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Temperature Dependence of Thermodynamic Properties of Thallium Chloride and Thallium Bromide

Abstract: Thermodynamic properties as lattice parameters, thermal expansion, heat capacities C_p and C_v, bulk modulus, and Gruneisen parameter of ionic halides TlCl and TlBr in solid and liquid phases were studied using classical molecular dynamics simulation (MD) with interionic Vashistha-Rahman (VR) model potential. In addition to the static and transport properties which have been previously reported by the author [13], this study further confirms that temperature dependence of the calculated thermophysical properties of TlCl and TlBr are in agreement with the available experimental data at both solid and liquid phases in terms of providing an alternative rigid ion potential. The results give a fairly good description of TlCl and TlBr in the temperature range 10–1000 K.

Keywords: thallium halides, thermophysical properties, molecular dynamics

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1 Introduction

Thallium halides TlCl and TlBr prove to be technologically useful materials due to their usage in a variety of applications such as radiation detectors and optical fibre crystals. Both thallium chloride and thallium bromide crystallize in the cubic CsCl structure with space group Pm3m (number 221). Since they possess elastic, electronic and optical properties, which provide relative stability, chemical bonding, relaxation of the atoms, phase transitions, electrical, mechanical, optical or magnetic behavior, there has been a lot of interest in their use [1]. With a coordination number of eighth, structure of thallium chloride and thallium bromide constitutes the most stable dense configuration for ionic crystals [2]. Neither TlCl nor TlBr is strictly ionic and they both exhibit partial covalency due to the presence of d-electrons in their cations [3]. Yet, they differ in terms of the very different mass ratios they contain; 5.76 and 2.56 for TlCl and TlBr, respectively. In an experiment carried out by Bashir et al., the aim was to provide information about the thermal parameters of thallium bromide and understand if the heavier Tl ion has larger mean square amplitude than the lighter Br ion, which applies to other thallium halide TlCl [4]. Using x-ray and neutron diffraction techniques, they found out that in TlBr, the heavier atom has larger mean square vibration amplitude than the lighter atom, which resembles TlCl.

Experimental and theoretical investigation of thermodynamic properties of alkali halides have resulted in the growth of a complete understanding of a number of the significant features of their dependence upon temperature [5]. Owing to their simple structures, there has been an intensive attention to the study of these solids. In normal circumstances, TlBr and TlCl have the CsCl type structure. However, the experiment by Blackman and Khan [6] demonstrated that evaporated layers of TlCl and TlBr could contain the rocksalt structure at low temperatures, which disappeared upon heating to room temperature whereas when TlI was kept at a suitable low temperature, it adopted the CsCl structure and turned into the orthorhombic form upon heating to room temperature [7]. In this study, TlI has not been included in the scope of this study due to its different behavior from TlCl and TlBr. The CsCl type structure of TlCl and TlBr do not change their structure up to their melting temperatures (704 K for TlCl; 733 K for TlBr) and neither do they undergo any structure transformation [8]. The cohesive and thermophysical properties of any material depend essentially on atomic interactions and hence on bonding. High polarizability implies a high electron cloud deformability and thus a large compressibility or low bulk modulus and thermal

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expansion in the ranges of temperature and pressure where covalent interactions operate [9].

In this paper, thermophysical properties of thallium halides (TlCl and TlBr) were calculated at solid and liquid phases; lattice parameter, thermal expansion, specific heats, bulk modulus, and Gruneisen parameter were calculated under different conditions of temperature and volume by performing MD simulation at constant volume-energy (NVE ensemble). The molecular dynamics simulations were performed both in solid and liquid phases. The results were compared with earlier theoretical and experimental data available in the literature.

2 Theory

2.1 Potential model

A semi empirical potential based on the functional form originally proposed by Vashistha-Rahman (VR) [10] has been re-parameterized for thallium halides [11]. VR potential is given by the expression

$$\phi_{ij}(r) = \frac{Z_i Z_j}{r} + \frac{A_{ij}(\sigma_i + \sigma_j)^{\eta_{ij}}}{r^{\eta_{ij}}} - \frac{P_{ij}}{r^4} - \frac{C_{ij}}{r^6}$$

Details of the potential have been given in Ref. [11–13]. The first term is the Coulomb interaction between effective charges, the second term is the repulsion between the ions arising from the overlap of the outer shell of electrons, the third term is the monopole-induced dipole attractive interaction, and the last is the dipole-dipole or van der Waals contribution. The repulsive hardness of the potential is determined by the parameter η_{ij}. Here, Z denotes effective charges, σ signifies ionic radius and A_{ij} represents strength parameters. The potential parameters used were adjusted so that minimum total energy corresponds to a_0 equilibrium lattice constant for both systems. The parameters of potentials are given in Table 1 and Table 2.

