



Theoretical investigations on structural, elastic and electronic properties of thallium halides

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ABSTRACT

Theoretical investigations on structural, elastic and electronic properties, viz. ground state lattice parameter, elastic moduli and density of states, of thallium halides (viz. TlCl and TlBr) have been made using the full potential linearized augmented plane wave method within the generalized gradient approximation (GGA). The ground state lattice parameter and bulk modulus and its pressure derivative have been obtained using optimization method. Young's modulus, shear modulus, Poisson ratio, sound velocities for longitudinal and shear waves, Debye average velocity, Debye temperature and Grüneisen parameter have also been calculated for these compounds. Calculated structural, elastic and other parameters are in good agreement with the available data.

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1. Introduction

Thallium halides are representative ionic crystals with simple cubic structure and crystallize in the CsCl type halides with space group Pm3m (number 221) and have attracted much attention due to their elastic, electronic and optical properties, which are responsible for relative stability, chemical bonding, relaxation of the atoms, phase transitions, electrical, mechanical, optical or magnetic behavior, etc. Thallium halides have promising technological applications in radiation detectors and as new optical fiber crystals. They are becoming technologically important for enthalpy stabilization in superconducting windings [1,2].

First principle quantum mechanical calculations based on the GGA have become one of the most frequently used theoretical tools in materials science and through the first principle calculations; we can obtain the information on structural, mechanical, electrical, vibrational, thermal and optical properties of the materials [3–5].

In the present paper, we report numerical investigations, based on a first-principles study of ground state properties, viz. structural, elastic and electronic properties, such as elastic moduli, density of states, charge density, etc., using generalized gradient approximation (GGA) functional. In addition, the influence of hybridization on chemical bonding and stability has been discussed in terms of the site projected densities of states as well as the crystal orbital overlap

population. Thus, in the present paper, we studied the elastic properties, as well as their electronic contribution behavior at ambient temperature and pressure for thallium halides (TlCl and TlBr). Principal features of the calculated band structures such as energy bandgaps have also been examined for both the compounds, TlCl and TlBr.

2. Computational approach

A number of methods are available for calculating the structural, elastic and electronic properties of solids. In the present paper, full potential linearized augmented plane wave method within the density functional theory, implemented in the WIEN2k code [6], has been used for the study of structural, elastic and electronic properties of B2 type (CsCl structured) thallium halides with space group Pm3m. Generalized Gradient Approximation based on Perdew–Burke–Ernzerhof (PBE–GGA) functional [7,8] has been used to determine the optimized structure of these compounds. This method has been chosen due to the following features: (i) it is a self-consistent method and it converges easily, (ii) it has good accuracy with experimental results and (iii) the method is physically transparent.

In the APW method, the unit cell is partitioned into two types of regions: (i) spheres centered around all constituent atomic sites r_α with a radius R_α and (ii) the remaining interstitial region. In this case, the wave functions are expanded into plane waves each of which is augmented by atomic solutions in the form of partial waves. In particular, radial solutions of Schrödinger's equation are

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employed inside non-overlapping atom centered spheres (Muffin-tin spheres) and plane waves in the remaining interstitial zone [9]. The basis set inside each Muffin-tin sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential only and are assumed to have a spherically symmetric charge density totally confined inside the Muffin-tin spheres [10–12]. The valence part is treated within a potential expanded into spherical harmonics up to $l=4$. The maximum one value for the wave function expansion inside the atomic spheres was confined to $l_{\max}=10$. In order to achieve energy eigen value convergence, the wave functions in the interstitial region are expanded in plane waves with a cutoff of $R_{\text{MT}}K_{\text{MAX}}=8$ (where K_{MAX} is the maximum modulus for the reciprocal lattice vector and R_{MT} is the average radius of the Muffin-tin spheres). The k integration over the Brillouin zone is performed using the Monkhorst and Pack [13] mesh, yielding to 10k points in the irreducible wedge of the Brillouin zone for both the compounds. The energy that separates the valence state from the core state has been taken as -6.0 Ryd. The leakage electrons from the Muffin-tin radius are found to be 0.0003 for Ti and 0.00001 for Cl.

