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Effect of pressure and temperature on CaF_2 and ZnO

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Simple theory based on the knowledge of Equation of State (EOS) has been developed to study the thermodynamic properties of CaF_2 with fluorite type structure and zinc oxide with wurtzite and rocksalt structure under varying conditions of pressure and temperature. The pressure and temperature dependence of V/V_0, thermal expansivity and isothermal bulk modulus, has been computed. The results are compared with the available experimental data. A good agreement obtained between theory and experiment supports the validity of the present approach.

Keywords: Equation of State, High pressure, High temperature, Thermodynamic properties

1 Introduction

The super ionic conductor CaF_2 is the well-known fluorite structure. This is a potentially useful material for lasers and there has been considerable interest to study the the crystal-doped with small amounts of rare earths. Besides the technological importance of such fluorite-type crystals as super ionic conductor, CaF_2 has been used as an internal pressure standard in single-crystal diffraction experiments covering simultaneously high-temperature and high pressure conditions[1]. In addition, CaF_2 also occurs naturally as a mineral and its high-pressure phase may be of geological importance as a component of the lower mantle[2]. Due to such reasons, the properties of CaF_2 are of current interest for experimental and theoretical investigations[3]. Similarly, zinc oxide (ZnO) a wide-band semiconductor and transition metal oxide have a range of technological applications. Moreover, natural ZnO represents an analogy for important constituent's phases of lower mantle. Therefore, a great interest has created to study this compound both theoretically and experimentally. There are continuous efforts to study the high pressure behaviour of ZnO for geophysical as well as fundamental material physics.

Kanchana *et al*[4]. studied the structural and electronic properties of CaF_2 using tight binding linear muffin tin orbital method. These researchers found that CaF_2 undergoes a structural phase transition at the pressure about 9.1 GPa. Pendas *et al*[5]. used first principle pair-wise simulations and quantum mechanical ab-initio method to obtain the static equation of state (EOS) of CaF_2. High pressure-high temperature EOS of CaF_2 has been reported by Angel[6] by combining room temperature single crystal X-ray diffraction (XRD) measurements up to 9 GPa with the thermodynamic data. The effect of pressure on CaF_2 has been studied by Gerward *et al*[7]. by performing synchrotron-radiation XRD. These studies are limited to study the equilibrium behaviour and not to explain the high pressure-high temperature behaviour of CaF_2 as required for geophysical applications. Recently, Sun *et al*[3]. studied the thermodynamic properties of CaF_2 using the constant temperature and pressure shell model molecular dynamics method with effective pair potential.

In addition to the experimental studies[8,9] on ZnO, theoretical efforts have also been made to understand the thermodynamic properties. Many studies on wurtzite-rocksalt phase transition of ZnO have been made using the linear combination of Gaussian-type orbital Hartree-Fock method[10], the linear augmented plane wave method[11], the Hartree-Fock method[12], the full potential linear muffin-till orbital approach[13], the correlated Hartree-Fock perturbed ion models[8]. The structural and dynamical properties of ZnO in wurtzite and rocksalt phase at finite temperature and ambient pressure have been investigated by Seko *et al*[14]. using first principle lattice dynamic calculations within the quasi-harmonic approximation. Sun *et al*[15,16]. predicted the thermodynamic properties of the high pressure rock-salt phase of ZnO using an effective pair potential model. Wu *et al*[17]. studied the structure and thermodynamic properties of ZnO at high pressure and high temperature using pseudo potential and plane wave basis on density functional theory.

The studies on high pressure-high temperature behaviour of solids demonstrate that the thermal expansivity is an important quality for geophysical analysis[18]. Due to the availability of diamond-anvil cells, considerable efforts have been made to determine EOS of minerals at very high pressures but not under high temperatures. Extrapolation may cause errors in the computation of thermodynamic quantities. Although good agreement is, generally, found for thermal expansion coefficient up to a limited range and deviations occur at high temperatures. This may be due to the fact that a volume error of 1% translates into differences up to 20% in thermal expansion coefficients as discussed by Fiquet *et al*[19].

It may also be discussed that potential based methods are tedious, involve heavy computational work based on various approximations. Thus, it may be useful to develop potential independent methods which are simpler in all respects. In the present paper, we therefore, introduce a simple and straightforward method to study CaF_2 with fluorite structure under varying conditions of pressure and temperature, which does involve any potential.