2.2 Simulation procedure

The intermetallic compound TlCl and TlBr have the cubic CsCl-type structure with lattice constants $a_0 = 3.84$ A for TlCl and $a_0 = 3.97$ A for TlBr [14]. The CsCl structure is a superposition of two simple cubic substructures. Both the cations and the anions occupy the cubic interstices present in each substructure. Each Tl ion is surrounded by eight anions. MD cell is constructed by 216 cations and 216 anions in six orthogonal directions ($6 \times 6 \times 6$) with a side of length $L = 6a_0$, which allows obtaining reliable data. The calculations were done by the molecular dynamics code called MOLDY [15]. The simulations were performed in the NVE through application of the temperature rescaling procedure. The temperature is varied at 20 K intervals. Calculations were carried out between 10 K and 1000 K, starting with CsCl crystal structure.

Table 1: The values of parameters of potential for TlCl.

	η_{ij}	$A_{ij}(\sigma_i+\sigma_j)^{\eta_{ij}}$	P_{ij}	C_{ij}	$\lvert Z_{eff}\rvert$
Tl-Tl	7	216.4	0.0	0.0	
Cl-Cl	7	1921.1	22.9	83.5	0.68
Tl-Cl	7	701.8	11.4	0.0	

in unit of $e^2/A = 14.399$ eV

Table 2: The values of parameters of potential for TlBr.

	η_{ij}	$A_{ij}(\sigma_i+\sigma_j)^{\eta_{ij}}$	P_{ij}	C_{ij}	$\lvert Z_{eff}\rvert$
Tl-Tl	6	137.9	0.0	0.0	
Br-Br	6	869.3	31.5	131.0	0.7
Tl-Br	6	378.1	15.7	0.0	

in unit of $e^2/A = 14.399$ eV

3 Results

Using various a_0 values and performing (EOS) simulation for each temperature within a range of 10 K and 1000 K, a_0 values that correspond to zero pressure were chosen. With the results obtained, lattice parameter, thermal expansion, specific heat capacity, bulk modulus, and Gruneisen parameter of the system at equilibrium state were calculated at zero pressure for each temperature. The values found are in line with the previous data reported in the literature. The bulk modulus and cohesive energy reflect important ground state properties of a material; the bulk modulus defines its resistance to volume change when compressed and cohesive energy is useful in understanding the binding forces and the potential function responsible for binding the ions in crystals. In this study, the cohesive energy (E_{coh} in eV/atom) of TlBr is calculated as 7.97 eV and TlCl as 8.86 eV at ambient temperature. These obtained values are in close agreement with values determined directly from earlier experiments and theoretical studies. Singh et al. [16] found $E_{coh,theo} = 7.37$ eV for TlBr and $E_{coh,theo} = 7.55$ eV for TlCl. Gupta et al. [17] indicated the

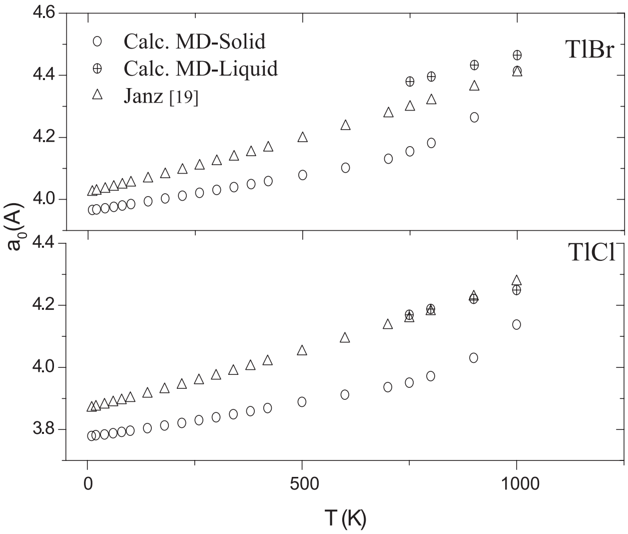

Fig. 1: Variation of lattice parameters with temperature for TlCl and TlBr.

