Thermal properties of a novel compound PbVO$_3$

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Abstract. Effect of pressure on thermal properties of a multiferroic (MF) novel compound PbVO$_3$ is studied using an atomistic approach. The temperature dependence of the specific heat ($C_P$) (20K $\leq T \leq$ 300 K) of PbVO$_3$ has been studied and compared with the earlier experimental work. Also, this work reports, probably for the first time the relation of pressure to the Debye temperature ($\theta_D$) along with other properties like bulk modulus (B), molecular force constant ($f$), Reststrahlen frequency ($\nu_0$), thermal expansion ($\alpha$) and Grüneisen parameter of PbVO$_3$ with the Modified Rigid Ion Model (MRIM).

1. Introduction
The AVO$_3$ (A = Sr, Ba, and Pb) type perovskite-based oxide compounds are very interesting. Among which the prototype PbVO$_3$ shows unusual behaviours at high pressure. PbVO$_3$ adopts a layered structure [1-5] with isolated layers of corner-shared VO$_5$ pyramids due to the strong tetragonal distortion (space group $P4mm$); Tetragonal PbVO$_3$ has attracted considerable attention as a promising candidate of MF material [1, 6-11]. Except for potential application as MF material, tetragonal PbVO$_3$ also exhibits intriguing and fantastic fundamental physics. The ABO$_3$-type FE perovskite materials often show a temperature- and/or pressure-induced tetragonal to cubic (T-to-C) structural transition, corresponding to ferroelectric to paraelectric (FE-to-PE) phase transition [4] which is an unusual metal to insulator transformation [1]. Quite recently, with the application of high-temperature and high-pressure techniques, PbVO$_3$ was successfully synthesized for the first time. The most pure PbVO$_3$ samples were obtained in 40-60 kbar pressure range and at 700-750°C [2]. This compound was found to possess a very large tetragonal distortion (c/a, 1.23) [5, 11]. Only at high pressure (about 2 GPa), can the T-to-C phase transition be realized at room temperature [5]. The well depth of V atoms in PbVO$_3$ decreases gradually when the lattice constant is suppressed. As a result, the ferroelectric instability of PbVO$_3$ is weakened and the tetragonal to cubic transition becomes available under pressure, being consistent with the experimental observations that the transition appears at about 2 GPa at room temperature [5].

The AVO$_3$ compounds are considered to possess many potential applications in fields such as multiferroic devices, high-temperature solid oxide fuel cells, high $T_c$ superconductivity, and so on [3]. Despite their potential importance, relevant investigations on the AVO$_3$ compounds are relatively scarce. The magnetic properties have been well studied; but a systematic study on the thermal properties on the compound is lacking. We present the cohesive and thermal properties of a novel compound PbVO$_3$ [1] in distorted tetragonal and cubic phase. Earlier we have successfully used MRIM to study the thermal properties of some perovskite manganites and other inorganic compounds [12-15] which motivated us to compute the pressure / temperature dependent thermal properties of...
PbVO₃. The essentials of the MRIM formalism and the results obtained from its application are presented in subsequent sections.

2. Formalism of RIM

We have formulated the modified rigid ion model (MRIM) by keeping the effect of long-range (LR) Coulomb attractions, the short-range (SR) Hafemeister–Flygare-type (HF) [16] overlap repulsion effective up to the next nearest neighbour atoms and the van der Waals attraction due to dipole–dipole (d–d) interactions. The potential describing the formalism of MRIM is expressed as

\[
\phi = \frac{-e^2}{2} \sum_{kk} Z_k Z'_k r^4_{kk} - \sum_{kk} C_{kk} r^6_{kk} + \sum_i \left[ n_i \beta_i^{1/v} \exp \left( \frac{r_k + r_k - r_{kk}}{\rho_i} \right) \right] + b_i \frac{n_i \beta_i^{1/v}}{2} \exp \left( \frac{2r_k - r_{kk}}{\rho_i} \right)
\]

(1)

The contribution of van der Waal’s (vdW) attraction for the dipole–dipole interaction is determined by using the Slater–Kirkwood Variational (SKV) method [17]. The various terms in Eq (1) have their usual meaning as defined in our earlier papers [12-14].

The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition.

\[
\left. \frac{d\phi}{dr} \right|_r = 0 \quad \text{and} \quad B = \frac{1}{9} K r_0 \left( \frac{d^2\phi}{dr^2} \right)_{r=r_0}
\]

(2)

Table 1. The average cation radius at A-site, Tolerance factor (t) and model parameters of PbVO₃

| r_k (Å) | Temp. (K) | Pressure (GPa)/ Structure | t   | ρ₁ (Å) (V-O) | b₁ × 10¹⁹ (J) (V-O) | ρ₂ (Å) (Pb-O) | b₂ × 10¹⁹ (J) (Pb-O) |
|--------|---------|-------------------------|-----|-------------|------------------|-------------|------------------|
| 1.49   | 295     | 4-6 /C                  | 0.999 | 0.374     | 1.877             | 0.644       | 0.235            |
| 1.29   | 90      | 0 /T                    | 0.930 | 0.195     | 0.145             | 0.490       | 0.022            |
| 1.29   | 530     | 2 /T                    | 0.930 | 0.183     | 0.107             | 0.465       | 0.016            |