2 Method of Analysis

The theory of EOS has been used and it predicts the properties of solids from atmospheric pressure up to the structural transition pressure by varying the temperatures from room temperature up to the melting temperature. A comparative study demonstrated that the theory is far better than the other relations available in the literature and agrees with the experimental data quite well. The detailed analysis is available[22,23] and the mathematical formulation reads as follows:

$$P=\frac{B_0}{A}\left[\exp A\left(1-\frac{V}{V_0}\right)-1\right]+\alpha_0 B_0\left(T-T_0\right) \quad \ldots (1)$$

or

$$\frac{V}{V_0}]1-\frac{1}{A}\ln\left[1+\frac{A}{B_0}\left\{P-\alpha_0 B_0\left(T-T_0\right)\right\}\right] \quad \ldots (2)$$

where V/V_0 is the relative change in volume, A is the parameter defined as, $\mathrm{A}=\left(\delta_T+1\right)$, B is the bulk modulus, P the pressure and α is defined as:

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (3)$$

Using the definition of α, Eq. (2) gives the following relation:

$$\frac{\alpha}{\alpha_0}=\left[1-\frac{1}{A}\ln\left\{1+\frac{AP}{B_0}-A\alpha_0\left(T-T_0\right)\right\}\right]^{-1} \times\left[1+\frac{AP}{B_0}-A\alpha_0\left(T-T_0\right)\right]^{-1} \quad \ldots (4)$$

or

$$\frac{\alpha}{\alpha_0}=\left(\frac{V_0}{V}\right)\left[\exp A\left(\frac{V}{V_0}-1\right)\right] \quad \ldots (5)$$

Eq. (4) or Eq. (5) may be used to study α/α_0 under varying conditions of P and T. At P=0, Eq. (4) may be rewritten as:

$$\frac{\alpha}{\alpha_0}=\left[1-\frac{1}{A}\ln\left\{1-A\alpha_0\left(T-T_0\right)\right\}\right]^{-1} \times\left[1-A\alpha_0\left(T-T_0\right)\right]^{-1} \quad \ldots (6)$$

The bulk modulus is defined as:

$$B=-V\left(\frac{\partial P}{\partial V}\right)_T \quad \ldots (7)$$

Thus, Eq. (1) and Eq. (7) give the following relation:

$$\frac{B}{B_0}=\left[1-\frac{1}{A}\ln\left\{1+\frac{AP}{B_0}-A\alpha_0\left(T-T_0\right)\right\}\right] \times\left[1+\frac{AP}{B_0}-A\alpha_0\left(T-T_0\right)\right] \quad \ldots (8)$$

At P=0, Eq. (8) may be rewritten as:

$$\frac{B}{B_0}=\left[1-\frac{1}{A}\ln\left\{1-A\alpha_0\left(T-T_0\right)\right\}\right] \times\left[1-A\alpha_0\left(T-T_0\right)\right] \quad \ldots (9)$$

3 Results and Discussion

The input parameters[3,8,9,20] required for the present work are given in Table 1. We used Eq. (1) to compute the values of pressure at different V/V_0 for CaF_2 (fluorite type structure) and ZnO with wurtzite and rocksalt structures at $T=T_0$=300K. The results obtained are reported in Figs 1-3 along with the experimental data[7-9]. It is found that results obtained are found to be in good agreement with the experimental data for the entire range of pressure. This encouraged the authors to extend the use of Eq. (1) for high pressure-high temperature range. The pressure dependence of V/V_0 at different temperatures computed for CaF_2 using Eq. (1) is shown in Fig. 4. It is found that V/V_0 depends on pressure, which is affected by the increase of temperature. This behaviour has been predicted from 300K to 1500K. We have also studied the temperature dependence of V/V_0 at different pressures for CaF_2 using Eq. (1) as shown in Fig. 5. It is found that V/V_0 increases as T increases. Moreover, pressure affects this behaviour, which decreases the values of V/V_0. We further extend this model (Eq. 1) to predict the values of V/V_0 as a function of temperature at different pressures for ZnO with wurtzite and rocksalt structure. The results obtained are shown in Figs 6 and 7. It is noted that

Table 1 — Input parameters used in the present work[3,8,9,20]

Material	B_0 (GPa)	B'_0	α_0 (10^{-5} K^{-1})
CaF_2	81.7	5.22	4.47
ZnO (wurtzite phase)	181.0	4.0	1.69
ZnO (rocksalt phase)	194	4.8	2.27