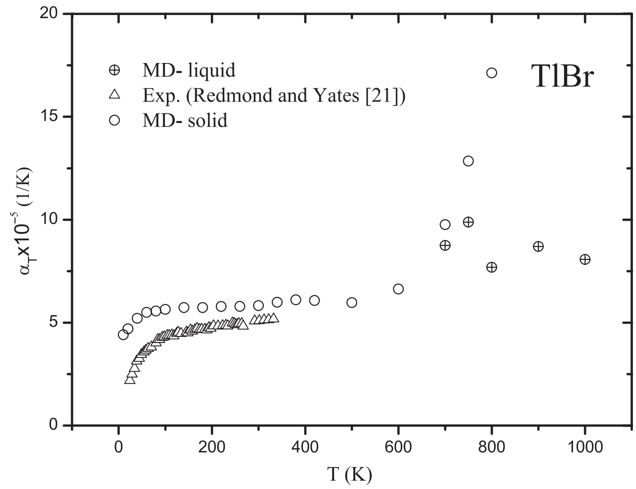

Fig. 2: Linear thermal expansion coefficient for TlBr.

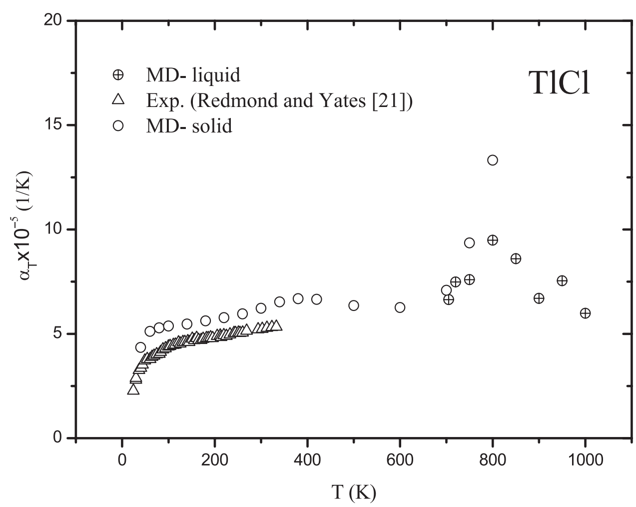

Fig. 3: Linear thermal expansion coefficient for TlCl.

values of TlBr and TlCl both theoretically and experimentally as follows: $E_{coh,theo} = 8.42$ eV for TlBr and $E_{coh,theo} = 8.76$ eV for TlCl, and $E_{coh,exp.} = 7.33$ eV for TlBr and $E_{coh,exp.} = 7.51$ eV for TlCl. In a similar vein, Schrciber and Schafer [18] found the following results: $E_{coh,theo} = 6.7$ eV for TlBr and $E_{coh,theo} = 6.4$ eV for TlCl, and $E_{coh,exp.} = 7.2$ eV for TlBr and $E_{coh,exp.} = 7.4$ eV for TlCl.

3.1 Lattice parameters and densities

The lattice parameters calculated for TlBr and TlCl at zero pressure $a_0 = \sqrt[3]{V(T,P=0)}$ and densities available in the literature [19, 20] are demonstrated in Fig. 1.

3.2 Thermal expansion

Variation of calculated and experimental linear thermal expansion and volume thermal expansion coefficients according to temperature for TlBr and TlCl systems are shown respectively in Fig. 2 and Fig. 3. Linear and volume thermal expansion coefficients are defined as below,

$$\alpha_P(T) = \frac{1}{L_0}\left(\frac{\partial L}{\partial T}\right)_P$$

$$\beta_P(T) = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$$

Here, L_0 and V_0, are values at 10 K. The experimental data was obtained from Ref. [21].

3.3 Heat capacities C_v and C_p

The heat capacities at constant volume and constant pressure can be evaluated from the variation in the internal energy with temperature as shown in the following equations:

$$C_V(T) = \left(\frac{\partial E}{\partial T}\right)_V$$

and

$$C_P(T) = \left(\frac{\partial E}{\partial T}\right)_P$$

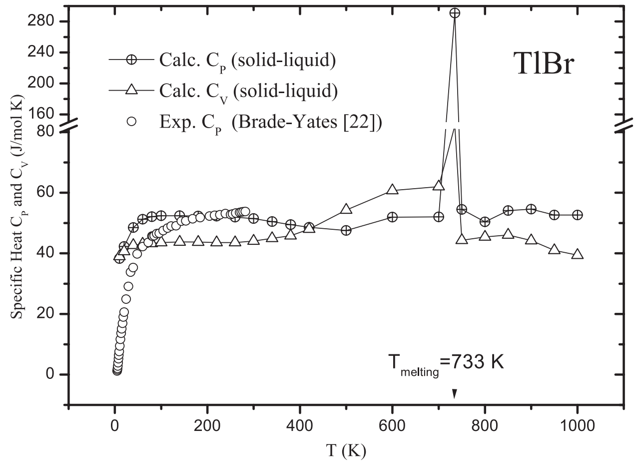

Fig. 4: Variation of specific heat constant pressure and constant volume with temperature for TlBr.

