

## A THEORETICAL STUDY OF THERMOPHYSICAL AND COHESIVE PROPERTIES OF $\text{KBr}_{1-x}\text{F}_x$ MIXED ALKALI HALIDE

A.K. DIXIT

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

RECEIVED : 23 February, 2019

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  $\text{KBr}_{1-x}\text{F}_x$  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 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 spirit we have used our three body force potential model (TBFP) for the calculation of lattice and thermo-physical properties of mixed alkali halides  $\text{KBr}_{1-x}\text{F}_x$ . 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 [10-36] 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 behavior of the ionic solids under some boundary conditions through some potential models. 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. Colombian 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

PCM019052/P019

elastic constants, lattice constants, ionic radii and vander-Waal's constants of host and dopant materials as-

$$C_{ij}(\text{mix}) = x c_{ij}(A) + (1-x) c_{ij}(B)$$

$$r_{ij}(\text{mix}) = x r_{ij}(A) + (1-x) r_{ij}(B)$$

$$\rho(\text{mix}) = x \rho(A) + (1-x) \rho(B)$$

$$C(\text{mix}) = x C(A) + (1-x) C(B)$$

$$D(\text{mix}) = x D(A) + (1-x) D(B)$$

**Table 1.1. Model parameters for mixed alkali halide  $\text{KBr}_{1-x}\text{F}_x$  at different compositions**

Composition (x)	$\rho$ ( $10^{-8}$ cm)	$b$ ( $10^{-12}$ ergs)	$f(r_0)$	$af'(r_0)$	$C$ ( $10^{-60}$ erg $\times$ cm <sup>6</sup> )	$D$ ( $10^{-76}$ erg $\times$ cm <sup>8</sup> )
0.0 (KBr)	0.256	0.264	-0.0012	0.0154	896	1521
0.2	0.320	0.283	-0.00012	0.0074	963	1274.6
0.4	0.384	0.302	0.00096	-0.0006	630	1028.2
0.6	0.449	0.320	0.0020	-0.0087	497	781.8
0.8	0.513	0.339	0.0031	-0.0167	364	535.4
1.0 (KF)	0.577	0.358	0.0042	-0.0247	231	289

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 ( $\gamma$ ), molecular force constant ( $f$ ) Debye Temperature ( $\theta_D$ ), Restrahl frequency ( $\nu_0$ ), ratio of volume thermal expansion coefficient to specific heat at constant volume ( $\alpha_V/C_V$ ), Compressibility ( $\beta$ ), Anderson-Gruneisen parameter ( $\delta_T$ ). The relevant expressions have been derived from three body potential model [25-36].

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

Gruneisen parameter

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

(i) Molecular force constant

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

(ii) Restrahl frequency

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

where  $\mu$  is the reduced mass of the crystal.

- (iii) Debye Temperature.

$$(\Theta_D) = h \nu_0/k$$

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

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

- (v) Compressibility

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

- (vi) The Anderson-Gruneisen Parameter

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

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 1.2. Thermophysical & cohesive properties of mixed halide  $KBr_{1-x}F_x$  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 $\gamma$	2.64	-	2.36	-	2.07	-	1.79	-	1.50	-	1.22	-
Molecular force constant $f$ ( $10^4$ dyn/cm)	3.73	-	3.18	-	2.63	-	2.076	-	1.52	-	0.974	-
Restrahl frequency $\nu_0$ (T Hertz)	1.33	-	1.74	-	2.15	-	2.55	-	2.96	-	3.37	-
Debye Temperature ( $\Theta_D$ ) (k)	63.8	-	83.2	-	102.74	-	122.21	-	141.69	-	161.69	-
Ratio of volume thermal expansion coefficient to specific heat at constant volume $\alpha_v/C_v$ ( $10^{10}$ ergs unit)	5.02	-	611	-	7.19	-	8.28	-	9.36	-	10.45	-
Compressibility ( $\beta$ ) ( $10^{-12}$ dyn/cm)	4.48	-	5.54	-	6.59	-	7.65	-	8.70	-	9.76	-
The Anderson-Gruneisen Parameter $\delta_T$	5.28	-	4.71	-	4.14	-	3.58	-	3.01	-	2.44	-

## RESULT AND DISCUSSION

**A** look at the table 1.2, it is clear that presently estimated end point values of Gruneisen parameter are very close to their experimental values. Some results of ours are still higher than the experimental values. The reason behind is to change in bond length in ionic solids. The compressibility and micro hardness and Ratio of volume thermal expansion coefficient to specific heat at constant volume 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 thermo physical properties of mixed alkali halides.