The elastic constants and related parameters play important role in determining the strength and stability of materials. Structural and elastic moduli can be obtained using the theory [14] discussed below. The total energy of a crystal in strained state is given by

$$E_{\text{total}} = E_{\text{total}}^0 + P(V - V_0) + \phi_{\text{elastic}} \quad (1)$$

Here E_{total}^0 is the total energy of unstrained crystal, V_0 is volume of crystal in initial state, V is the volume of the strained lattice and P and ϕ_{elastic} are the pressure and elastic energy, respectively, defined by

$$P = - \left(\frac{\partial E_{\text{total}}^0}{\partial V} \right)_{V=V_0} \quad (2)$$

$$\phi_{\text{elastic}} = \frac{V}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \quad (\text{Here } i, j, k, l = 1, 2, 3) \quad (3)$$

In Voigt two suffix notation, ϕ_{elastic} is given by

$$\phi_{\text{elastic}} = \frac{V}{2} C_{ij} \varepsilon_i \varepsilon_j$$

Here C_{ij} are elastic moduli derived from the second order derivative of E_{total} given by

$$C_{ij} = \left(\frac{1}{V_0} \frac{\partial^2 E_{\text{total}}}{\partial \varepsilon_i \partial \varepsilon_j} \right)_{\varepsilon=0} \quad (4)$$

A cubic crystal has only three independent elastic constants, namely, C_{11} , C_{12} and C_{44} . As a result, a set of three equations is needed to determine all the constants. Hence, three types of strain must be applied to the starting crystal [15,16]:

- (i) First type strain involves calculating the bulk modulus, given by

$$B_0 = (C_{11} + 2C_{12})/3 \quad (5)$$

- (ii) Second type strain involves performing volume conservative tetragonal strain given by the following tensor:

$$\begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \frac{1}{(1+\varepsilon)^2} - 1 \end{bmatrix} \quad (6)$$

This strain has an effect on the total energy from its unstrained state given by

$$E(\varepsilon) = E(0) + 3(C_{11} - C_{12})V_0\varepsilon^2 + o(\varepsilon^3) \quad (7)$$

- (iii) Finally, for the third type of deformation, we use the volume conserving rhombohedral strain tensor given by

$$\frac{\varepsilon}{3} \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (8)$$

This volume conserving rhombohedral strain transforms the total energy to the energy, given by

$$E(\varepsilon) = E(0) + \frac{1}{6}(C_{11} + 2C_{12} + 4C_{44})V_0\varepsilon^2 + o(\varepsilon^3) \quad (9)$$

Once we have calculated three elastic constants, namely C_{11} , C_{12} and C_{44} , bulk modulus, B ; isotropic shear modulus, G ; Young's modulus, Y and Poisson ratio, ν can be calculated easily using the following explicit expressions [17]:

$$B = (C_{11} + 2C_{12})/3 \quad (10)$$

$$G = (G_V + G_R)/2 \quad (11)$$

Here G_V is Voigt's shear modulus corresponding to the upper bound of G values and G_R is Reuss's shear modulus for cubic crystals corresponding to the lower bound values, expressed as

$$G_V = (C_{11} - C_{12} + 2C_{44})/4$$

and

$$G_R = 5[(C_{11} - C_{12})C_{44}]/[4C_{44} + 3(C_{11} - C_{12})]$$

$$Y = \frac{9GB}{G + 3B} \quad (12)$$

$$\nu = (3B - 2G)/(6B + 2G) \quad (13)$$

Sound velocity for longitudinal and shear waves (V_L and V_S) and Debye average velocity (V_m) can be obtained using bulk modulus, isotropic shear modulus and mass density. The explicit expressions are as follows [18]:

$$V_L = \sqrt{\frac{3B + 2G}{3\rho}} \quad (14)$$

$$V_S = \sqrt{\frac{G}{\rho}} \quad (15)$$

and

$$V_m = \left[\frac{1}{3} \left(\frac{1}{V_L^3} + \frac{2}{V_S^3} \right) \right]^{-1/3} \quad (16)$$

The Debye temperature, θ_D , and Grüneisen parameter, ζ , are two useful parameters in solid-state problems because of their inherent relationship with lattice vibrations. The Debye temperature, θ_D , can be used in characterizing the excitation of phonons and describing various lattice thermal phenomena, and the Grüneisen parameter describes the phonons contribution to specific heat.

Debye temperature, θ_D [18], and the Grüneisen parameter, ζ [19], are sound velocity and mass density dependent, and can be calculated using

$$\theta_D = \left(\frac{h}{k_B} \right) \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} V_m \quad (17)$$

$$\zeta = \frac{9(V_L^2 - 4V_S^2/3)}{2(V_L^3 + 2V_S^3)} \quad (18)$$

Here $h = h/2\pi$, where h is Planck's constant and k_B is the Boltzmann constant.