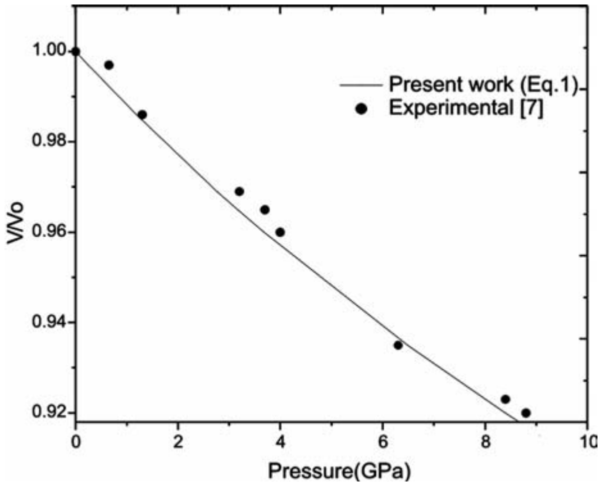

Fig. 1 — Pressure dependence of V/V_0 of CaF_2

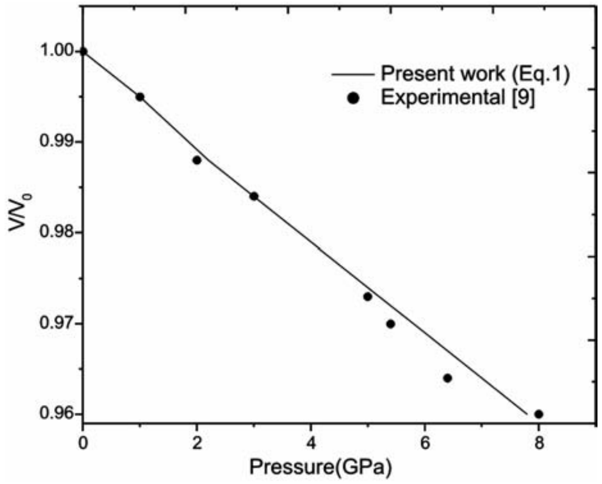

Fig. 2 — Pressure dependence of V/V_0 of ZnO (wurtzite structure)

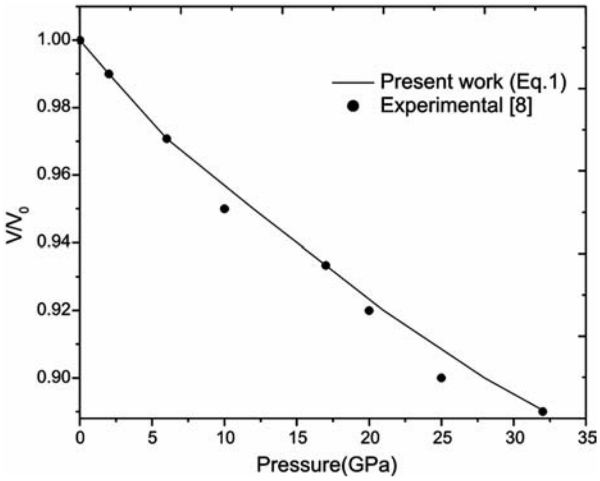

Fig. 3 — Pressure dependence of V/V_0 of ZnO (rocksalt structure)

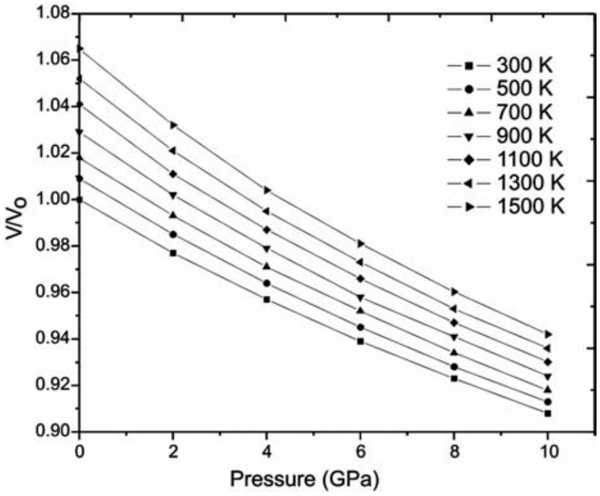

Fig. 4 — Pressure dependence of V/V_0 of CaF_2 using Eq. (1) at different temperatures

