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First principles calculations on thermodynamic properties of $\alpha - \mathrm{Al_2O_3}$under pressure and temperature

S. J. MOUSAVI*
Department of Physics, Rasht Branch, Islamic Azad University, Rasht, Iran

By employing the first principles method of the full potential linearized augmented plane waves (FP-LAPW) approach based on density functional theory and Debye model the thermodynamic properties of $\alpha - Al_2O_3$ are investigated. The exchange correlation potential was calculated in framework of generalized gradient approximation (GGA). Through the quasi-harmonic Debye model, in which the phononic effects are considered, we have obtained successfully the thermodynamic parameters including the relative volume, heat capacity and volume expansion coefficient over a pressure range 0-70 Gpa and a wide temperature range of 0-2000 K.

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1. Introduction

The advanced of new materials improved the science and life qualities during the past several decades. One of these materials is alpha phase of Alumina$\alpha - Al_2O_3$. The$\alpha - Al_2O_3$ is an important ceramic material in its pure forms and is widely used in a range of industrial applications such as a substrate for the growth of thin metal, semiconductor, and insulator films in the microelectronics industry [1,2]. The study of thermodynamic properties of materials is of great importance in order to extend our knowledge about there specific behaviors when put under sever constraints such as a high pressure and high temperature. The properties of materials under high pressure have attracted much attentions because of their relevance for understanding the compositions of the earth's interior.The microscopic investigation of solid, either by means of an ab initio quantum mechanical method at zero temperature which neglecting zero point vibrational effect, i.e. in the static approximation. In order to proceed the thermodynamic calculations for solving problems in geophysics, particles accelerator,fission and fusion reactor, and etc, one needs an accurate knowledge of equation of state (EOS) and related thermodynamic properties. The EOS and chemical potential are two of key thermodynamic properties of a solid. The EOS of a given crystalline phase determines its behavior with respect to change in the macroscopic variables, mainly pressure and temperature. The chemical potential μ is the magnitude governing phase stability and change. To obtain the determination of the EOS and μ from first principle one has to pay particular attention to the concept of thermodynamic equilibrium state.

2. Method of calculations

In recent years, ab initio total energy calculations based on density functional theory have been very successful in predicting crystal structures, electronic and optical properties of $\alpha - Al_2O_3$ but in our knowledge a complete study about thermodynamics properties of the alpha phase of Alumina have not been reported. In the present work, we have investigated the thermodynamics properties of $\alpha - \mathrm{Al_2O_3}$, using the density functional theory by full potential linearized augmented plane waves (FP-LAPW) method. The first principles calculations described here are performed with the Wien2k code [3] based on DFT. We use the the generalized gradient approximation (GGA) in the scheme of Perdew – Burke – Ernzerhof [4,5] to describe the exchange and correlation potential. Inside the muffin-tin spheres, the wave functions, electron charge density and potentials were expanded in terms of spherical harmonics, whereas for the interstitial region between the spheres plane wave expansions were used. The core states were treated fully relativistically. To confirm the convergence of our calculations cut-off energy and the k-point set mesh according the minkhorst-pack grid [6] are investigated carefully.

The thermodynamic properties of material are the basis of solid state physics and chemistry and industrial applications. The quasi-harmonic Debye model was applied to calculate thermodynamic properties of α-Al2O3 by using GIBBS program [7]. In this model, the non equilibrium Gibbs function $G^*(V;P,T)$ can be written as [8]

$$G^*(V;P,T)=E(V)+PV+A^*_{vib}(\Theta_D(v);T) \qquad (1)$$

where E(v), is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, Θ_D(v) is the Debye temperature and A^*_{vib} is the vibrational Helmholtz free energy. The vibrational contribution A^*_{vib} is given as [9-12]:

$$A^*_{vib}(\theta_D;T) = nK_BT\left[\frac{9\theta_D}{8T} + 3\ln\left(1 - e^{-\theta_D/T}\right) + D\left(\frac{\theta_D}{T}\right)\right] \tag{2}$$

where n, is the number of atoms per formula unit, K_B is Boltzmann's constant, $D(\frac{\theta_D}{T})$ represents the Debye integral. The Debye temperature, θ_D, is expressed as [12]:

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

where M, is molecular mass per unit cell, B_s is the adiabatic bulk modulus measuring the compressibility of crystal which is defined by [7]:

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

$f(\sigma)$is given by [9-10]:

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

The poisson's ratio σ is taken as 0.25 [13], 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:

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

The thermal equation of state (EOS) V(P,T) can be obtained. The thermal expansion coefficient, α, can be expressed as [7]:

$$\alpha = \frac{\gamma C_V}{B_T V} \tag{7}$$

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 [7]:

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

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

$$\gamma = -\frac{d ln\theta_D(V)}{d\ln V} \tag{10}$$

$$S = nK\left[4D\left(\frac{\theta_D}{T}\right) - 3\ln(1 - e^{\frac{\theta_D}{T}})\right] \tag{11}$$

3. Results and discussion

The total energy of $\alpha - Al_2O_3$ are calculated for different volumes around the equilibrium lattice constant a, bulk modulus B_0 and its pressure derivative B'. We have fitted the curve $E = f(V)$ to Murnaghan equation of stste [14].In Fig. 1. The plot of calculated total energy versus reduced volume is given.