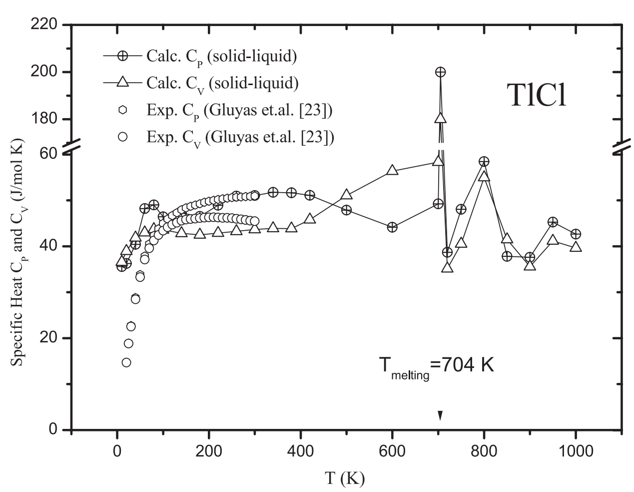

Fig. 5: Variation of specific heat constant pressure and constant volume with temperature for TlCl.

Calculated heat capacities at constant volume for TlCl and TlBr are shown in Fig. 4 and Fig. 5 together with experimental results [22–23]. Up to the melting point, MD calculations were done in solid phase whereas above melting temperature, they were measured in liquid phase. A typical λ-lambda curve was observed for specific heat curves. The transition shows a slight premonitory rise prior to the relatively sharp peak with a heat capacity greater than 200 J/mol K. Fig. 4 and Fig. 5 display calculated specific heats at constant volume C_v and constant pressure C_p respectively with respect to temperature range 10 K–1000 K. λ-lambda peak is produced at melting temperatures for each C_v and C_p. This jump in λ-lambda curve indicates a first order phase transition. Above melting temperature (733 K for TlBr and 704 K for TlCl), specific heats descend to the level of Dulong and Petit. From 10 K to ~150 K, calculated C_p increases with temperature, which is interpreted as progressive excitation of the harmonic lattice vibrations. The anharmonicity of the vibrations is reflected as a weak increase and decrease in C_p from 150 K to melting temperature. At liquid phase, contribution to the specific heat comes only from atomic vibrations and all thermally created defects are completely saturated. We note that, the classical MD approach is suitable below the Debye temperature as all modes are excited almost equally in a classical system, while the modes are quantized at very low temperature. Therefore, the quantum correction has very significant effect for calculating the thermophysical properties such as specific heats [24].

3.4 The Grüneisen parameter

The volume dependence of the lattice vibrations of solid may be obtained from the Grüneisen parameter γ which has been calculated by using the equation

$$\gamma = \frac{\beta V}{C_v \chi_T}$$

in which β is the thermal coefficient of volume expansion, C_v the heat capacity of volume V of material at constant volume and χ_T the isothermal compressibility.

The values calculated for TlBr and TlCl and the experimental data [22–23] are plotted in Fig. 6 and Fig. 7.

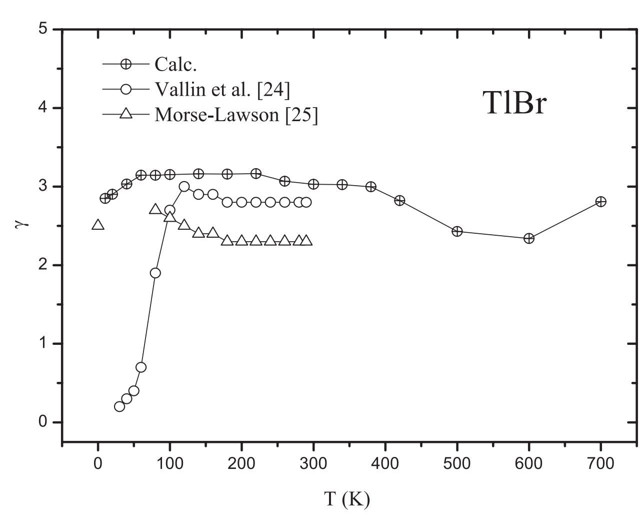

Fig. 6: The Grüneisen constant γ for TlBr.