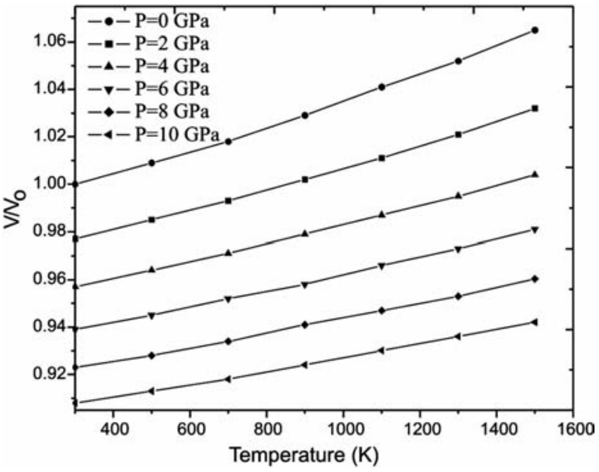

Fig. 5 — Temperature dependence of V/V_0 of CaF_2 using Eq. (1) at different pressures

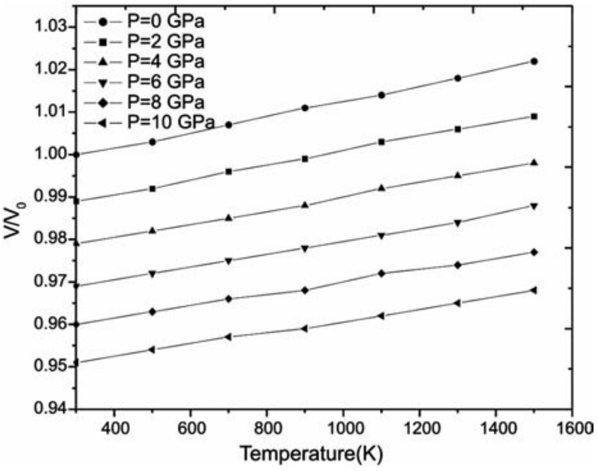

Fig. 6 — Temperature dependence of V/V_0 of ZnO at different pressures (wurtzite structure)

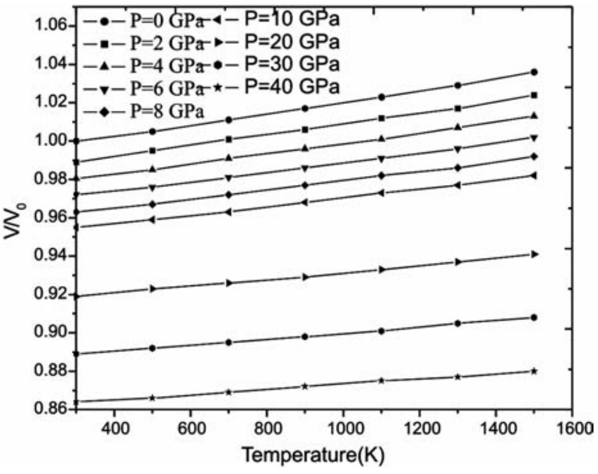

Fig. 7 — Temperature dependence of V/V_0 of ZnO at different pressures (rocksalt structure)

V/V_0 increases with temperature, which is affected by pressure.

Now, we extend the model to study the coefficient of volume thermal expansion and bulk modulus. Eq. (1) gives Eq. (4) for α as a function of pressure and temperature. We used Eq. (4) to predict the values of α as a function of pressure at different temperatures for CaF_2, and ZnO. The results obtained are reported in Figs 8-10. It is found that the value of α decreases with increasing pressure. Moreover, the variation is affected by the application of temperature. The similar trend of variation is found for all three cases considered in the present paper. We have also studied temperature dependence of α at different pressures using Eq. (4) as shown in Figs 11-13.

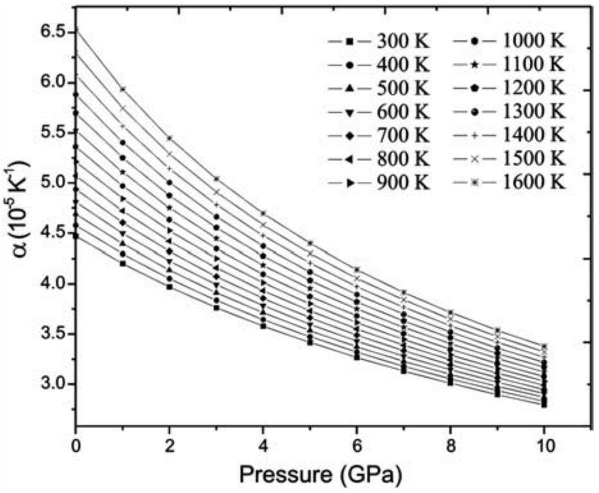

Fig. 8 — Pressure dependence of α at different temperature for CaF_2 using Eq. (4)