3. Results and discussion

Total energies have been plotted as a function of reduced volume for TlCl and TlBr, and the graph connecting the total energies to the relative volumes for these compounds is shown in Fig. 1 with their equilibrium volume $V(0)$, bulk modulus B (GPa), pressure derivative of bulk modulus (BP) and equilibrium energy $E(0)$. The calculated total energies are fitted to the Murnaghan equation of state [20] to obtain the equilibrium properties. The calculated ground state properties, viz. equilibrium lattice constant, bulk modulus and its pressure derivative, are tabulated in Table 1. The calculated lattice parameter is in good agreement with the experimental/theoretical results [21]. However, experimental values of the equilibrium bulk modulus (B_0) and its pressure derivative (B_0') are not available; thus, no comparison can be made for B_0 and B_0' for TlCl and TlBr, respectively. Present calculations show that the total energy calculations based on the density functional theory within the framework of the GGA are sufficiently accurate in predicting the ground state properties.

The elastic stability criteria for a cubic crystal [22] at ambient conditions are $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. Our calculated elastic moduli satisfy these stability conditions, including the conditions $C_{12} < C_{11}$ and $C_{12} < B < C_{11}$. In the present work, the elastic moduli are calculated using the tetrahedral and rhombohedral distortions on the cubic structure and are given in Table 2. The systems are fully relaxed after each distortion in order to reach the equilibrium state. The calculated values of C_{11} and C_{44} are underestimated compared to the experimental values [23] (obtained using ultrasonic wave transit times method for TlCl) by about 27% and 31%, while C_{12} is overestimated by about 6%. Similarly, calculated values of C_{11} and C_{44} are underestimated to the experimental values [24] by about 8% and 19%, while C_{12} is overestimated by about 24% for TlBr. These values of

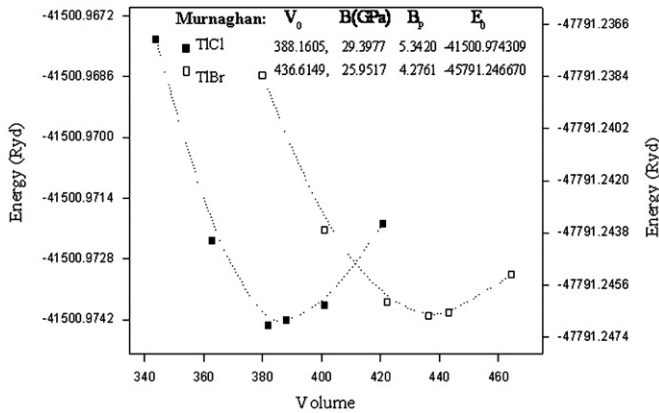


Fig. 1. Total energy as a function of volume for TlCl and TlBr with GGA calculation.

Table 1

Calculated lattice constant, a_0 (Å), bulk modulus, B_0 (GPa), its pressure derivative, B_0' for TlCl and TlBr using GGA functional.

		TlCl	TlBr
a_0	Present	3.86	4.01
	Other	3.84 ^a	3.97 ^a
B_0	Present	29.39	25.95
	Other	–	–
B_0'	Present	5.34	4.21
	Other	–	–

^a Ref. [3].

Table 2

Calculated elastic moduli, C_{ij} (GPa), bulk modulus, B (GPa), Young's modulus, Y (GPa), isotropic shear modulus, G (GPa), Poisson ratio, ν , using GGA.

		TlCl	TlBr
C_{11}	Present	35.33	34.80
	Other	40.40 ^a , 48.00 ^b	37.8 ^a , 37.60 ^c
C_{12}	Present	20.86	19.21
	Other	15.80, 19.5 ^b	14.50 ^c
C_{44}	Present	6.92	6.26
	Other	7.60, 10.1 ^b	7.50 ^c
B	Present	25.6	24.40
	Other	–	22.47 ^c
Y	Present	19.20	18.75
	Other	–	19.50 ^c
G	Present	6.98	6.83
	Other	–	7.58 ^c
ν	Present	0.37	0.37
	Other	–	0.28 ^c

^a Ref. [3].

^b Ref. [4].

^c Ref. [5].

Table 3

Calculated mass density, ρ (gm/cm³), sound velocities (10^3 m/s) for longitudinal and shear wave (V_L and V_S), Debye average velocity, V_m (10^3 m/s), Debye temperature, θ_D (K) and the Grüneisen parameter.

		TlCl	TlBr
ρ	Present	6.92	7.29
	Other	7.00 ^a	7.54 ^a
V_L	Present	2.24	2.14
	Other	2.26 ^b	2.13 ^b
V_S	Present	1.00	0.96
	Other	1.15 ^b	1.08 ^b
V_m	Present	1.13	1.09
	Other	–	–
θ_D	Present	181	167
	Other	120 ^c , 141 ^d	115 ^c
ζ	Present	2.36	2.32
	Other	2.47 ^e , 1.94 ^b , 2.60 ^b , 2.99 ^f	2.54 ^e , 1.94 ^b , 2.47 ^b , 2.50 ^f

^a Ref. [6].