## REFERENCES

1. Kennedy, S.W., *J. Appl. Cryst.*, **6**, 293 (1973); *J. Mat. Sci.*, **9**, 1043 (1974).
2. Basset, W.A. and Takahashi, T., "Advance in high pressure research", Vol. **4**, R.H. Wentorf (Academic Press London, 1974); *Rev. Sci. Instr.*, **38**, 37 (1967); Liu, Ling and W.A. Bassett, *J. Geophys. Res.*, **77**, 4934 (1972).
3. Singh, R.K. and Agrawal, M.K., *Solid State Communication*, **17**, 991 (1975).
4. Singh, R.K. and Gupta, D.C., *Phase Transition*, **53**, 39 (1995).
5. Singh, R.K., *Phys. Report*, **85**, 259 (1982).
6. Hafemeister, A.M., *Phys. Rev.*, **B 56**, 5835 (1997).
7. Tosi, M.P., *Solid State Physics*, **16**, 1 (1964).
8. Cohen, A.J., *Physical Rev.*, **B 12**, (1975).
9. Tranquada, J.M. and Ingalls, *Phys. Rev.*, **B34**, 4267 (1986); *Phys. Lett.*, **94 A**, 441 (1983).
10. Singh, R.K. and Singh, Sadhana, Phase Transitions, *Phys. Rev.*, **B39**, 761 (1989).
11. Jog, K.N. Singh R.K. and Sanyal, S.P., *Phys. Rev.*, **B35**, 5235 (1987); **B31**, 6047 (1985).
12. Singh, R.K. and Gupta, D.C., *Nuovo Cimento*, **D2**, 1235 (1987).
13. Singh, R.K. and Gupta, D.C. and Sanyal, S.P., *Physics Status Solidi*, **B149**, 356 (1988).
14. Ladd, M.F.C., *J. Chem. Phys. Solids*, **60**, 1954 (1974).
15. Fumi, F.G. and Tosi, M.P., *Ibid*, **25**, 345 (1964).
16. Tosi, M.P., *J. Phys. Chem. Solids*, **24**, 956 (1963).
17. Fumi, F.G. and Tosi, M.P., *Ibid*, **25**, 31 45 (1964).
18. Born, M. and Huang, K., "Dyanamic theory of Crystal lattices" (Oxford U. Press London 1945).
19. Vaidya, S.N. and Kennedy, G.C., *J. Phys. Chem. Solids*, **31**, 2329 (1970).
20. Vaidya, S.N. and Kennedy, G.C., *J. Phys. Chem. Solids*, **32**, 951 (1971).
21. Bridgeman, P.W., *Proc. Am. Acad. Arts. Sci.*, **77**, 189 (1949); **72**, 45 (1937); **74**, 21 (1940); **76**, 1 (1945).
22. Anderson, O.L., *J. Phys. Chem. Solids*, **27**, 547 (1966).
23. Lewis, J.T., *et. al.* *Phys. Rev.* **161**, 877 (1967).
24. Jayaraman, A., Klement, W. and Kennedy, G.C., *Phys. Rev.*, **30**, 2277.
25. Munson, D.E. and May, R.P., *AIAAJ*, **14**, 235 (1976).
26. Mequene, R.G., Marsh, S.P., Taylor, J.W., Fritz, J. N. and Carter, W.J., Academic Press, New York (1970).
27. Obsenschain, S.P., Green, J., Ripin, B.H. and McLwan, E.A., *Phys. Rev. Lett.*, **46**, 1402 (1981).
28. Holmes, N.C., *GPP Sala*, P-164 (1982).
29. Rashleigh, S. C. and Marshall, R. A., *J. Appl. Phys.*, **49**, 2540 (1978).
30. Dixit, A.K., Sinha, B.K. Gupta, J.P., Sharma, S.K., *Napier Indian Research Journal of Science*, Vol. **6**, (pp 83-86) June (2011).
31. Dixit, A.K., Gupta, J.P., Sharma, S.K., *Napier Indian Research Journal of Science*, Vol. **6**, (pp 75-78) June (2011).
32. Dixit, A.K., Gupta, J.P., Sharma, S.K., *Acta Ciencia Indica*, Vol. **XXXVII**, No. **4**, 415 (2011).
33. Gour, Atul, Singh, Sadhana, Singh, R.K., *Journal of Physics & Chemistry of Solids*, Vol. **69**, (pp 1669-1675) July (2008).
34. Dixit, A.K. and Sharma, S.K., *Acta Ciencia Indica*, Vol. **XXXVIII** P, No. **4**, 289 (2012).
35. Dixit, A.K., Chaturvedi, S.D. and Dixit, R.C., *International Advanced Journal of Science*, Vol. **2**, pp. 15-18 July (2013).

36. Dixit, A.K., Chaturvedi, S.D. and Dixit, R.C., *Acta Ciencia Indica*, Vol. **XXXIX** P., No. 4 (2013).
37. Dixit, A.K., *Acta Ciencia Indica*, Vol. **XL** P, No. **4**, 169 (2014).
38. Dixit, A.K., *Acta Ciencia Indica*, Vol. **XL** P, No. 4, 135 (2014).
39. Dixit, A.K., Chaturvedi. S.D. and Dixit, R.C., *Naveen Shodh Sansar*, ISSN 2320 – 8767, Vol. **1**, Jan. to March (2015).
40. Dixit, A.K., *Acta Ciencia Indica*, Vol. **XLI** P, No. **2**, 101 (2015).
41. Dixit, A.K., *Acta Ciencia Indica*, Vol. **XLI** P, No. **2**, 79 (2015).