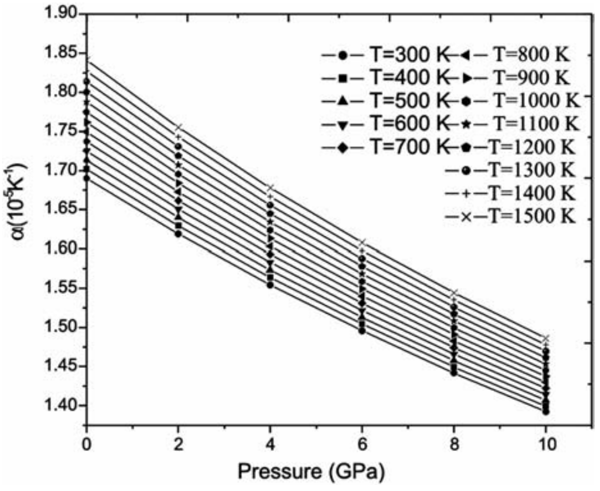

Fig. 9 — Pressure dependence of a at different temperature for ZnO (wurtzite structure) using Eq. (4)

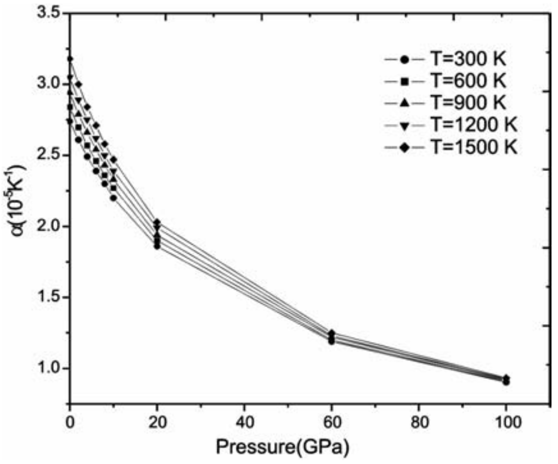

Fig. 10 — Pressure dependence of α at different temperature for ZnO (rocksalt structure) using Eq. (4)

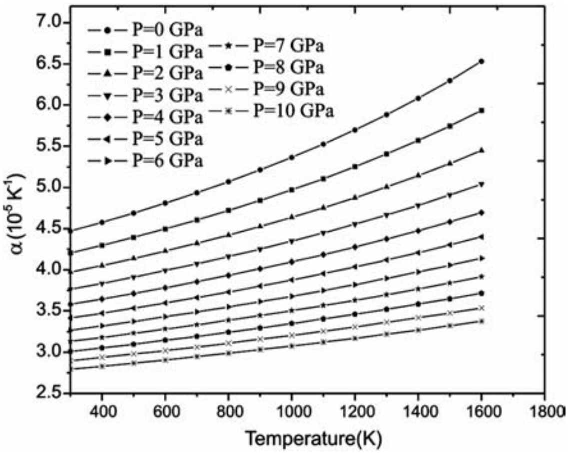

Fig. 11 — Temperature dependence of α at different pressure for CaF_2 using Eq. (4)

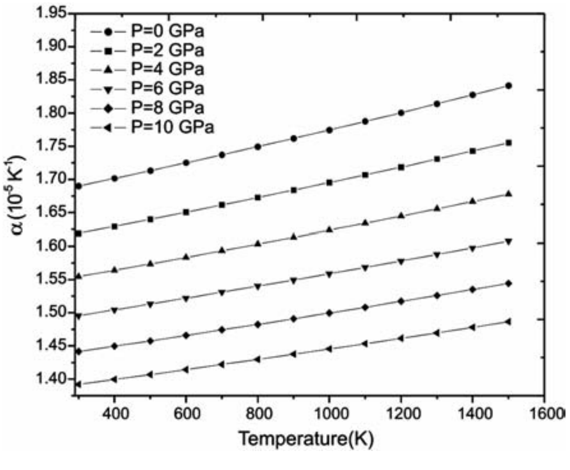

Fig. 12 — Temperature dependence of α at different pressure for ZnO (wurtzite structure) using Eq. (4)