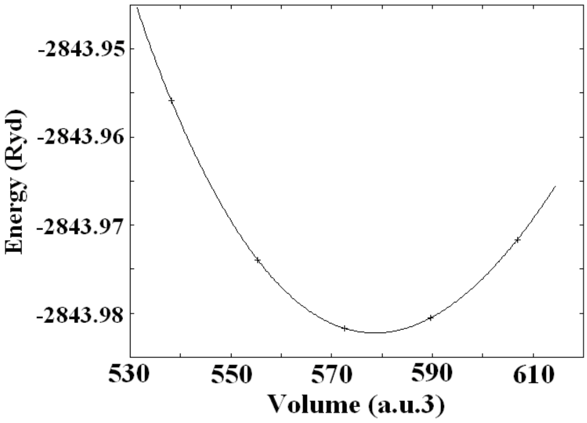

Fig. 1.Total energy versus reduced volume.

The thermal properties of $\alpha - Al_2O_3$ are determined in the temperature range from 0 to 2000 K where the quasi-harmonic Debye model remains fully valid and the pressure effect was studied in 0 -70 Gpa range. The relationship between relative volume and pressure at different temperature are shown in Fig. 2. It is seen that when the pressure increase from 0 to 70 Gpa, the volume decreases. This can be attributed to that the atoms in the interlayer become closer and their interaction become stronger. It is clear that the relative volume increases with increasing temperature moderately.

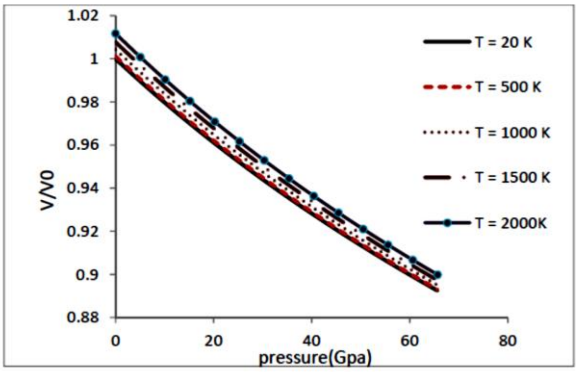

Fig. 2.The relationship between relative volume and pressure at different temperature.

In fact the temperature has tendency to increase the lattice parameter and the pressure decreases it and we can note trough the variation the effect of temperature remains dominant.

The relationship between bulk modulus$B$ and pressure at different temperature are shown in Fig. 3. These results indicate that bulk modulus decreases with temperature at a given pressure and increases with pressure at a given temperature. The results are due to the fact that the effect of increasing pressure on material is similar as decreasing temperature of material.

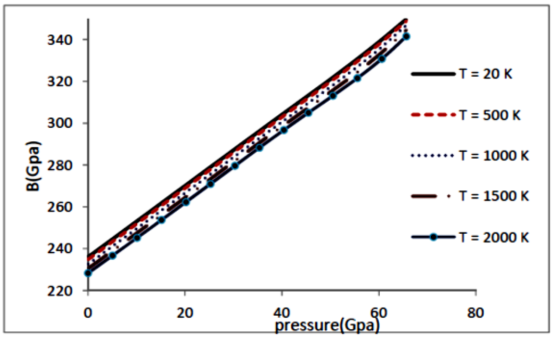

Fig. 3.The relationship between bulk modulus and pressure at different temperature.

The specific heat of a metal is due essentially to the vibrational motion of the ions. The heat capacity of a substance is a measure of how well the substance stores heat. The temperature dependence behaviors of the constant volume heat capacity at various pressures are shown in Fig. 4. As we can see from Fig. 4.when$T < 500\,K$, $C_V$increases rapidly with temperature at a given pressure which is due to the anharmonic approximation of the Debye model and decreases with pressure at a given temperature. At high temperature, the constant volume heat capacity tend to the Dulong-petit limit[15] which is common to all solid at high temperatures. At sufficiently low temperature, however, the C_V is proportional to T^3 [15].At intermediate temperature, the temperature dependence of $C_V$is governed by the details of vibrations of the atoms.

