

## Structural and thermodynamic properties of Alumina

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### ABSTRACT

We have investigated the electronic structure and thermodynamic properties of supercell of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by first-principles calculation in framework of density functional theory (DFT) and full potential linearized augmented plane wave (FP-LAPW) with generalized gradient approximation (GGA) and by quasi-harmonic Debye model. Our calculated value for direct band gap of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is 7.2 eV which is very close to its experimental measurement. Through the quasi-harmonic Debye model, in which the phononic effects are considered, we have obtained successfully the thermodynamic parameters including the relative volume and heat capacity over a pressure range 0-70 Gpa and a wide temperature range of 0-2000 K.

**Keywords:** Band structure; Electric and thermodynamics properties; Density functional theory

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### 1. INTRODUCTION

Alumina (Al<sub>2</sub>O<sub>3</sub>) is an extremely important material due to its great hardness, high thermal stability, chemical inertness and high melting temperature. Corundum can also be used in combination with silicon dioxide layers to form multilayer structure with high damage thresholds in UV laser applications. Besides the stable phase  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, alumina exhibit a number of different metastable or transition phases, such as  $\gamma$ ,  $\kappa$ ,  $\lambda$ ,  $\eta$ ,  $\theta$  and  $\chi$  alumina. The metastable-alumina can be divided into two major groups, depending on the stacking of their O anions: face-centered cubic (fcc) packing ( $\gamma$ ,  $\theta$ ,  $\eta$  and  $\lambda$ ) and hexagonal close packing (hcp) ( $\kappa$  and  $\chi$ ) [1]. The electronic structure of alumina (Al<sub>2</sub>O<sub>3</sub>) is increasingly of interest for its various applications in optical, electronic and structural devices.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is an insulator with measured value of its direct band gap of 8.8 eV [2]. The best

calculated value for band gap which has been reported is 6.6 eV [3]. Our calculated band gap, density of state for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is very close to the experimental measurements. The unit cell of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is rhombohedral, composed of two Al<sub>2</sub>O<sub>3</sub> molecular units (i.e. 10 atoms). It can be more easily visualized, however, with a trigonal unit cell, that is, a hexagonal coordinate system, composed of six molecular units (30 atoms). The crystal structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is described as an almost close-packed ABAB stacking of oxygen ions in planes that are perpendicular to the [0001] direction (the c axes of the hexagonal coordinate system). Smaller aluminum ions occupy two thirds of the six-foldly coordinated interstitial sites present between the oxygen layers. Then  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> belongs to the trigonal crystal system and has a rhombohedral lattice with space groups  $R\bar{3}c$ .

The aim of this paper is to determine some of the basic electronic and thermodynamic properties of supercell of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by first principles methods based on density functional theory (DFT) with full potential linearized augmented plane wave (FP-LAPW) method and with exchange-correlation potential of generalized gradient approximation (GGA) and gibbs approximation [4-6].

## 2. METHOD OF CALCULATION

We have calculated the electrical and thermodynamic properties of supercell of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by self-consistent scheme with solving the Kohn-Sham equations, in the framework of density functional theory (DFT) by means of full potential augmented plane wave method (FP-LAPW) with generalized gradient approximation (GGA [7] and by quasi-harmonic Debye model. In the full potential method, space is divided into two regions, a spherical muffin-tin (MT) around the nuclei and aninterstitial region between the muffin-tin spheres (I). In the first region the redial solution of Schrodinger equation and their energy derivatives are used as basic functions and for interstitial region basis set consist of plane waves. Core states are treated fully relativistically, while valence and semi-core states are treated semi-relativistically. We have used a periodic supercell approach to study the electronic and thermodynamic properties of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The supercell is in the hexagonal lattice and it contains 12 Al<sub>2</sub>O<sub>3</sub> molecules. The study of thermodynamic properties of materials is of great importance in order to extend our knowledge about their specific behaviors when put under sever constraints such as high pressure and high temperature. The properties of materials under high pressure have attracted much attention 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 neglects zero point vibrational effect, i.e. in the static approximation. The EOS and chemical potential are two 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 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by using GIBBS program [8]. In this model, the non equilibrium Gibbs function  $G^*(V;P,T)$  can be written as [9].

