

The effect of pressure on thermodynamic properties of Barium titanate

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In this paper the structural and thermodynamics properties of Barium titanate have been studied in the tetragonal phase by first principle approach. The full potential linearized augmented plane waves and Debye model through the quasi harmonic Debye model, in which the phononic effect are considered, have been employed to calculate the fundamental thermodynamic properties. Heat capacity at constant volume, Debye temperature and thermal expansion coefficient over a wide temperatures range of 1K to 1000 K and pressures range 0 GPa to 30 GPa were successfully calculated.

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1. Introduction

Barium titanate (BaTiO_3) is as one of the most technologically importance ferroelectric material with three different ferroelectric phases. It has a variety of physical properties so can be used in devices such as capacitors, components of nonlinear optical devices, piezoelectric and data storage. At ambient pressure and above 393 K, a tetragonal distortion of unit cell is observed and Barium titanate changes to a tetragonal phase with dipole moment. At lower temperatures BaTiO_3 has two other phase transitions to orthorhombic (273 K) and rhombohedral (183 K). The crystal structure of BaTiO_3 single crystal in paraelectric and ferroelectric phases has been reported by X-ray diffractions [1-3].

As we know, we can extend our knowledge about specific behaviors of different materials under Special conditions such as high temperature and high pressure by study of thermodynamic properties [4-6]. Temperature-pressure phase diagram of Barium titanate has been determined by Ishidate et al [7]. They showed that by means of experimental dielectric measurement, the critical pressures for transition from cubic to tetragonal, from tetragonal to orthorhombic and finally from orthorhombic to rhombohedral at 0 K are 6.5, 6.0 and 5.4 GPa respectively. Pressure-induced phase transformation of Barium titanate from rhombohedral to orthorhombic, from orthorhombic to tetragonal and from tetragonal to cubic at 273 °C have been reported 5.0, 6.0 and 7.5 GPa respectively. Bandura et al [8] have performed a first principles study of the thermodynamic properties of BaTiO_3 rhombohedral phase by means of quasiharmonic approximation. They considered hybrid PBEO exchange-correlation functional for estimation of heat capacity at zero pressure and temperature from 0 K to 200 K. In addition, many other ab initio calculations have mainly reported the thermodynamic properties of cubic phase of barium titanate but to our knowledge, thermodynamic properties of tetragonal phase of BaTiO_3 in different

pressure and temperature have not been reported. The aim of our study is to investigate the change of the bulk modulus, volume thermal expansion coefficient and heat capacity of Barium titanate with pressure and temperature.

2. Computational details

First principle total energy calculation based on density functional theory is a very successful way to predicting crystal structures, electronic and optical properties of BaTiO_3 in different phases, but to our knowledge a complete study of thermodynamics properties of the tetragonal phase of BaTiO_3 have not been reported. In this study we have computed thermodynamic properties of Barium titanate in tetragonal phase using the density functional theory (DFT) by generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof [9, 10] to describe the exchange and correlation potential.

The quasi-harmonic Debye model (QHA) [11] was applied to calculate thermodynamic properties of Barium titanate by using GIBBS II package [12].

The calculations were started with a full structural relaxation of the tetragonal phase of BaTiO_3 . For the structural optimization, different exchange correlation functional within local density approximation (LDA) and generalized gradient approximation (GGA) were used. The electronic wave functions are expanded in a plane wave for the interstitial region between the spheres, and inside the muffin-tin spheres, the wave function, electron charge density were expanded in terms of spherical harmonics. We evaluated different thermodynamic properties of tetragonal phase of Barium titanate such as heat capacity at constant volume, thermal expansion coefficient and bulk modulus by employing QHA. In this model, the nonequilibrium Gibbs function $G(v; P, T)$ under a given pressure P and temperature T can be written as [13]:

$$G^*(V;P,T)=E(V)+PV+A_{\text{vib}}^*(\Theta D(v);T) \quad (1)$$

$E(v)$, is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta D(v)$ is the Debye temperature and A_{vib}^* is the vibrational Helmholtz free energy. The vibrational contribution A_{vib}^* is given as [14-17]:

$$A_{\text{vib}}^*(\theta_D;T) = nK_B T \left[\frac{9\theta_D}{8T} + 3 \ln \left(1 - e^{-\theta_D/T} \right) + D \left(\frac{\theta_D}{T} \right) \right] \quad (2)$$

where n , is the number of atoms per formula unit, K_B is Boltzmann's constant, $D \left(\frac{\theta_D}{T} \right)$ represents the Debye integral. The Debye temperature, θ_D , is expressed as:

$$\theta = \frac{\hbar}{K_B} \left[6\pi^2 V^{\frac{1}{3}} n \right] f(\sigma) \sqrt{\frac{B_s}{M}} \quad (3)$$

where M , is molecular mass per unit cell, B_s is the adiabatic bulk modulus measuring compressibility of crystal which is defined by [12]:

$$B_s \cong B(V) = V \frac{d^2 E(V)}{dV^2} \quad (4)$$

$f(\sigma)$ is given by [11-12]:

