

**A THEORETICAL STUDY OF PHASE TRANSITION
PRESSURE, THERMOPHYSICAL AND COHESIVE PROPERTIES
OF $\text{NaBr}_{1-x}\text{F}_x$ MIXED ALKALI HALIDE**

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I have studied the phase transition pressure, thermophysical and cohesive properties such as Gruneisen parameter, molecular force constant, Restrahl frequency, Debye temperature, compressibility and Anderson-Gruneisen parameter etc of $\text{NaBr}_{1-x}\text{F}_x$ mixed alkali halide under the banner of three body force potential model. Three body force potential (TBFP) model contains long- range forces (colombian and three body interactions) as well as short range forces (vander-Waal's and overlap repulsive forces) [10-15]. I have selected the mixed alkali halide 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. Recently many workers have devoted their efforts in providing some in-sights to pressure induced behaviour particularly phase transition phenomenon in mixed alkali halides. They observed the structural phase transformation from B_1 to B_2 structure. In the present note, we have made a comparative analysis of the prediction of the phase transition pressure, thermophysical and cohesive properties with the three-body interactions and without three-body interactions model described else where. The observation shows that the micro hardness of mixed alkali halides is larger than the pure crystals. Some results are very close to their experimental value and better than others which shows the superiority of this model over the other models.

INTRODUCTION

Ionic solids are model crystals for the analysis of lattice properties and phase transition pressure. In the same spirit I have used our three body force potential model (TBFP) for the calculation of thermo-physical properties, cohesive properties and phase transition pressure of mixed alkali halide $\text{NaBr}_{1-x}\text{F}_x$. This potential model consists long-range (colombian 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 [10-45] have explained the elastic and thermophysical properties of the ionic solids.

Table 1.1. Model Parameters for mixed Alkali Halide $\text{NaBr}_{1-x}\text{F}_x$ at different compositions

Composition (x)	ρ (10^{-8}cm)	b (10^{-12}ergs)	$f(r_0)$	$af'(r_0)$	C ($10^{-60}\text{erg} \times \text{cm}^6$)	D ($10^{-76}\text{erg} \times \text{cm}^8$)
0.0 (NaBr)	0.390	0.363	0.00130	-0.012	930	537
0.2	0.373	0.397	0.00134	-0.0192	759	445
0.4	0.357	0.433	0.00138	-0.0264	589	353
0.6	0.341	0.467	0.00142	-0.0336	418	262
0.8	0.325	0.502	0.00146	-0.0408	248	170
1.0 (NaF)	0.309	0.537	0.00150	-0.048	77	78

THEORY AND METHOD OF CALCULATION

From the early history of science and its evolution, attempts have been made to explain the behavior of the ionic solids under some boundary conditions through different potential models. I have applied the TBP model for the calculation of phase transition pressure and thermophysical properties of mixed alkali halide. Coloumbian force associated with three body force is long-range force while vander-Waal's and Hafemeister – Flygare forces 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 constituents 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 (ν_0), ratio of volume thermal expansion coefficient to specific heat at constant volume (α_v/C_v), Compressibility (β), Anderson-Gruneisen parameter (δ_T). The relevent expressions have been derived from three body potential model [25-45]

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

- (i) Gruneisen parameter

$$\gamma = -r_0/6 [U'''(r)/U''(r)]_{r=r_0}$$

- (ii) Molecular force constant

$$f = 1/3 [U''_{\text{SR}}(r) + 2/r U'_{\text{SR}}(r)]_{r=r_0}$$

- (iii) Restrahl frequency

$$\nu_0 = 1/2\pi\sqrt{f/\mu}$$

where μ is the reduced mass of the crystal.

(iv) Debye Temperature. $(\Theta_D) = h \nu_0/k$

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

$$\alpha_v/C_v = -U'''(r_0)/2r_0 U''(r_0)^2$$

(vi) Compressibility $\beta = 18r_0/U''(r_0)$

(vii) The Anderson-Gruneisen Parameter

$$\delta_T = -\beta r_0^3/27V U'''(r_0)$$

Table 1.2. Thermophysical & cohesive properties of mixed alkali halide NaBr_{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 Parameter γ	2.24	1.81 ^c	2.09	-	1.95	-	1.80	-	1.66	-	1.51	1.39 ^b
Molecular force constant f (10 ⁴ dyn/cm)	5.37	-	6.51	-	7.28	-	8.06	-	8.83	-	9.61	-
Restrahl frequency ν_0 (T Hertz)	6.69	-	7.69	-	8.69	-	9.70	-	10.69	-	11.7	-
Debye Temperature (Θ_D) (k)	370.8	280 ^e	409	-	447	-	485	-	523.58	-	561.77	492 ^h
Ratio of volume thermal expansion coefficient to specific heat at constant volume α_v/C_v (10 ¹⁰ ergs unit)	3.16	-	3.14	-	3.12	-	3.10	-	3.09	-	3.07	-
Compressibility (β) (10 ⁻¹² dyn/cm)	2.83	-	2.27	-	2.30	-	2.04	-	1.77	-	1.51	-
The Anderson-Gruneisen Parameter δ_T	3.58	-	3.47	-	3.36	-	3.24	-	3.13	-	3.02	3.37 ⁱ