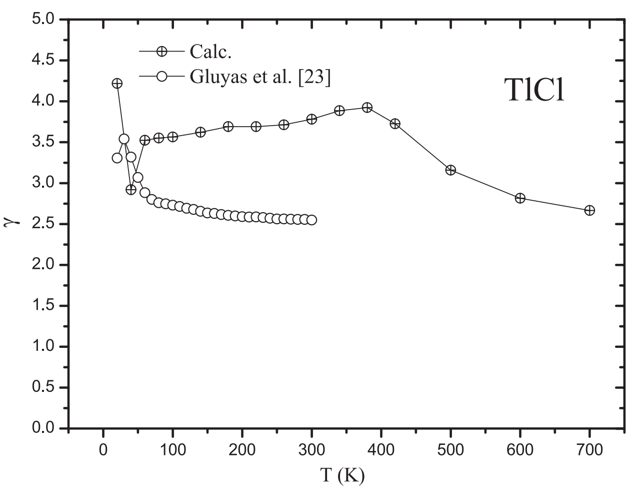

Fig. 7: The Grüneisen constant γ for TlCl.

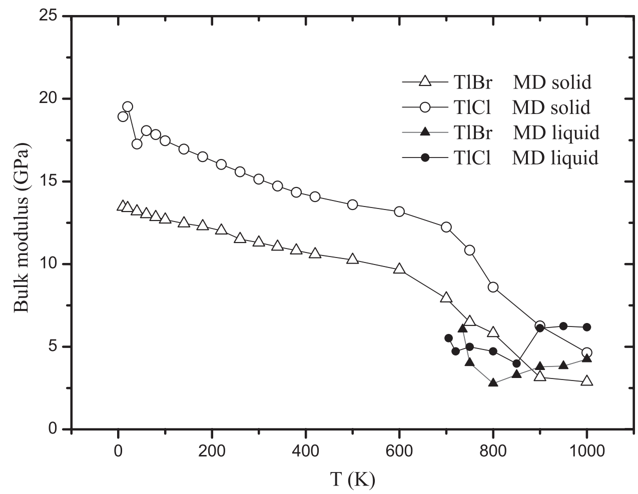

Fig. 8: The variation of bulk modulus with temperature for TlBr and TlCl.

3.5 The bulk modulus

The bulk modulus is a macroscopic property of materials and an ideal solid which depends on the nature of its chemical bonds and thus reflects the ability of solids to resist compression deformation within the limits of the elastic regime [27]. Recent studies have revealed that different relations exist between bulk modulus and interionic distance or volume per atom pair for crystals with different crystal structure [27–28]. The isothermal bulk modulus have been calculated by use of the equation

$$B_T(T) = -V(T)\left(\frac{\partial P}{\partial V}\right)_T .$$

The isothermal bulk modulus B_T of TlCl and TlBr are plotted in Fig. 8 and compared with previously reported data in Table 3 at solid phase. The B_0 values given in the table are calculated by fitting Murnaghan Equation to the total energy found in molecular dynamics simulations.

Table 3: Bulk Modulus B(GPa) at T = 0 K.

	Ref. [29]	Ref. [16]	Ref. [7]	Ref. [2]	Ref. [1]	Ref. [26]	B_0 Murnaghan EOS	Calc.
TlBr	19.9	18	21	18.8	24.4	17.7	15.8	13.5
TlCl	22.3	19	23	20.8	25.7	19.3	18.5	19.5

4 Conclusion

In the investigation of thermophysical properties of thallium halides (TlCl and TlBr) at solid and liquid phases; lattice parameter, thermal expansion, specific heats, bulk modulus, and Gruneisen parameter under different conditions of temperature and volume were calculated by performing MD simulation at constant volume-energy (NVE ensemble). Even though the same calculations were conducted for constant pressure-temperature (NPT ensemble), only the results obtained for NVE ensemble were reported in this study. The lattice parameter that corresponds to the minimum of total energy and zero pressure yielded the same results for both NVE and NPT. For the thermodynamic analysis of solids, the temperature variations of three properties, the thermal expansion, the heat capacity, and bulk modulus are required. Evaluation of cohesive energy as a function of temperature is a very important feature in theoretical studies because studies on the temperature dependence of total energy provide a better understanding in the anharmonic nature of lattice vibrations and mutual interaction of anions and cations of the crystals.

The calculated thermophysical properties agree well with the available experimental values. Vashistha-Rahman type effective ionic pair potential proves to be a reliable model to calculate the structure and thermophysical properties of both TlCl and TlBr. We believe that the essential features of Thallium halides are reproduced by our simulation. Yet, larger scale simulations that are carried out with more advanced computers may be necessary to achieve more reliable results.

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