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A THEORETICAL STUDY OF THERMOPHYSICAL AND COHESIVE PROPERTIES OF $NaCl_{1-X}F_X$ MIXED ALKALI HALIDE

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I 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 $NaCl_{1-x}F_x$ mixed alkali halide under the banner of three body force potential model. Three body force potential (TBFP) model contains long-range forces (coloumbian and three body interactions) as well as short range forces (vander-Waal's and overlap repulsive forces) [10-15]. I have selected mixed alkali halides for the discussion because mixed crystals are very useful and known as solid solutions. Mixed alkali halides have received considerable attention of investigators [1-9] due to their scientific and technological importance. The observations show 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 I have used three body force potential model (TBFP) for the calculation of lattice and thermophysical properties of mixed alkali halides $NaCl_{1-x}F_x$. This potential model consists long-range (coloumbian and three body interaction) forces as well as short range forces (overlap repulsive force operating upto next nearest neighbour ions and vander-Waal's interaction) [25-30]. 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 and experimental workers [10-36] have explained the elastic and thermophysical properties of the ionic solids.

THEORY AND METHOD OF CALCULATIONS

From the early history of science and its evolution attempts have been made to explain the behaviour of the ionic solids under some boundary conditions through some potential models. I have applied the TBP model for the calculation of thermophysical properties of mixed alkali halide. 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-Waal's 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-Waal's 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 table 1.1. Thermophysical properties included in the discussion are Gruneisen parameter (γ), molecular force constant (***f***) Debye Temperature (θ_D), Restrahl frequency (υo), ratio of volume thermal expansion coeffcient to specific heat at constant volume (α_v/Cv), Compressibility (β), Anderson-Gruneisen parameter (δ_T). The relevent expressions have been derived from three body potential model. [25-36] --

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

(i) Gruneisen parameter

$$\gamma = -r_o/6\,[U'''(r)/U''(r)]\;r = ro$$

(ii) Molecular force constant

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

(iii) Restrahl frequency

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

where μ is the reduced mass of the crystal.

(iv) Debye Temperature.

$$(\Theta_D) = h\,\upsilon o/k$$

(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 $\beta = 18r_o/U''(r_o)$

(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 model parameters are given in table 1.1 and calculated thermophysical properties of mixed alkali halide are given in table 1.2.

Table 1.1. Model parameters for mixed Alkali Halide $NaCl_{1-x}F_x$ 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 (NACl)	0.313	0.377	0.0026	– 0.024	561	455
0.2	0.3122	0.409	0.00238	– 0.0288	464	380
0.4	0.3114	0.441	0.00216	– 0.0336	367	304
0.6	0.3106	0.473	0.00194	– 0.0384	271	229
0.8	0.3098	0.505	0.00172	– 0.0432	174	153
1.0 (NaF)	0.309	0.537	0.0015	– 0.048	77	78

Table 1.2. Thermophysical & Cohesive properties of mixed halide $NaCl_{1-x}F_x$ 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 Prarmeter γ	2.19	2.25[6]	2.055	–	1.92	–	1.785	–	1.65	1.39	1.515	–
Molecular force constant f (10^4 dyn/cm)	6.46		7.09	–	7.72	–	8.35	–	8.98	–	9.61	
Restrahl frequency υo (T Hertz)	8.31	–	8.98	–	9.66	–	10.34	–	11.02	–	11.7	–
Debye Temperature (Θ_D) (k)	398.7	333	431.3	–	463.9	–	496.5	–	529.2	492	561.77	–
Ratio of volume thermal expression coefficient to specific heat at constant volume α_v/C_v(10^{10} ergs unit)	5.81	–	5.26	–	4.71	–	4.16	–	3.62	–	3.07	–
Compressibility (β) (10^{-12} dyn/cm)	3.55	4.17	3.14	–	2.73	–	2.33	–	1.92	–	1.51	–
The Anderson-Gruneisen Prarmeter δ_T	4.40	3.94	4.12	–	3.85	–	3.57	–	3.30	3.37	3.02	–

Result and discussion

A look at the table 1.2, it is clear that the estimated end points values of Gruneisen parameter and Anderson – Gruneisen parameter are very close to their experimental values. Some results are still higher than the experimental values. The reason behind is to change in bond length in ionic solids. The compressibility and microhardness of mixed halide is higher than pure crystals. So this mixed halide is very important for industrial purpose. 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 thermophysical properties of mixed alkali halides.

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