3. Results and discussions

The input data like the lattice parameters and interatomic distances at various pressures and temperatures are taken from [2, 4 and 5]. The ionic radii for distorted tetragonal and cubic structure of PbVO₃ with coordination no. 8 and 12 respectively were taken from [18] (Table1). Using the input data and the vanderwaals coefficients (using SKV method [17]) we computed the model parameters, hardness (b₁, b₂) and range (ρ₁, ρ₂) corresponding to the ionic pairs V⁴⁺-O²⁻ and Pb²⁺-O²⁻. The bulk modulus calculated on the basis of AIM theory [19] similar to our previous work [12-14] could not be compared due to lack of experimental data. But the calculated bulk modulus, 91.5GPa for cubic PbVO₃ is in fair agreement with the bulk modulus, 97.3GPa for multiferroic BeFeO₃ [20] (Table 2). The cohesive energy of PbVO₃ is computed using eqn. (1) and is reported in table 2. The negative value of the cohesive energy indicates that this compound is stable at ambient temperature and pressure. Calculated cohesive energy of PbVO₃ is quite comparable with the reported value of the lattice energy for LaVO₃, -140.07eV [21]. Further, to ascertain the validity of the MRIM we have used the generalized Kapustinskii equation [22] on the lines of our earlier work [12-14]. The lattice energy obtained using the Kapustinskii equation is close to the MRIM results (average deviation being less than 3%). The cohesive energy results conclude that tetragonal PbVO₃ is more stable than cubic PbVO₃. An empirical prediction for the size of the distortion is given by the tolerance factor, t (t = (r_p+b) / 2(r_v+r_d)). The tolerance factor t (Table 1) satisfies the condition that it lies between 0.8 and 1 for orthorhombic and is almost 1 for cubic structure [23].

Our results on Debye temperatures correlate well with the earlier experimental results on CaVO₃ [24]. Also it can be clearly seen in Table 2 that the Debye temperature (θ₀) of the tetragonal PbVO₃ is...
higher than that of cubic and \( \theta_D \) increases slightly with increase in temperature and pressure for tetragonal \( \text{PbVO}_3 \). The value of Gruneisen parameter (Table 2) seems to be reasonable since its value ranges from 2 - 3 for perovskite type compounds as reported earlier [25].

**Table 2.** Bulk modulus, Cohesive and Thermal properties of \( \text{PbVO}_3 \) (Cubic-C, Tetragonal-T)

| Temp. (K) | Pressure (GPa)/ Structure | \( B_T \) (GPa) | \( \phi \) (eV) | \( \phi \) (eV) (kapustinskii equation) | \( f \) (Nm\(^{-1}\)) | \( \nu \) (THz) | \( \theta_D \) (K) | \( \gamma \) |
|----------|--------------------------|-----------------|----------------|--------------------------------------|-----------------|---------|---------------|-------|
| 295      | 4-6 /C                   | 91.5            | -131.19        | -132.93                              | 18.08           | 7.74    | 393.27        | 1.15  |
|          |                          | 97.3\(^a\)      |                |                                      |                  |         |               |       |
| 90       | 0 /T                     | 116.7           | -138.62        | -140.57                              | 27.31           | 9.52    | 483.38        | 2.10  |
| 530      | 2 /T                     | 119.77          | -138.81        | -140.89                              | 28.69           | 9.75    | 495.38        | 2.18  |
|          |                          | -140.07\(^b\)  |                |                                      |                  |         |               |       |

\(^a\)ref [20], \(^b\)ref [21], \(^c\)ref [24], \(^d\)ref [25]

**Figure. 1** Variation of calculated heat capacity (\( C_p \)) with temperature compared with the experimental data of Tsirlin et al. [1] (left) and Comparison of specific heat of \( \text{PbVO}_3 \) in tetragonal and cubic phases (right).

The heat capacity (\( C_p \)) (20K \( \leq T \leq 300 \) K) for this multiferroic compound is shown in Figure 1. Also we have compared the specific heat for the two pressure-induced phases (tetragonal and cubic), Figure 1 concludes that higher the pressure, higher is the specific heat of \( \text{PbVO}_3 \). The specific heat curve is smooth between 1.8 and 270 K and suggests the absence of phase transitions in \( \text{PbVO}_3 \) in this temperature range. The conclusion is supported by thermal expansion curve depicted in Figure 2. Our
results on specific heat have quite good match with the experimental work of Tsirlin et al [1]. Besides we have computed the $C_p/T$ curve at temperature $20K \leq T \leq 300$ K and displayed in Figure 2.

Thus, a satisfactory prediction of the cohesive and thermal properties for the multiferroic compound attained by us is remarkable in view of inherent simplicity and less parametric nature of Modified Rigid Ion Model (MRIM). Our results on specific heat can be further improved by including the magnetic contribution. The theoretical values of thermal properties presented in this paper can serve as a guide to the experimental workers in the future.

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