBr	6.6434	6.6104	-	-	-	-
$\text{KCl}_{0.2}\text{KBr}_{0.8}$	6.5601	6.5420	6.5994	-	-	-
$\text{KCl}_{0.4}\text{KBr}_{0.6}$	6.4581	6.4293	6.5346	6.6011	0.0393	0.0410
$\text{KCl}_{0.5}\text{KBr}_{0.5}$	6.3922	6.4119	6.5055	6.5378	0.0765	0.0797
$\text{KCl}_{0.6}\text{KBr}_{0.4}$	6.3622	6.3747	6.4447	6.5089	0.1133	0.1167
$\text{KCl}_{0.8}\text{KBr}_{0.2}$	6.3348	6.3327	6.3890	6.4479	0.0825	0.0857
				6.3908	0.0542	0.0560

### 3.4 Debye temperature calculation

#### 3.4.1 Melting Point

Molecular weight, lattice parameter, melting point and the calculated Debye temperature are provided in Table 3. The observed melting point of  $KCl_{0.5}KBr_{0.5}$  Crystal well agreed with those value reported by Jeya Kumari [5]. The Debye temperature thus calculated from melting point varies linearly with composition in the present study is shown in the figure 4. In the case of ZnO added systems the observed melting point remains same and also the calculated Debye temperature from the melting point vary linearly with composition of KCl and KBr. The measured melting point of the end member crystals well agreed with the literature value which is provided in the bracket.

**Table 3. Molecular weight, Lattice constant, Melting point and Debye temperature together with the composition taken for pure and doped crystals**

System	Molecular Weight M (gm)	Lattice Constant Å	Melting Point K	$\theta_m$ (°C)
Undoped mixed crystals KCl	74.56	6.3433 [6.2931] [25]	1048.5 [1043] [25]	228.7890 [19]
KBr	119.02	6.6434 [6.600] [25]	1015.3 [1006] [25]	169.1616 [20]
$KCl_{0.2}KBr_{0.8}$	112.4977	6.5601	1002.6	174.6918
$KCl_{0.4}KBr_{0.6}$	102.9033	6.4581	1004.1	185.7297
$KCl_{0.5}KBr_{0.5}$	98.5998	6.3922	1022.4 [1083] [5]	194.0800
$KCl_{0.6}KBr_{0.4}$	89.5863	6.3622	1033.5	206.0791
$KCl_{0.8}KBr_{0.2}$	81.331	6.3348	1026.1	216.1619
ZnO doped mixed crystals				
KCl	74.56	6.3199	1045.3	229.1619
KBr	119.02	6.6104	1010.7	169.4785
$KCl_{0.2}KBr_{0.8}$	112.179	6.5420	1001	175.2317
$KCl_{0.4}KBr_{0.6}$	102.886	6.4293	1003.8	186.5396
$KCl_{0.5}KBr_{0.5}$	94.585	6.4119	1012.6	196.2519
$KCl_{0.6}KBr_{0.4}$	88.4031	6.3747	1026.7	206.1191
$KCl_{0.8}KBr_{0.2}$	81.9151	6.3327	1036.1	216.8864

#### 3.4.2 From Micro hardness

The measured hardness values and the Debye temperatures calculated are provided in Table 4. Here also the calculated Debye temperature varies non-linearly with composition. In the case of ZnO added crystals the Debye temperature values increased. The increase in Debye temperature may be due to the increase in hardness values during dopant addition.

**Table 4. The values of hardness number and Debye temperature along with system**

System	Hardness Number for 25gm (Kg/mm <sup>2</sup> )	$\theta_H$ (°C)
Undoped mixed crystals		
KCl	8.265	291.8135
KBr	31.1	160.7404
$KCl_{0.2}KBr_{0.8}$	11.3	190.7613
$KCl_{0.4}KBr_{0.6}$	11.45	199.2087
$KCl_{0.5}KBr_{0.5}$	9.055	180.0525
$KCl_{0.6}KBr_{0.4}$	7.65	173.2134
$KCl_{0.8}KBr_{0.2}$	9.34	200.4384
ZnO doped mixed crystals		
KCl	10.8	332.9609
KBr	54.7	212.6461
$KCl_{0.2}KBr_{0.8}$	12.5	200.6427
$KCl_{0.4}KBr_{0.6}$	15.25	229.4075
$KCl_{0.5}KBr_{0.5}$	11.25	205.2235
$KCl_{0.6}KBr_{0.4}$	13.35	230.5709
$KCl_{0.8}KBr_{0.2}$	11.15	218.1814

#### 3.4.3 From Debye Waller factor

The thermal parameters obtained in the present study Viz Debye Waller factor ( $B_{\text{Observed}}$ ,  $B_{\text{Static}}$  and  $B_{\text{Thermal}}$ ) mean Square amplitude of vibration Debye temperature and Debye frequency are given in Table 5. The Wilson plot of the sample  $KCl_{0.5}KBr_{0.5}$  is shown fig 3.