^b Ref. [7].

^c Ref. [8].

^d Ref. [9].

^e Ref. [4].

^f Ref. [10].

C_{11} , C_{12} and C_{44} satisfy the elastic stability criteria, justifying the calculated values.

Bulk modulus (B), isotropic shear modulus (G), Young's modulus (Y) and Poisson ratio (ν) are also the important physical parameters, which tell more about the mechanical stability, hardness, brittleness and ductile properties of materials and are defined by Eqs. (10), (11), (12) and (13), respectively. The calculated values of B , G , Y and ν are given in Table 2 along with available experimental/theoretical values [24], which are in good agreement with the available results. The sound velocities for longitudinal and shear waves (V_L and V_S), Debye average velocity (V_m), Debye temperature (θ_D) and acoustic Grüneisen parameter (ζ) of a crystal are also the material parameters associated with lattice vibrations. These basically depend on the elastic moduli. In the present work, V_L , V_S , V_m , θ_D and ζ have been calculated using Eqs. (14), (15), (16), (17) and (18), respectively, and presented in Table 3 along with their experimental/theoretical values [23,25–29]. These values are inconsistent with the available literature values, justifying our results.

Figs. 2 and 3 show the self-consistent electron dispersion curve along the symmetry direction in the Brillouin zone for TlCl and TlBr. Fig. 4 shows calculated total density of states for (a) TlCl, Tl and Cl

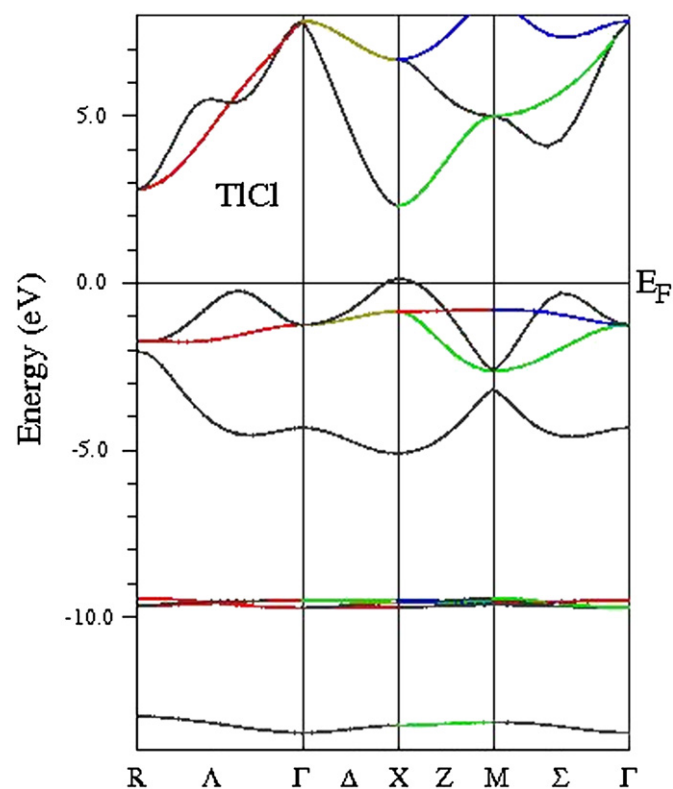


Fig. 2. Electron dispersion curve along high symmetry direction in the Brillouin zone for TlCl with GGA calculation.

