Low Temperature Thermoelastic and static properties of $(NaCN)_x (NaCl)_{1-x}$

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Abstract—The evolution of thermal and elastic properties of $(NaCN)_x(NaCl)_{1-x}$ with temperature is investigated by means of Extended Three Body Force Shell Model (ETSM). The temperature dependence of anharmonic elastic properties over composition dependence is confirmed through the investigation on different compositions at different temperature and the purpose of study is to test the mechanical stabilities of the potential. In addition, the thermodynamic properties such as molecular force constant (f), Restrahlen frequency (ν_0), cohesive energy (ϕ), Debye temperature (θ_D) and Gruneisen parameter (γ) are also reported for different compositions for the first time.

Index Terms—Elastic constants, Cohesive energy, Thermodynamic properties

I. INTRODUCTION

Recently, we have described the cohesive and thermoelastic properties of orientationally disordered mixed halide cyanide crystal $(KCN)_x(KCl)_{1-x}$ satisfactorily by means of ETSM. This model which was designed by incorporating Translational-Rotational coupling effect in the framework of Three Body Force Shell Model was found to be excellent in explaining the static, dynamic, dielectric and optic properties of ODMs. Inspired by the great success of ETSM [1] in explaining these properties of ODMs we thought it appropriate to extend the investigation to thermoelastic and cohesive behaviour of $(NaCN)_x(NaCl)_{1-x}$ which also belongs to the mixed alkali halide-cyanide family.

The various structures associated with crystalline solids are ultimately related to bonding mechanisms between atoms. An understanding of why nature selects certain preferred crystal structures will lead to explanation of elastic properties of the solids. Mixed crystals having the structure $(MCN)_x (MX)_{1-x}$ where M is an alkali metal and X is a halogen ion is called as mixed alkali halide – cyanide crystals. These crystals are orientationally disordered crystals where X randomly substitutes for CN⁻ on the anion sublattice[15].

When a dump – bell shaped cyanide ion replaces chloride (Cl⁻) ion in NaCl system a $(NaCN)_x(NaCl)_{1-x}$ mixed system is obtained. The $(NaCN)_x(NaCl)_{1-x}$ shows plastic phase transitions from an orientationally ordered cubic phase to rhombohedral or orthorhombic phases where the CN⁻ groups are orientationally ordered for higher concentrations[2]. In this crystal there are high temperature cubic phases on the CN⁻ rich side stabilized by the rapid reorientation of the CN⁻ and low temperature glass like (x $\leq$ xc) ordered phases, where x_c is the critical concentration below which phase transitions into ordered phases are suppressed. This feature is brought about by the dumbbell shaped CN⁻ ions forming elastic quadrupoles, which determine the anomalous static and dynamic properties. As compared to other mixed systems i.e. $(KCN)_x(KCl)_{1-x}$, $(KCN)_x(KBr)_{1-x}$ and $(RbCN)_x(RbBr)_{1-x}$ less studies have been done on $(NaCN)_x(NaCl)_{1-x}$. The theory of ETSM is given in 2. We present the results and related discussions about the thermoelastic and cohesive properties in section 3. Concluding remarks are given in Section 4.

II. ESSENTIAL THEORY OF ESTM

The formalism of the Extended Three Body Force Shell Model has been derived from the following interatomic interaction [3-8]

$$\Phi = \frac{e^2}{2} \Sigma Z_k Z_{k'} \; r_{kk'}^{-1} \; [1+\Sigma_{kk'}f(r_{kk'})]-\Sigma_{kk'}c_{kk'}r_{kk'}^{-6}-\Sigma_{kk'}d_{kk'}r_{kk'}^{-8}+b\,\Sigma_{kk'}\,\beta_{kk'}\exp(r_k+r_{k'}-r_{kk'}/\rho)+\phi^{TR} \quad (1)$$

Here, the first term is attractive long range (LR) coulomb interactions energy and the second term is the three body interaction potential. The third and fourth term represents the contributions of Van der Waals (vdW) attraction for the dipole-dipole interaction and dipole-quadrupole interactions and the fifth term is short range (SR) overlap repulsive energy represented by the

Hafemeister–Flygare type (HF) interaction extended up to the second neighbor. $\emptyset^{TR}$ is the contribution due to translational rotational coupling. In expression (1), other symbols involved are the same as those defined in our earlier papers [3-8]. b_i and ρ_i are the hardness and range parameters for the ith cation–anion pair (i = 1, 2) respectively and $\beta_i^{kk'}$ is the Pauling coefficient [9] given by

$$\beta_i^{kk'} = 1 + (Z_k / N_k) + (Z_{k'} / N_{k'})$$

(2)