The reported values of Debye-Waller factors and Debye temperatures for the end member crystals are provided in bracket. Large difference in these values obtained may be attributed to the difference in the method of preparation of crystals and method of estimation of these parameters. The bulk composition dependence of Debye-Waller factor in the case of undoped mixed crystals is highly non-linear.

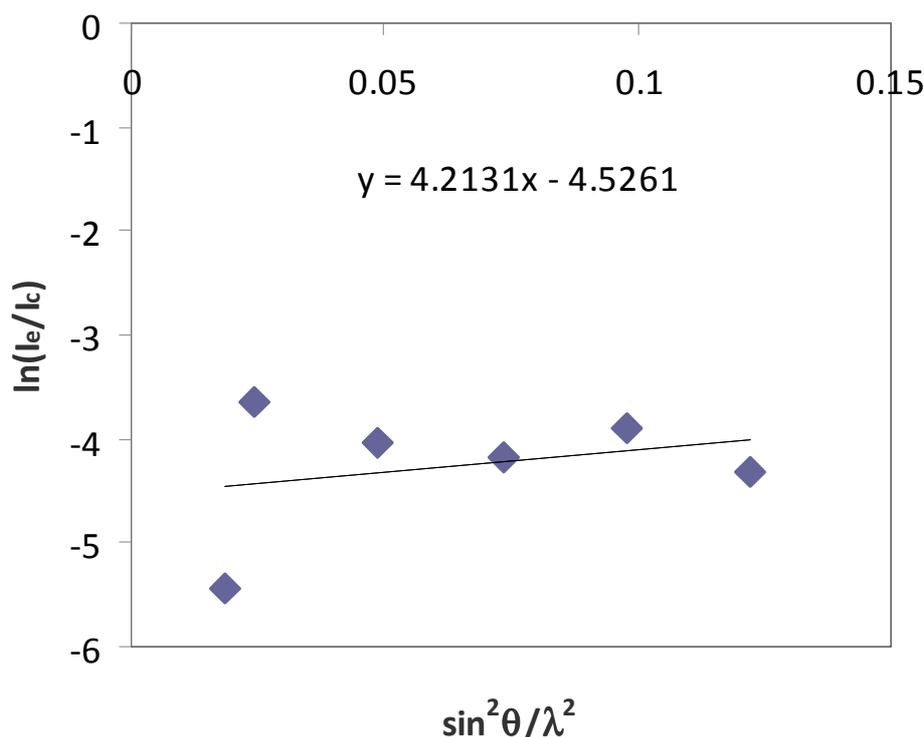


Fig :3 Wilson plot of the sample  $KCl_{0.5}KBr_{0.5}$

Table 5. The values of Debye Waller factor ( $B_{Observed}$ ,  $B_{Static}$  and  $B_{Thermal}$ ), mean square amplitude of vibration, Debye temperature and Debye frequency along with system

System	$B_{Static}$ $\text{\AA}^2$	$B_{Observed}$ $\text{\AA}^2$	$B_{Thermal}$ $\text{\AA}^2$	Mean square amplitude of vibration $\text{\AA}^2$	Debye Temperature $\theta_D$ ( $^{\circ}C$ )	Debye frequency $f_D \times 10^{12}$
Undoped mixed crystals						
KCl	-	0.5455	0.5455	0.0069158	292.189 (231)[26]	6.085433
KBr	-	1.8205	1.8205(1.742)[6]	0.0230803	125.309 (155)[6]	2.60982
$KCl_{0.2}KBr_{0.8}$	0.002817	0.6975	0.694683	0.0088072	298	6.20646
$KCl_{0.4}KBr_{0.6}$	0.0051996	1.695	1.6898	0.0214233	198.468	4.1335
$KCl_{0.5}KBr_{0.5}$	0.0055883	2.1065	2.100912	0.0266354	181.631	3.78284
$KCl_{0.6}KBr_{0.4}$	0.0050344	2.5465	2.541466	0.0322207	173.287	3.60906
$KCl_{0.8}KBr_{0.2}$	0.0029048	1.6065	1.603595	0.0203304	229.609	4.78208
ZnO doped mixed crystals						
KCl	-	0.8015	0.8015	0.0101614	240.039	4.9993
KBr	-	1.926	1.926	0.0244177	121.882	2.53844
$KCl_{0.2}KBr_{0.8}$	0.002924	1.4225	1.419576	0.0179974	207.557	4.322799
$KCl_{0.4}KBr_{0.6}$	0.0052021	2.5345	2.529298	0.03206644	161.963	3.37321
$KCl_{0.5}KBr_{0.5}$	0.00557	1.871	1.86543	0.02364992	196.978	4.10247
$KCl_{0.6}KBr_{0.4}$	0.004826	0.5225	0.517674	0.0065631	394.85	8.22356
$KCl_{0.8}KBr_{0.2}$	0.0031086	0.6105	0.607391	0.00770051	376.97	7.8737