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

where  $E(v)$ , is the total energy per unit cell,  $PV$  corresponds to the constant hydrostatic pressure condition,  $\Theta_D(v)$  is the Debye temperature and  $A_{\text{vib}}^*$  is the vibrational Helmholtz free energy. In the calculations, we use a parameter  $R_{\text{MT}}K_{\text{max}}=7$  is the plane wave cutoff and  $R_{\text{MT}}$  is the smallest of all atomic sphere radii. We choose the muffin-tin radii of Al and O to be 2.4 Å and 0.846 Å, respectively. The self-consistent calculations are considered to be converged when the charge difference was less than 0.0001 e between steps. The separation of the valence and core states was chosen -8 Ry. Since calculations of the optical properties require a more dense k-space matrix, we have used 400 k points in reciprocal space.

### 3. RESULTS AND DISCUSSION

The calculation were first carried out applying the experimental data for lattice constants then by minimizing the ratio of the total energy of the crystal to its volume (volume optimization) the theoretical lattice constants were obtained. The total energy of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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 state [10]. In Fig. 1, the plot of calculated total energy versus reduced volume is given. The band structures of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been calculated with FP-

LAPW-GGA method and are shown in Fig. 2. There is a direct band gap which separates the valence and conduction bands with 7.2 eV at the  $\Gamma$  point. The experimental value for direct band gap of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is 8.8 eV by French [2]. Our calculated value for band gap is very close to experimental value and is very better than other theoretically calculated values that have been reported. Our calculations with DFT are fundamentally ground-state calculation and therefore, tend to underestimate the band gap energy since this energy corresponds to a transition to a higher energy excited state of the solid.

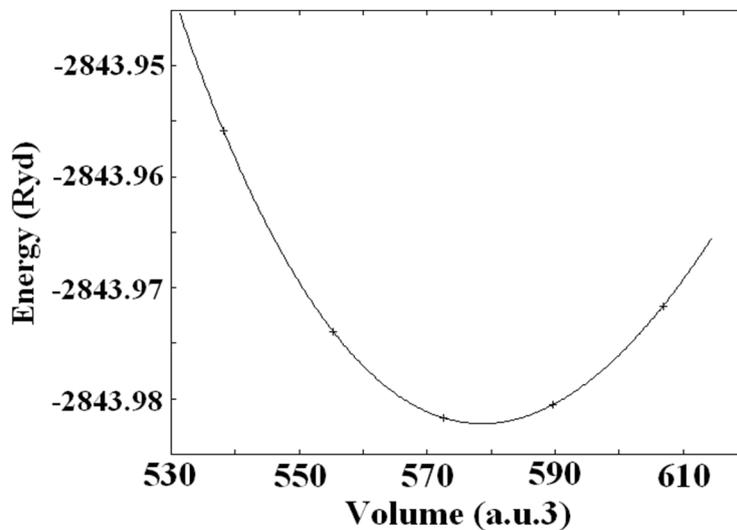


Fig. 1. Total energy versus reduced volume.

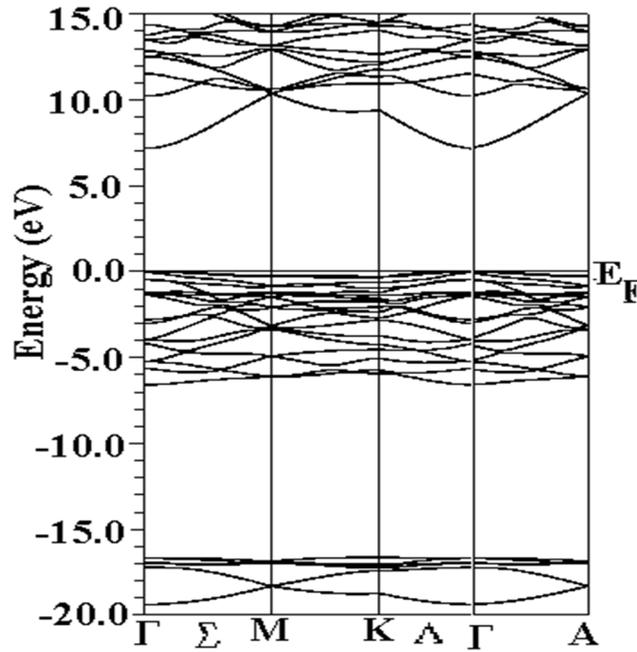


Fig. 2. Band structure of (a)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

The top of the valence bands (VB) is very flat, indicating a very large effective hole mass. On the other hand conduction bands show a large curvature, especially at the  $\Gamma$  point, indicating a good mobility for electron if they only could be excited across the wide band gap. Fig.3 shows the calculated total density of state (DOS) of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The width of the upper valence bands (UVB) are about 6.7 eV. There are many peaks in this region which are the sources of electrons that can do transition to the conduction band. The width of LVB is calculated to be 3.1 eV. Experimental value for LVB width for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is about 6.0 eV and thus LVB difference may be due to correlation effects in these deep-lying semicore-like states. LVB have two peaks that located at around 16.5 eV and 19.0 eV. The width between UVB and LVB is about 9.71.