Z_k ($Z_{k'}$) and N_k ($N_{k'}$) are the valence and the number of electrons in the outermost orbit of the k (k') ion respectively. The contributions of van der Waals (vdW) attraction for the dipole-dipole interaction is determined by using the Slater- Kirkwood Variational (SKV) method [10]. The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition.

$$[d\phi/dr]_{r=r_0} = 0$$

(3)

and the bulk modulus

$$B = 1/9Kr_0 [d^2\phi/dr^2]_{r=r_0}$$

(4)

where K is the crystal-structure-dependent constant and r_0 is the equilibrium nearest neighbour distance. The expressions for calculating the thermodynamic properties like Debye temperature (θ_D), Restrahalen frequency (v), molecular force constant (f), and Gruneisen parameter (γ) are taken from our earlier papers [3-8]. The present model (ETSM)) described above for the $(NaCN)_x(NaCl)_{1-x}$ contains three model parameters $(b, \rho$ and $f)$, which are used to determine the second- order (SOECs), third order (TOECs) and fourth order (FOECs) elastic constants of $(NaCN)_x(NaCl)_{1-x}$.

III. RESULTS AND DISCUSSIONS

We have obtained the model parameters (b, ρ and f) as a function of temperature using input data (Table 1) taken from Ref. [11-13] and the Van der Waals coefficients. The model parameters computed for $(NaCN)_x(NaCl)_{1-x}$ for the concentrations x=0, 0.04 ,0.7 and 0.95 are given in Table 2. Using the model parameters we have calculated the second order (SOEC), third order (TOEC) and fourth order (FOEC) elastic constants of $(NaCN)_x(NaCl)_{1-x}$ and the values are plotted in Figures 1-3.

c_{11} & c_{12} shows quasilinear behaviour except for x = 0. No drastic change in elastic constants is observed since the temperature variation is small. It is very interesting to note that the dominating coupling of orientational degrees of freedom of the CN molecules to elastic waves give rise to an enormous softening of c_{44}[15-17]. Due to lack of experimental results the values of SOECs are not compared.

The computed values of third and fourth order elastic constants are presented in Figures 4-7. Our results on anharmonic elastic constants show that the magnitudes all the values of TOECS decreases with increase in temperature near room temperature. Its variation plays a significant role in explaining the anharmonic properties. The variation of TOECs follows the same trend for all compositions. The values of all the FOECs also decrease in magnitude with increase in temperature. These values could not be compared due to the lack of experimental data.

The thermophysical properties of $(NaCN)_x (NaCl)_{1-x}$ cohesive energy ϕ, compressibility β , molecular force constant f and Restrahalen frequency v_0, the Debye temperature θ_D and Gruniesen parameter γ, α_v / c_v are calculated for concentrations x = 0, 0.04, 0.7 and 0.95 for temperature range 50K $\leq$T$\leq$ 90K and are listed in Table 3. From Table 3 it is clear that cohesive energy ϕ , Gruneisen parameter and Debye temperature θ_D are decreasing with increase in temperature but are increasing with increase in concentration of CN- ions. There were no experimental results available and so the results could not be compared. The experimental values of cohesive energy for pure NaCN is -738kJ/mol [14] respectively. The negative values of cohesive energy show that the stability of these compounds is intact. All other thermophysical properties like compressibility β and molecular force constant f, Restrahalen frequency and α_v / c_v are found to increase with increase in temperature. The Debye temperature calculated by us is elastic constant dependent and hence is more accurate.

IV. CONCLUSION

The elastic and thermodynamic properties of the orientationally disordered $(NaCN)_x(NaCl)_{1-x}$ mixed crystal are investigated with the help of ETSM. Our calculated results on shear elastic constant c_{44} are in fairly good agreement with the available experimental data. Also, the values of cohesive energy obtained from ETSM are in good agreement with the experimental value of this parameter for pure NaCN crystals. Our comments on the other results are restricted until the report of experimental data on them but these results will serve as a guide to the experimental workers in future. A successful description of mechanical properties achieved for such complicated $(NaCN)_x(NaCl)_{1-x}$ can be considered remarkable in view of the inherent simplicity of the ETSM and its less parametric nature.

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