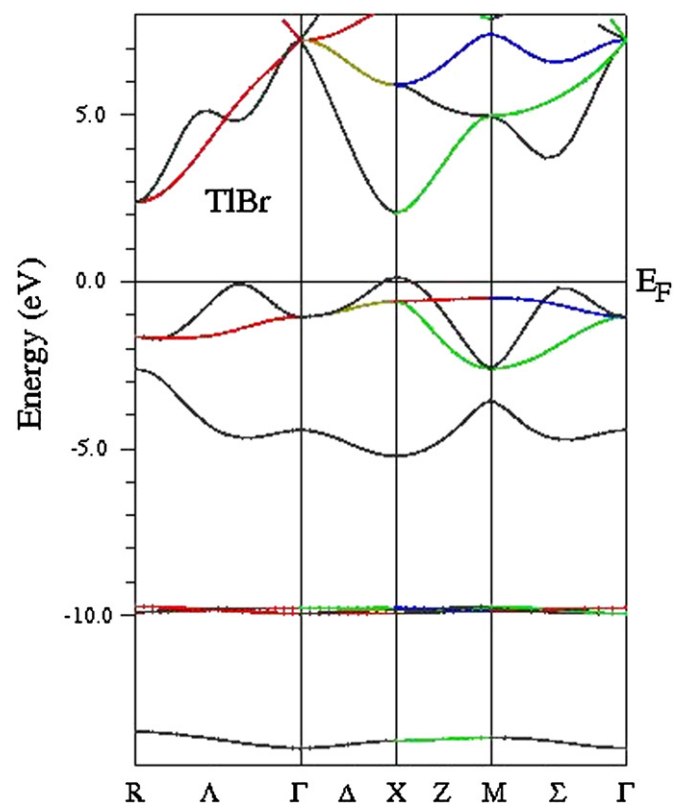


Fig. 3. Electron dispersion curve along high symmetry direction in the Brillouin zone for TlBr with GGA calculation.

and (b) TlBr, Tl and Br. It is clear from Figs. 2–4 that there are total four bands at around -14 , -10 , -5 and -2 eV. The lowest-lying band (at around -14 eV) arises from the Cl 3s-states; the bands

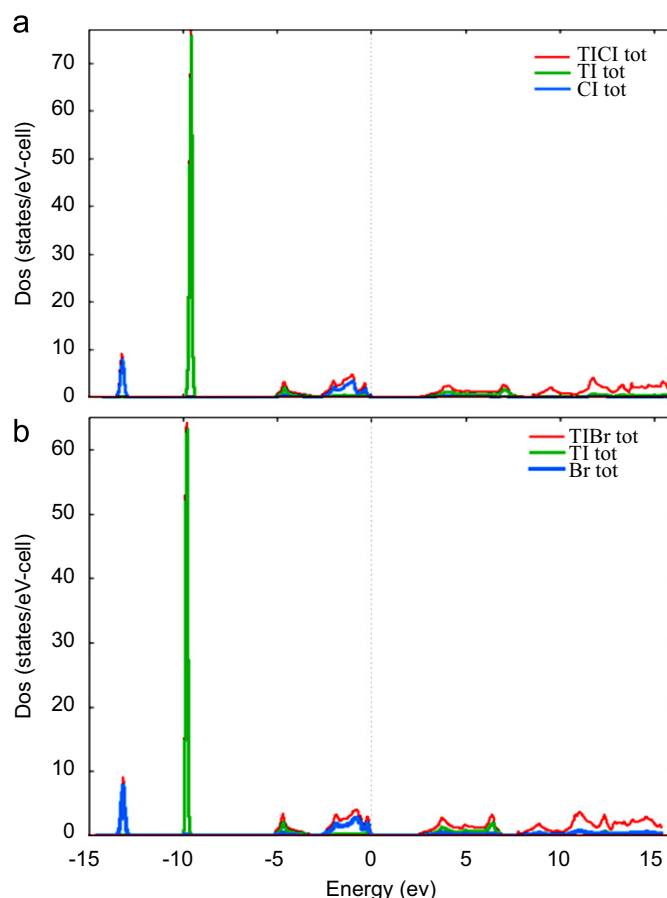


Fig. 4. Calculated total density of states for (a) TlCl, Tl and Cl and (b) TlBr, Tl and Br.

lying above this (at around -10 eV) are mainly contributed by the d-like states of the Tl atom. Well above these, the bands (at around -5 eV) arising from the Tl '6s' states with small contribution of Cl (or Br) p-states, while the bands at around -2 eV are entirely derived from Cl (or Br) p-states.

From Figs. 2 and 3 it can also be seen that there is a band gap ($E_g \approx 2.4$ eV) for TlCl and ($E_g \approx 2.2$ eV) for TlBr. The literature value of band gap is 2.7 eV for TlCl [30] and 2.68 eV for TlBr [5]. The close agreement between experimental and theoretical values justifies first principle electron dispersion calculations for band gap. The band gap value leads to semiconducting behavior of TlCl and TlBr.

4. Conclusion

From the total energy calculations, the ground state properties are calculated; the results are in good agreement with the literature values. The band structures for these compounds are plotted at ambient conditions. The overall band profiles are found to be the same, with the band gap occurring between the 'p'-like states of the halogen atom and the 'sd'-like states of the metal atom. The close agreement between literature and our calculated bandgap values of TlCl and TlBr justifies the band structure calculations. The wide bandgap semiconducting properties of these single crystals (TlCl and TlBr) with their high stopping power and density make these materials the leader among other materials and these properties could be utilized compact and mobile devices that are needed for express analysis and military applications.

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