The region between the upper and lower valence bands is referred to as the ionicity gap and the lack of any electronic states in these regions are a demonstration of the ionicity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Partial DOS of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for Aluminum and Oxygen atoms are shown in Fig. 4 and Fig. 5. The electronic states below the Fermi levels are dominated by oxygen states. The lower valence bands (LVB) are composed of O-2s orbital, and the upper valence bands (UVB) consists mostly of the O-2p orbital, with small mixing from Al-3s, -3p and -3d hybridized orbital. Upper part of UVB corresponds to the O-2p nonbonding states and the lower part is the O-2p bonding states. All states contribute mainly to the conduction band (CB) DOS.

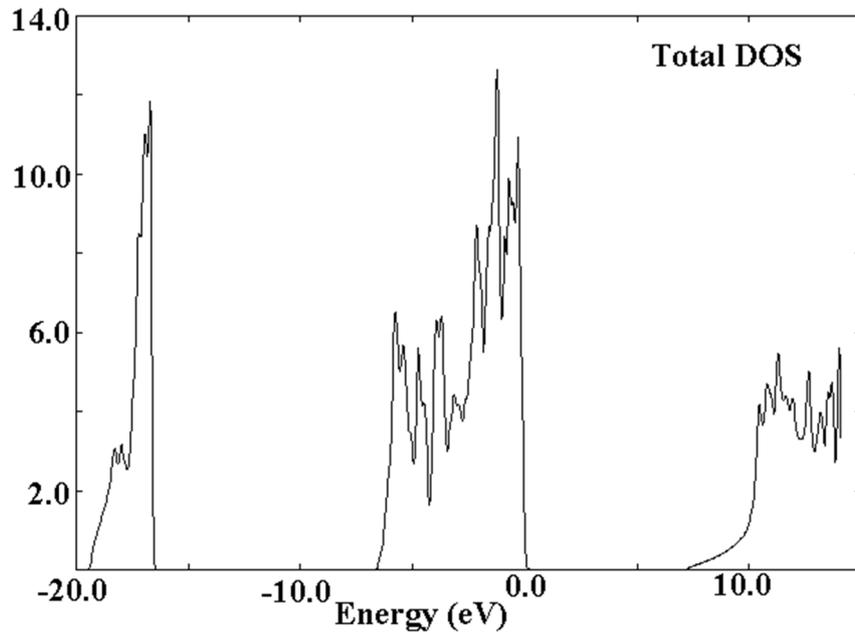


Fig. 3. Total DOS for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

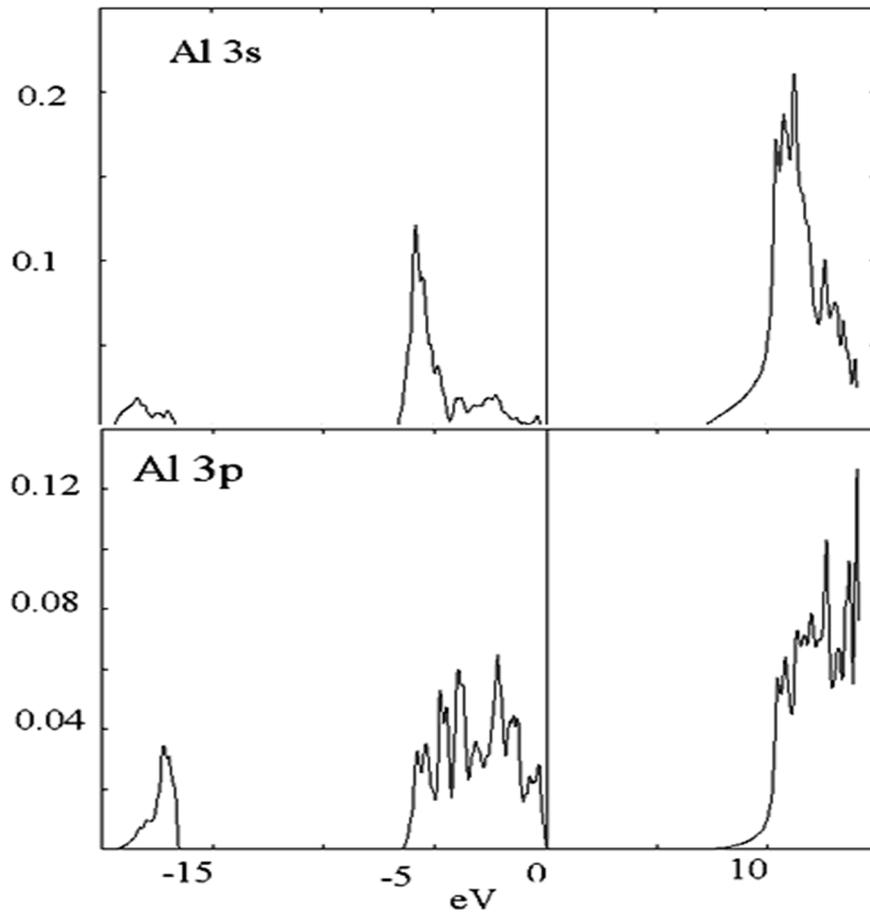


Fig. 4. Partial DOS of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for aluminum atoms.

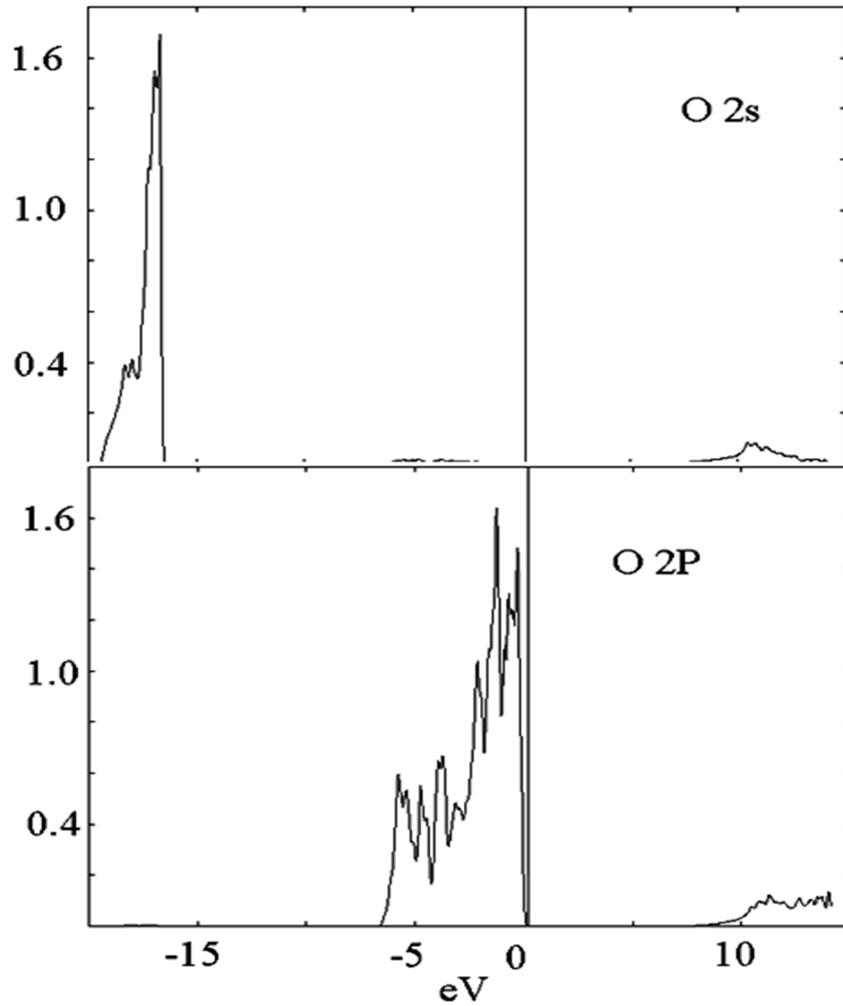
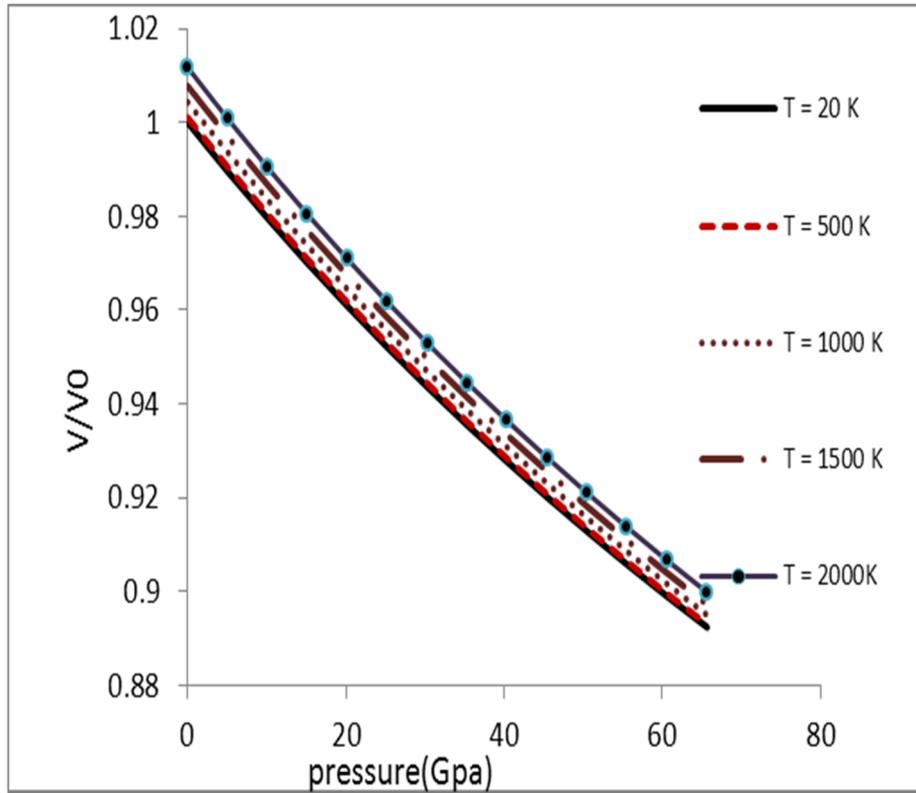