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2-1+\sigma}{3-1-2\sigma} \right)^{\frac{3}{2}} + \left(\frac{1-1+\sigma}{3-1-\sigma} \right)^{\frac{3}{2}} \right]^{-1} \right\}^{\frac{1}{3}} \quad (5)$$

The poisson's ratio σ is taken as 0.25 [18], therefore, the non-equilibrium gibbs function $G^*(V;P,T)$ can be minimized as a function of $(V;P,T)$ with respect to volume V :

$$\left(\frac{\partial G^*(V;P,T)}{\partial V} \right)_{P,T} = 0 \quad (6)$$

The thermal equation of state (EOS) $V(P,T)$ can be obtained. The thermal expansion coefficient, α , can be expressed as [12]:

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (7)$$

where B_T is isothermal bulk modulus, C_V , is the heat capacity at constant volume, γ is the Gruniesen parameter and S entropy which are given by [12]:

$$B_T(T, P) = V \left(\frac{\partial^2 G^*(V,P,T)}{\partial V^2} \right)_{P,T} \quad (8)$$

$$C_V = 3nk \left[4D \left(\frac{\theta_D}{T} \right) - \frac{3 \frac{\theta_D}{T}}{e^{\frac{\theta_D}{T}} - 1} \right] \quad (9)$$

3. Results and discussion

In this study the total energy of BaTiO_3 in tetragonal phase was calculated for different volumes around the equilibrium lattice constants. In Fig. 1, calculated total energy versus reduced volume has been shown.

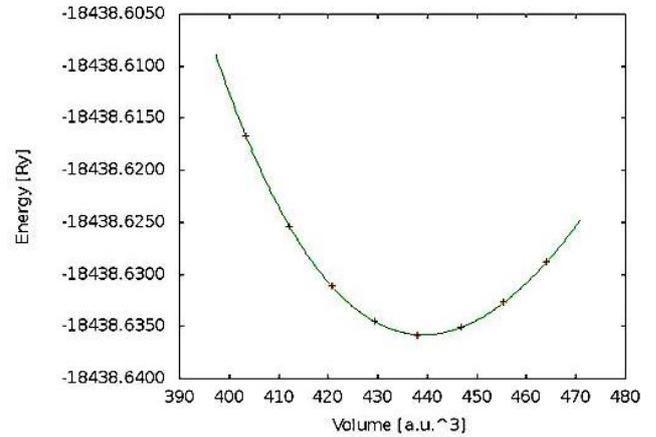


Fig. 1. Total energy versus reduced volume of BaTiO_3 in tetragonal phase

The experimental lattice constants values a and c are 3.997 Ao and 4.031Ao respectively. The structural parameters including lattice constants a and c and bulk modulus were calculated by performing structural optimization and the resulted values are listed in Table 1.

Table 1. The structural parameters including lattice constants a and c and bulk modulus

	a (Ao)	c (Ao)	B (GPa)
Theoretical work [19]	4.013	4.0153	-
Theoretical work [20]	4.050	4.205	-
Exp [21]	3.943	3.994	98
Present work (LDA)	3.888	4.012	116
Present work (GGA)	3.990	4.023	112

The quasi-harmonic Debye model is fully valid in the temperature range from 0 to 2000 K, so, the thermal properties of Barium titanate were determined these range and the pressure effect was studied in range of 0 GPa to 30 GPa. In Fig. 2, we show the temperature dependence of the bulk modulus in different pressure. It can be seen that bulk modulus decreases with temperature at a given pressure and increases with temperature at a given pressure.

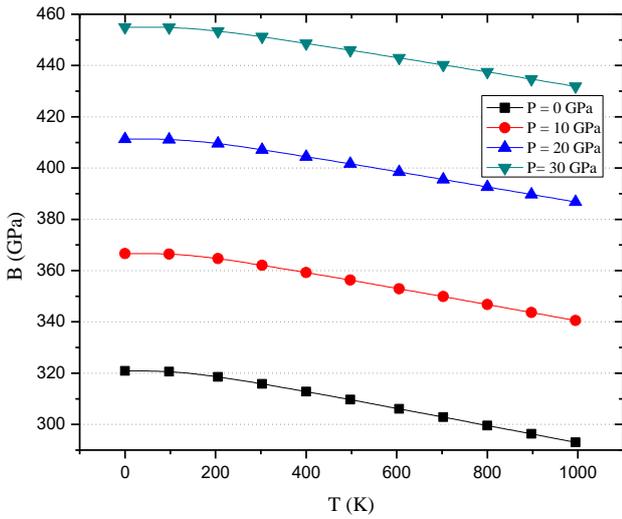


Fig. 2. Temperature dependence of the bulk modulus with temperature in different pressure

Variation of specific heat at constant volume for temperatures from 0K to 1000 K at pressures from 0 GPa to 30 GPa for Barium titanate has been shown in Fig. 3. As we know the specific heat of a material is due to vibrational motion of the ions. At low temperatures strength of binding represents Hook's law and acoustic modes. At sufficiently low temperature, the heat capacity at constant pressure is proportional to T^3 . At higher temperatures, the optical modes become very important and C_v tends to the Dulong-petit limit [22]. At intermediate temperatures, C_v behaves by the details of vibrations of the atoms.