The Debye-Waller factors of  $KCl_{0.5}KBr_{0.5}$  were determined by Wasastjerna [21] and Ahtee et al [22] from X-ray intensities. Mohanlal et al [23] determined the Debye-Waller factors for two compositions in the KCl-KBr system from neutron diffraction intensities. All these studies indicate that Debye-Waller factors of mixed crystals are larger than those expected from additivity. Also the enhancement of Debye-Waller factor may be attributed due to increase in the vibrational entropy due to mixing [24]. But in the case of ZnO added  $KCl_{0.6}KBr_{0.4}$  and  $KCl_{0.8}KBr_{0.2}$  systems the calculated Debye-Waller factor nearly agreed with the end member crystal KCl. For other doped crystals the calculated Debye-Waller factors are greater than either end member except for the system  $KCl_{0.2}KBr_{0.8}$  in which it is less than the either end member.

Debye temperature of the mixed crystals shows a non-linear variation with composition. Debye temperature determined for the equimolar system agreed exactly with the value reported by K. Jeyakumari[5] grown from

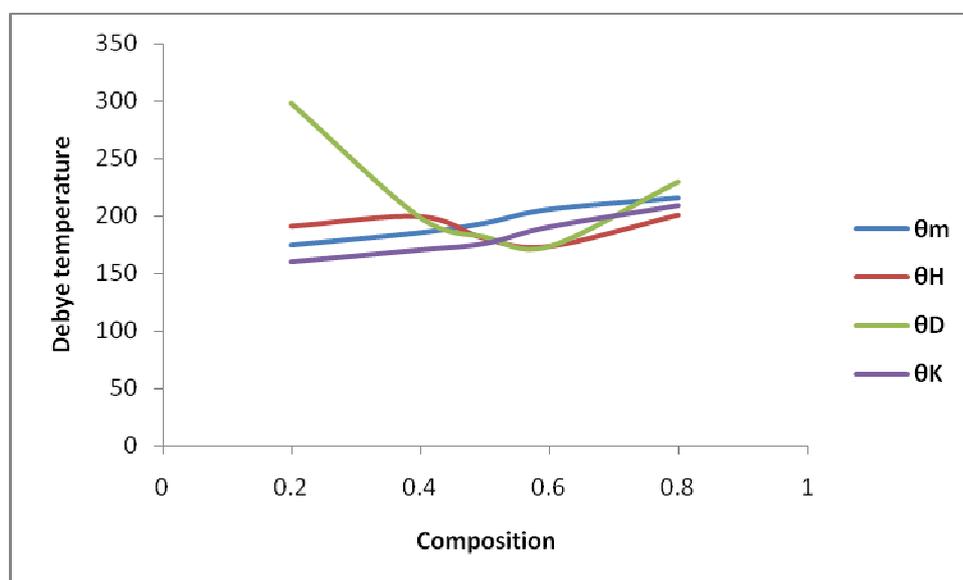
pulling method. Debye frequencies obtained for pure and doped crystals lie in the infrared range. The variation of Debye frequency with composition is not in any order similar to Debye temperature.

### 3.4.4 Comparison of calculated Debye temperatures with Kopp-Neumann relation

The Debye temperatures calculated from the melting point, micro hardness and from Debye-Waller factor are provided in Table 6 along with those calculated from Kopp-Neumann relation. Variation of Debye temperatures obtained from the above four methods with composition is shown in figure 4 and figure 5. It is found that Debye temperatures calculated from the melting point and micro hardness varies linearly with composition and nearly match with those estimated from Kopp-Neumann relation. But obtained from Debye Waller factor shows non linear variation and deviating highly from the Kopp-Neumann relation. This may be related to increase in the vibrational entropy due to mixing. Mahadevan and his co-workers [2,5-11] observed the Debye temperature for ternary mixed crystals of alkali halide crystals, they have also reported that the Debye temperature varies non-linearly with composition.