Fig. 5. Partial DOS of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for Oxygen atoms.

The thermal properties of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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 temperatures are shown in Fig. 6.

It is seen that when the pressure increases 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. 6.** The relationship between relative volume and pressure at different temperatures.

In fact the temperature has tendency to increase the lattice parameter and the pressure decreases it and we can note through the variation that the effect of temperature remains dominant. The relationship between bulk modulus  $B$  and pressure at different temperatures are shown in Fig. 7. These results indicate that bulk modulus decreases with temperature at 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. 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. 8. As we can see from Fig. 8, when  $T < 500\text{ K}$ ,  $C_V$  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 tends to the Dulong-petit limit [11] which is common to all solids at high temperatures. At sufficiently low temperature, however, the  $C_V$  is proportional to  $T^3$  [11]. At intermediate temperature, the temperature dependence of  $C_V$  is governed by the details of vibrations of the atoms.

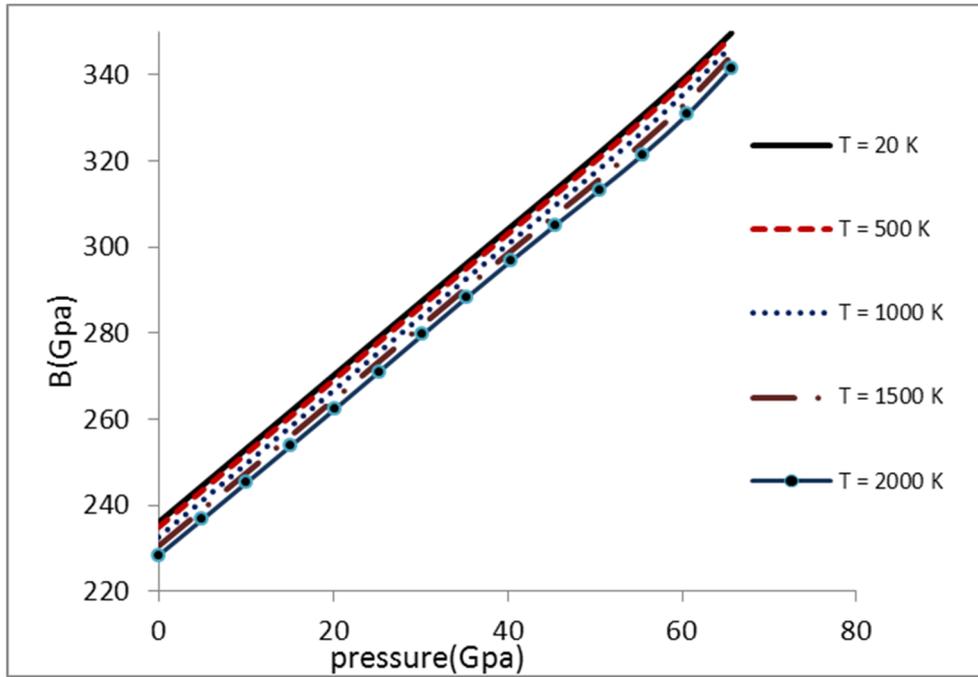


Fig. 7. The relationship between bulk modulus and pressure at different temperatures.

