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A STUDY OF THERMOPHYSICAL AND COHESIVE PROPERTIES OF $NaBr_{1-x}I_x$ AND $KBr_{1-x}I_x$ MIXED ALKALI HALIDES

A.K. DIXIT

Professor of Physics, Govt. P.G. College, Satna (M.P.)

R.C. DIXIT

Asstt. Professor of Physics, Govt. Holkar Science College, Indore (M.P.)

AND

S.D. CHATURVEDI

Asstt.Professor of Physics, Govt. Maharaja College, Chhatarpur (M.P.)

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We have studied the thermophysical and cohesive properties such as Gruneisen parameter, molecular force constant, Restrahl frequency, Debye temperature compressibility and Anderson-Gruneisen parameter etc of mixed $NaBr_{1-x}I_x$ and $KBr_{1-x}I_x$ mixed alkali halides under the banner of three body force potential model. This three body force potential (TBFP) model contains long-range forces (Coulombian and three body interactions) as well as short range forces (Vander-Waals and overlap repulsive forces) [10-15]. We have selected mixed alkali halides for the discussion because mixed crystals are more precisely known as solid solutions. So mixed alkali halides have received considerable attention of investigators [1-9] due to their scientific and technological importance. The observations shows that the micro hardness of mixed alkali halides is larger than the pure crystals. Some results are very close to their experimental value which shows the superiority of this model over other models.

INTRODUCTION

Ionic solids are model crystal for the analysis of lattice properties. In the same sprit we have used our three body force potential model (TBFP) for the calculation of lattice and thermo-physical properties of mixed alkali halides $NaBr_{1-x}I_x$ and $KBr_{1-x}I_x$. This potential model consists long-range (Coulombian and three body interaction) forces as well as short range forces (overlap repulsive force operating upto next nearest neighbour ions and Vander-Waals interaction) [31-35]. This shows that the inclusion of three body interaction effect makes the present model suitable for the study of thermophysical properties of mixed alkali halides. Most of the theoretical [10-25] and experimental workers [26-30] have explained the elastic and thermophysical properties of the ionic solids.

Theory and method of Calculations:

We have applied the TBP model for the calculation of thermophysical properties of mixed alkali halides. Three body potential model contains long-range forces as well as short-range

forces. Coloumbian force associated with three body force is long-range force while Vander-Waals and Hafemeister-Flygare are short-range forces. The values of input data for different concentrations(x) have been evaluated by applying Vegard's law for second order elastic constants, lattice constants, ionic radii and Vander-Waals constants of host and dopant materials as-

$$C_{ij}\,(\text{mix}) = x\,c_{ij}\,(A) + (1-x)\,c_{ij}\,(B)$$
$$r_{ij}\,(\text{mix}) = x\,r_{ij}\,(A) + (1-x)\,r_{ij}\,(B)$$
$$\rho\,(\text{mix}) = x\,\rho\,(A) + (1-x)\,\rho\,(B)$$
$$C\,(\text{mix}) = x\,C\,(A) + (1-x)\,C\,(B)$$
$$D\,(\text{mix}) = x\,D\,(A) + (1-x)\,D\,(B)$$

The constituent of mixed crystals are held together by the harmonic elastic forces with no internal stress within the crystal. The values of input data are given in tables 1.1 and 1.2. Thermophysical properties include in the discussion are Gruneisen parameter (γ), molecular force constants (f), Debye Temperature (θ_D), Restrahl frequency (υ_0), ratio of volume thermal expansion coeffcient to specific heat at constant volume ($\alpha v/Cv$), Compressibility (β), Anderson-Gruneisen parameter (δ_T). The relevent expressions have been derived [31-35] from three body potential [31-35] —

$$U(r) = -\alpha_m ze^2/r\,[z + 12\,f(r)] + 6b\beta + -\exp[(r_1 + r_2 - r)/\rho] + 6b\,\beta_{++}\exp[(2r_1 - 1.4142r)/\rho] + 6b\,\beta - \exp[(2r_2 - 1.4142r)/\rho] - C/r^6 - D/r^8$$

(i) Gruneisen parameter

$$\gamma = -r_0/6[U'''(r)/U''(r)]\;r = r_0$$

(ii) Molecular force constant

$$f = 1/3[U''_{SR}(r) + 2/r\;U'_{SR}(r)]_{r=r0}$$

(iii) Restrahl frequency

$$\upsilon_0 = 1/2\pi\sqrt{f/\mu}$$

where μ is the reduced mass of the crystal.

(iv) Debye Temperature. $(\Theta_D) = h\,\upsilon_0/k$

(v) Ratio of volume thermal expression coefficient to specific heat at constant volume

$$\alpha_v/C_v = -U'''(r_o)/2r_o\,U''(r_o)^2$$

(vi) Compressibility $\beta = 18\,r_o/U''(r_o)$

(vii) The Anderson-Gruneisen Parameter

$$\delta_T = -\beta r_o^3/27V\,U'''(r_o)$$

The above relations have been used to calculate the thermophysical properties of mixed halides. The input parameters are given in tables 1.1 and 1.2. Calculated thermophysical properties of mixed alkali halides are given in tables 1.3 and 1.4.