The above relations are used to calculate the thermophysical properties of mixed alkali halide. The phase transition is a phenomenon where the parental structure transforms to the most stable at elevated pressure and temperature. The sodium halides undergoes to structure phase transformation from B_1 to B_2 structure. If $G(B_1)$ and $G(B_2)$ are the Gibb's free energies of parental B_1 and finally stable B_2 structure at absolute 0 K, the phase transformation can be found as :

$$G_{B_1} - G_{B_2} = 0$$

or
$$U_{B_1} + PV_{B_1} = U_{B_2} + PV_{B_2}$$

or

$$P = U_{B1} - U_{B2}/V_{B2} - V_{B1}$$

Here $V_{B1} (= 2r_0^3)$ and $V_{B2} (= 1.54r_0'^3)$ are the unit cell volumes of the respective structures. B_1 and B_2 , r_0 and r_0' are the nearest neighbour distances at equilibrium. So U_{B1} and U_{B2} can be expressed as

$$U_{B1} = -(\alpha_m z e^2/r) (z + 12f(r)) + 6b\beta_{+-} \exp((r_1 + r_2 - r)/\rho) \\ + 6b\beta_{--} \exp((2r_2 - 1.4142r)/\rho) \\ + 6b\beta_{++} \exp((2r_1 - 1.4142r)/\rho) - C/r^6 - D/r^8 \\ U_{B2} = -(\alpha_m z e^2/r') (z + 16f(r')) + 8b\beta_{+-} \exp((r'_1 + r'_2 - r')/\rho) \\ + 3b\beta_{--} \exp((2r'_2 - 1.1547r')/\rho) \\ + 3b\beta_{++} \exp((2r'_1 - 1.1547r')/\rho) - C'/r'^6 - D'/r'^8$$

Cohesive energies as expressed by above equations contain only three-model parameters b , r and $f(r)$ have been computed with the help of equilibrium conditions:

$$[dU_{B1}/dr]_{r=r_0} = 0 \text{ and } [dU_{B2}/dr']_{r'=r_0'} = 0$$

The values of model parameters given in table 1.1 have been computed by initial thermodynamic conditions and then the pressure variations of the model parameters have been computed, so different lattice energies corresponding various pressure. When the difference in two competitive structural energies comes out to zero, the phase transitions phenomenon occurs. The computed internal energy difference ΔU and phase transition pressure (P_i) are given table 1.3. Calculated thermophysical properties of mixed alkali halide are given in table 1.2.

Table 1.3. Lattice energy and phase transition pressure of mixed alkali halide $\text{NaBr}_{1-x}\text{F}_x$ at different compositions.

Compositions	U_{B1} (Kcal/mol)			Phase Transition Pressure P_T (GPa)			ΔU (Kcal/mol)	
	Calc	Exp.	Other	Calc	Exp.	Other	Calc	Exp.
$X = 0$ (NaBr)	-183.20	-173.6 ⁷	-	21.7	>10	7.9 ¹⁶ 39.2 ³⁰	9.63	-
$X = 0.2$	-188.68	-	-	34		-	10.06	-
$X = 0.4$	-194.16	-	-	46.3		-	10.49	-
$X = 0.6$	-199.64	-	-	58.6		-	10.92	-
$X = 0.8$	-205.12	-	-	70.9		-	11.35	-
$X = 1.0$ (NaF)	-210.6	-214.4 ⁷	219.3 ³⁰	83.2	>20 ³¹	82.4 ³²	11.78	-

RESULT AND DISCUSSION

We have observed the phase transitions from B_1 to B_2 in mixed alkali halide. A look the calculated values given in table 1.3 shows that the positive lattice energy difference in mixed solids very well supports the relative stability criteria for the competitive structure. The reported phase transition pressure for the compounds are in good agreement with their available experimental results than the other workers. It is also clear from table 1.2 that presently estimated end point values of Gruneisen parameter are very close to its experimental values. Some results are still higher than the experimental values. The reason behind is to change in bondlength in ionic solids. The compressibility 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 than others which shows the superiority of this model over other models. On the basis of over all achievements TBP model can be regarded to be adequately suitable for the prediction of phase transition pressure and thermophysical properties of mixed alkali halides.

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