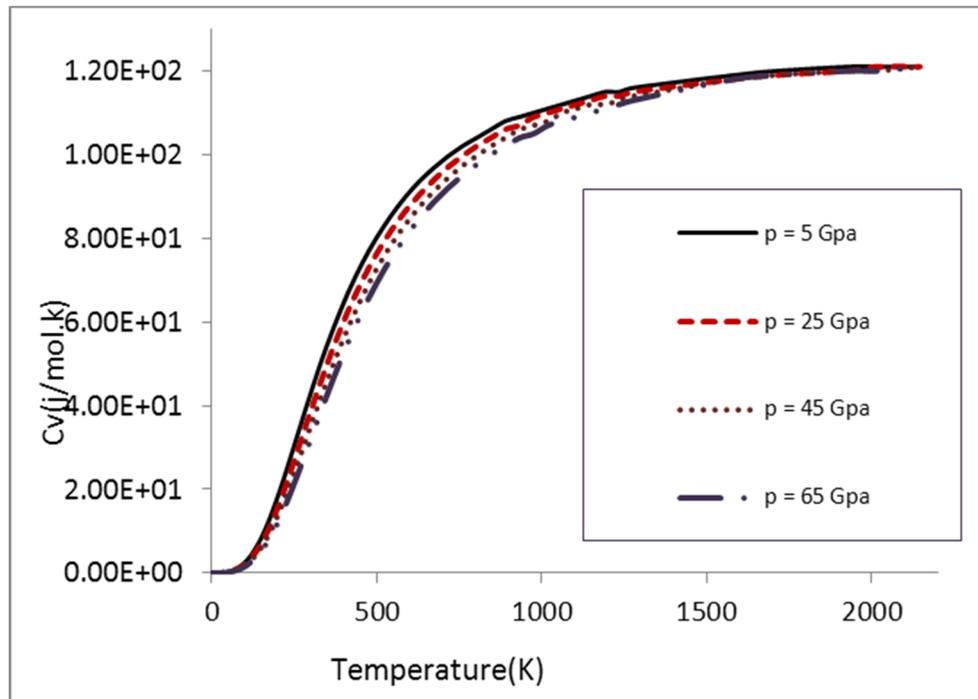


Fig. 8. The relationship between thermal expansion and pressure at different temperatures.

#### 4. CONCLUSION

We have calculated the electronic and thermodynamic properties of supercell of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> using full potential linearized augmented plane wave (FP-LAPW) with generalized gradient approximation (GGA) and quasi-harmonic Debye model in the framework of density functional theory (DFT). Our calculated results show a very excellent agreement with experimental findings. Total density of state calculations show that the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> below the Fermi level, O-2p and O-2s states are dominated. The calculations show a direct band gap 7.2 eV for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. 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 and heat capacity decreases with increasing pressure, the bulk modulus increases with the increase of pressure. Increase the high temperature leads to a smaller adiabatic bulk modulus and a larger heat capacity.

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## ساختار و خواص ترمودینامیکی آلومینا

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### چکیده:

ویژگیهای ترمودینامیکی و ساختار الکترونی ابر سلول  $\alpha\text{-Al}_2\text{O}_3$  با استفاده از محاسبات ابتدا به ساکن در چارچوب نظریه تابعی و پتانسیل کامل امواج خطی تخت بهبود یافته با تقریب شیب گرادیان و مدل شبه هارمونیک دبای مورد بررسی قرار گرفت. مقدار محاسبه شده برای گاف مستقیم انرژی  $\alpha\text{-Al}_2\text{O}_3$  برابر  $7/2$  الکترون ولت شد که به مقدار تجربی بسیار نزدیک است. با استفاده از مدل شبه هارمونیک دبای که در آن آثار فونونی هم دیده شده است، توانستیم به صورت مناسبی پارامترهای ترمودینامیکی شامل حجم نسبی و ظرفیت گرمایی را در محدوده فشار  $0-70$  گیگا پاسکال و دمای  $0-2000$  کلوین به دست آوریم.

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