Table 1.1. Model parameters for mixed halide $NaBr_{(1-x)}I_{(x)}$ at different compositions

Composition (x)	ρ (10^{-8}cm)	b (10^{-12} ergs)	$f(r_0)$	$af'(r_0)$	C (10^{-60} erg × cm^6)	D (10^{-76}erg × cm^8)
0.0 NaBr	0.329	0.363	0.0013	– 0.012	930	537
0.2	0.347	0.361	0.0012	– 0.012	1097	618
0.4	0.365	0.358	0.0018	– 0.013	1264	699
0.6	0.383	0.355	0.0047	– 0.039	1431	780
0.8	0.401	0.360	0.0048	– 0.038	158	861
1.0 NaI	0.420	0.351	– 0.0046	– 0.028	1765	942

Table 1.2. Model parameters for mixed halide $KBr_{(1-x)}I_{(x)}$ at different compositions

Composition (x)	ρ (10^{-8}cm)	b (10^{-12}ergs)	$f(r_0)$	$af'(r_0)$	C (10^{-60}erg × cm^6)	D (10^{-76}erg × cm^8)
0.0 (KBr)	0.265	0.264	– 0.0012	+0.0154	896	1521
0.2	0.232	0.247	– 0.0075	0.0106	1156	2074
0.4	0.231	0.323	0.0020	– 0.019	1417	2626
0.6	0.215	0.352	0.0059	– 0.050	1678	3179
0.8	0.199	0.381	0.0013	– 0.0101	1938	3731
1.0 (KI)	0.183	0.410	– 0.0015	– 0.019	2199	4284

Table 1.3. Thermophysical & cohesive properties of mixed halide $NaBr_{(1-x)}I_{(x)}$ at different compositions

Cohesive Property	$X = 0$		$X = 0.2$		$X = 0.4$		$X = 0.6$		$X = 0.8$		$X = 1.0$	
	Calc	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp.
Gruneisen Pararmeter γ	2.24	-	2.18	-	2.20	-	2.31	-	2.44	-	1.80	
Molecular force constant f (10^4 dyn/cm)	5.73	-	5.046	-	4.45	-	3.93	-	3.22	-	3.34	-
Restrahl frequency υ_o (T Hertz)	6.69	-	6.43	-	5.98	-	5.58	-	5.01	-	5.05	-
Debye Temperature (Θ_D) (k)	320.8	-	308.4	-	286.8	-	267.6	-	240.3	-	242.3	-
Ratio of volume thermal expression coefficient to specific heat at cons tant volume α_v/C_v (10^{10}ergs unit)	3.16	-	3.21	-	3.264	-	3.316	-	3.368	-	3.42	-
Compressibility (β) (10^{-12} dyn/cm)	2.83	3.94	4.11	-	5.55	-	9.16	-	10.19	-	3.87	-
The Anderson-Gruneisen Pararmeter δ_T	3.58	-	4.37	-	4.42	-	4.63	-	4.89	-	3.59	-

Table 1.4. Thermophysical & cohesive properties of mixed halide $KBr_{(1-x)}I_{(x)}$ at different compositions

Cohesive Property	$X = 0$		$X = 0.2$		$X = 0.4$		$X = 0.6$		$X = 0.8$		$X = 1.0$	
	Calc.	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**
Gruneisen Pararmeter γ	2.64	2.01	2.34	-	2.05	-	1.76	-	1.46	-	1.17	1.60
Molecular force constant f (10^4 dyn/cm)	3.73	-	4.55	-	5.35	-	6.16	-	6.95	-	7.73	-
Restrahl frequency υ_0 (T Hertz)	1.33	-	2.31	-	3.28	-	4.25	-	5.23	-	6.21	-
Debye Temperature (Θ_D) (k)	63.8	-	110.6	-	157.4	-	204.2	-	251.1	-	297.9	-
Ratio of volume thermal expression coefficient to specific heat at cons tant volume α_v/C_v(10^{10}ergs unit)	5.02	-	4.40	-	3.77	-	3.15	-	2.52	-	1.90	-
Compressibility (β) (10^{-12} dyn/cm)	4.48	3.94	3.97	-	3.46	-	2.96	-	2.45	-	1.94	-
The Anderson-Gruneisen Pararmeter δ_T	5.28	-	4.69	-	4.11	-	3.52	-	2.94	-	2.35	-

Result and discussion

A look at the tables 1.3 and 1.4, it is clear that presently estimated end point values of Gruneisen parameter and Anderson–Gruneisen parameter are very close to their experimental values. The end point values of Debye temperature show a good agreement with their available experimental values [21-22]. Some results of ours are still higher than the experimental values. The reason behind is to change in bond length in ionic solids. The observations shows that the micro hardness of mixed alkali halides is larger than the pure crystals. Some results are very close to their experimental value which shows the superiority of this model over other models. On the basis of over all achievements the present TBP model can be regarded to be adequately suitable for the prediction of thermo physical properties of mixed alkali halides.

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