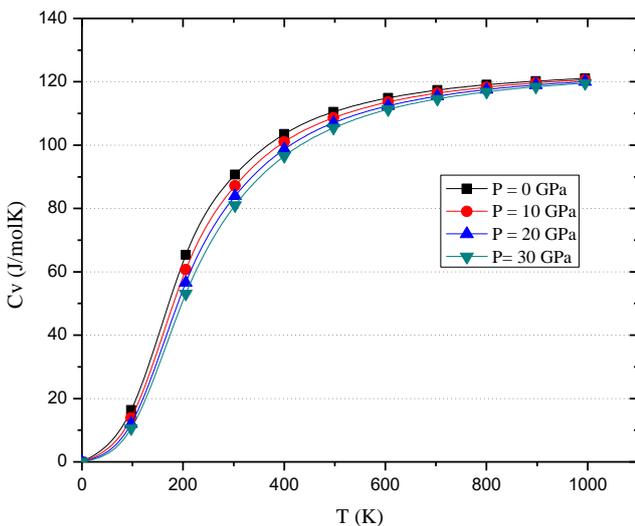


Fig. 3. Variation of specific heat at constant volume with temperature in different pressure

As we can see from the Fig. 3, heat capacity at constant volume decreases with pressure at a given temperature.

As we know from the literatures, the Debye temperature is the temperature of highest normal mode of vibration of a solid. In Fig. 4 diagram of Debye temperature versus temperature for different pressure have been plotted. It is seen that the Debye temperature decreases with increasing temperature as well as pressure.

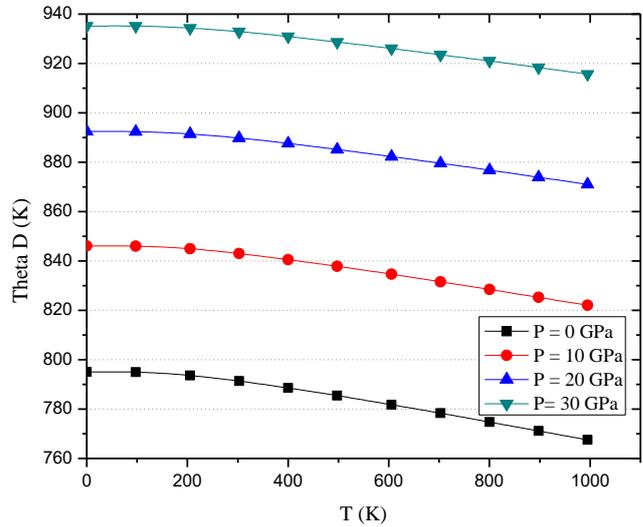


Fig. 4. Variation of Debye temperature with temperature in different pressure

For indication of expansion of $BaTiO_3$ upon heating, the volume thermal expansion, α of Barium titanate have been calculated and the results shown in Fig. 5.

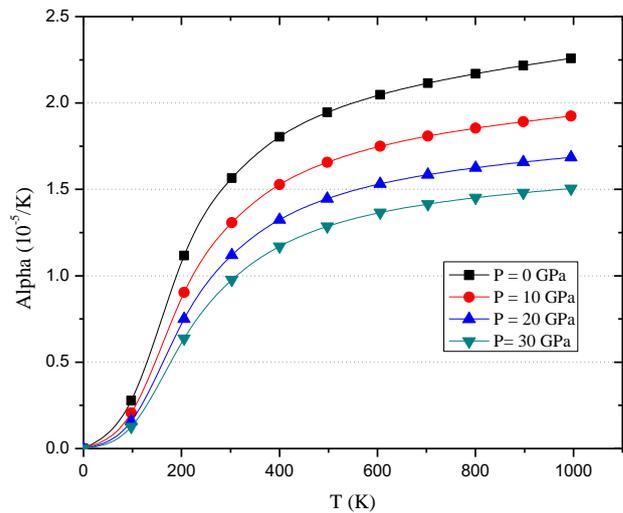


Fig. 5. Variation of volume thermal expansion with temperature in different pressure

It is seen that at a given temperature, volume thermal expansion decreases with the increasing of the pressures.

4. Conclusion

In brief, we investigated the thermodynamics properties of Barium titanate in the tetragonal phase using full potential augmented plane waves approach in the framework of density functional theory and Debye model. Thermodynamic properties such bulk modulus, heat capacity at constant volume, Debye temperature and thermal expansion coefficient have been calculated in temperature ranges 0K to 1000 K and pressure ranges of 0 GPa to 30 GPa. It is found that the effect of temperature on the relative volume is not significant as that of pressure. Also the heat capacity at constant volume and thermal expansion coefficient decrease with increasing pressure, while bulk modulus and Debye temperature increase with increasing pressure.

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