**Table 6. The Debye temperatures calculated from the melting point, micro hardness, Debye-Waller factor and Kopp-Neumann along with system**

System	Debye temperature			
	$\theta_m$ (°C)	$\theta_H$ (°C)	$\theta_D$ (°C)	$\theta_K$ (°C)
Undoped mixed crystals				
KCl	228.7890	291.8135	292.189	231
KBr	169.1616	160.7404	125.309	155
KCl <sub>0.2</sub> KBr <sub>0.8</sub>	174.6918	190.7613	298	160.6822
KCl <sub>0.4</sub> KBr <sub>0.6</sub>	185.7297	199.2087	198.468	170.82663
KCl <sub>0.5</sub> KBr <sub>0.5</sub>	194.0800	180.0525	181.631	176.31633
KCl <sub>0.6</sub> KBr <sub>0.4</sub>	206.0791	173.2134	173.287	190.5791
KCl <sub>0.8</sub> KBr <sub>0.2</sub>	216.1619	200.4384	229.609	208.9164
ZnO doped mixed crystals				
KCl	229.1619	332.9609	240.039	231
KBr	169.4785	212.6461	121.882	155
KCl <sub>0.2</sub> KBr <sub>0.8</sub>	175.2317	200.6427	207.557	160.9663
KCl <sub>0.4</sub> KBr <sub>0.6</sub>	186.5396	229.4075	161.963	170.8479
KCl <sub>0.5</sub> KBr <sub>0.5</sub>	196.2519	205.2235	196.978	182.11089
KCl <sub>0.6</sub> KBr <sub>0.4</sub>	206.1191	230.5709	394.85	192.8131
KCl <sub>0.8</sub> KBr <sub>0.2</sub>	216.8864	218.1814	376.97	207.36173



**Fig :4 For undoped mixed crystal**

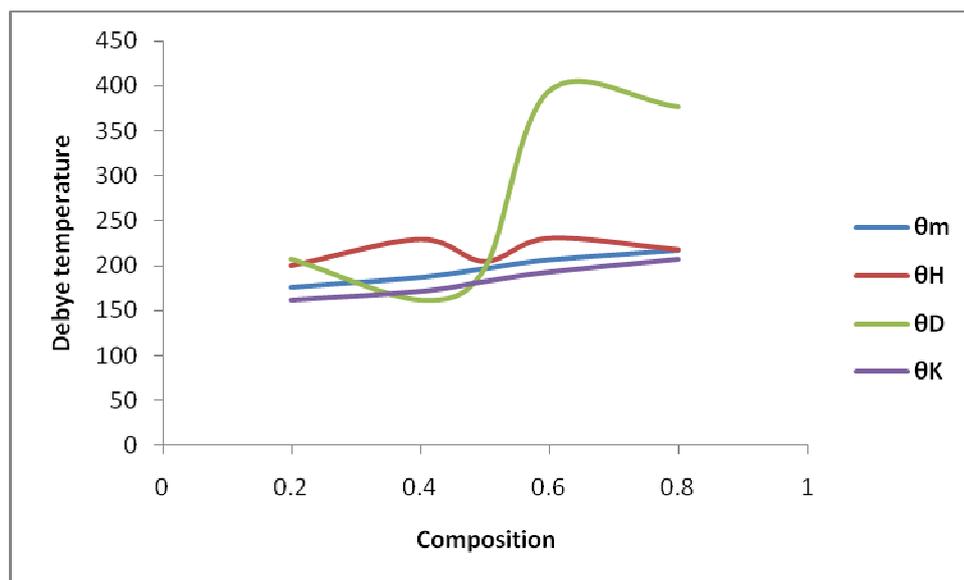


Fig: 5 For ZnO doped mixed crystal

### CONCLUSION

Undoped and ZnO added mixed crystals of  $KCl_xBr_{1-x}$  were grown from the aqueous solution. Composition of the grown crystals were determined from the EDAX data. The lattice parameters estimated from the X-ray diffraction data shows that the system exhibits only a single f.c.c phase and the lattice parameters almost obey the Vegard's law for all the grown mixed crystals. In the case of doped crystals the deviation of lattice parameter from Vegard's law is high except those for intermediate composition. Thermal parameters Viz Debye-Waller factor, mean square amplitude of vibration and Debye frequency were determined for all the grown crystals from X-ray powder diffraction data. Debye temperatures were determined from the melting point, hardness value and Debye-Waller factor. Debye temperatures calculated from the melting point and hardness value are found to vary linearly with composition where as those calculated from the Debye -Waller factor found vary non linearly with composition which may be attributed to the increase in vibrational entropy due to mixing.

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