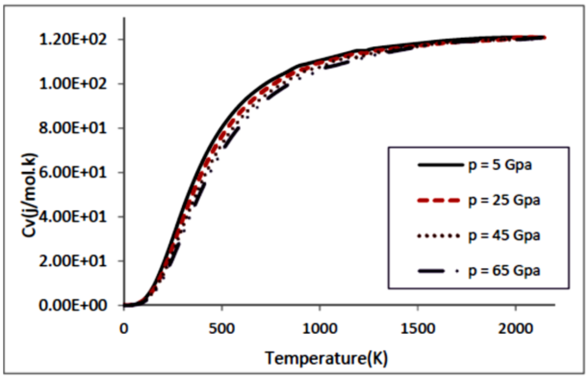

Fig. 4.The relationship between heat capacity and temperature at different pressure.

The volume thermal expansion coefficient α is a material property that is indicative of the extent to which a material expands upon heating. The variation of thermal expansion α with temperature and pressure are shown in Fig. 5. It can be directly obtained from Eq. (7). It can be seen that at a given temperature, α decreases drastically with the increasing of the pressure and increases with increasing temperature at different pressures. These indicate that the anharmonic effects are important at low pressure and high temperatures for $\alpha - Al_2O_3$.

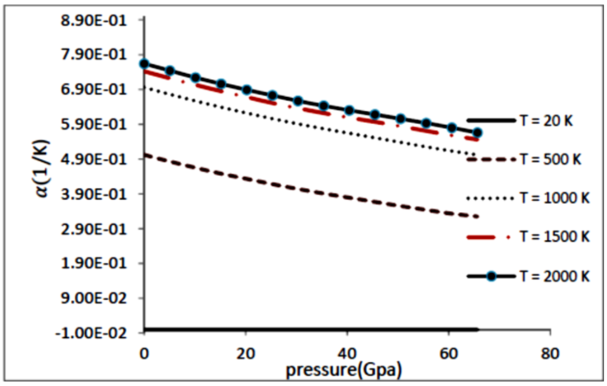

Fig. 5. The relationship between thermal expansion and pressure at different temperature

4. Conclusions

In this study, the thermodynamic properties of $\alpha - Al_2O_3$ are investigated using full potential linearized augmented plane waves (FP-LAPW) approach based on density functional theory and Debye model. The exchange correlation potential was calculated in framework of generalized gradient approximation (GGA). We analyzed the thermodynamic parameters over a pressure range 0-70 Gpa and a wide temperature range of 0-2000 K. It is found that the effect of temperature on the relative volume is not as significant as that of pressure while the relative volume, heat capacity and volume thermal expansion decreases with increasing pressure, the bulk modulus increases with the increase of pressure. The high temperature leads to a smaller adiabatic bulk modulus, a larger heat capacity and a bigger volume thermal expansion coefficient.

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References

[1] T. J. Godin, J. P. LaFemina, Phys. Rev. B: Condens. Matter, **49**(11), 7691 (1994).
[2] T. Fujii, D. Alders, F. C. Voogt, T. Hibma, B. T.

Thole, G. A. SawatzkySurf.Sci., **366**(3), 579 (1996).
[3] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, Inst. f. Materials Chemistry, TU Vienna, http://www.wien2k.at/
[4] K. Schwarz, P. Blaha, Comput. Mater. Sci. **28**, 259 (2003).
[5] K. Schwarz, P. Blaha, G. K. H. Madsen, Comput. Phys. Commun. **147**, 71 (2002).
[6] H. J. Monkhorst, J. D. Pack, Phys. Rev. B **13,** 5188 (1976).
[7] M. A. Blanco, E. Francisco, V. Luana, Comput. Phys. Commun. **158,** 57 (2004).
[8] A. A. Maradudin, E. W. Montroll, G. H. Weiss, I. P. Ipatova, Theory of Lattice Dynamics in the Harmonic Approximation, Academic Press, New York, 1971.
[9] M. A. Blanco, A. Martin Pendas, E. Francisco, J. M. Recio, R. Franco, J. Mol. Struct .(Theochem.), **368,** 245 (1996).
[10] E. Francisco, J. M. Recio, M. A. Blanco, A. Martin Pendas, J. Phys. Chem. **102,** 1595 (1998).
[11] E. Francisco, M. A. Blanco, G. Sanjurjo, Phys. Rev. B **63,** 094107 (2001).
[12] M. Florez, J. M. Recio, E. Francisco, M. A. Blanco, A. Martin Pendas, Phys. Rev. B**66,** 144112 (2002).
[13] J. P. Poirier, Introduction to the Physics of the Earth's Interior, 39, Cambridge University Press, Oxford, 2000.
[14] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30,** 5390 (1944).
[15] A. T. Petit, P. L. Dulong, Ann. Chim. Phys. **10,** 395 (1819).

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*Corresponding author: j_mousavi@iaurasht.ac.ir