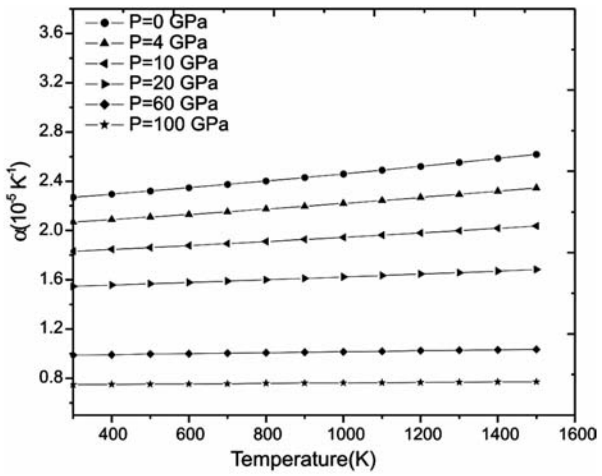

Fig. 13 — emperature dependence of α at different pressure for ZnO (rocksalt structure) using Eq. (4)

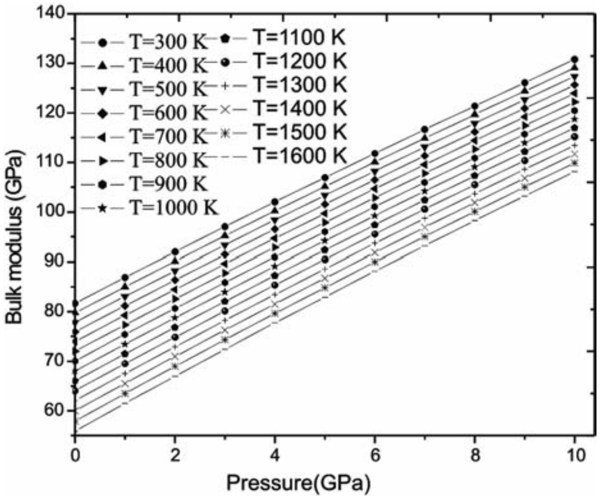

Fig. 14 — Pressure dependence of bulk modulus at different temperature for CaF_2 using Eq. (8)

The model can also be used to obtain the relation for bulk modulus as a function of pressure and temperature in the form of Eq. (8). We used this equation to compute bulk modulus as a function of pressure at different temperatures for CaF_2 and ZnO. The results obtained are shown in Figs 14-16. It is found that bulk modulus increases with pressure, which is affected by the application of temperature. Eq. (8) can also be used to study the temperature dependence of bulk modulus at different pressures. The results obtained are shown in Figs 17-19. The experimental data for temperature dependence of bulk modulus are available for ZnO (rocksalt phase) at room pressure. We have included these results for comparison purposes in Fig. 19. There is a good

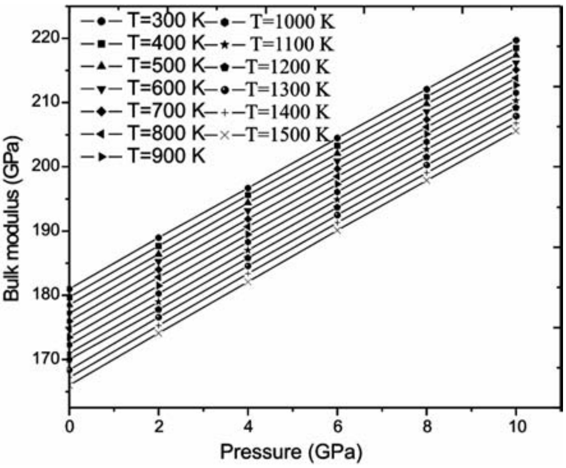

Fig. 15 — Pressure dependence of bulk modulus at different temperature for ZnO (wurtzite structure) using Eq. (9)

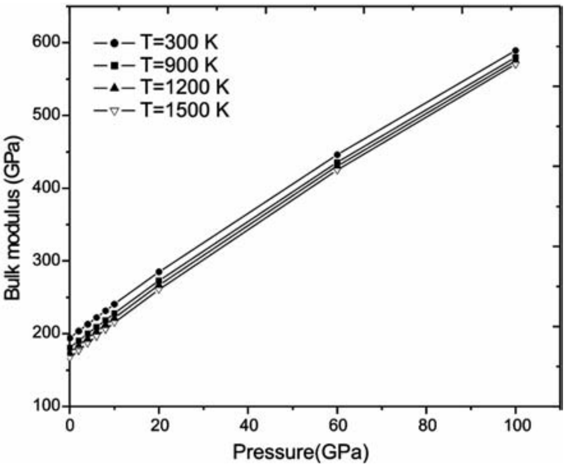

Fig. 16 — Pressure dependence of bulk modulus at different temperature for ZnO (rocksalt structure) using Eq. (9)

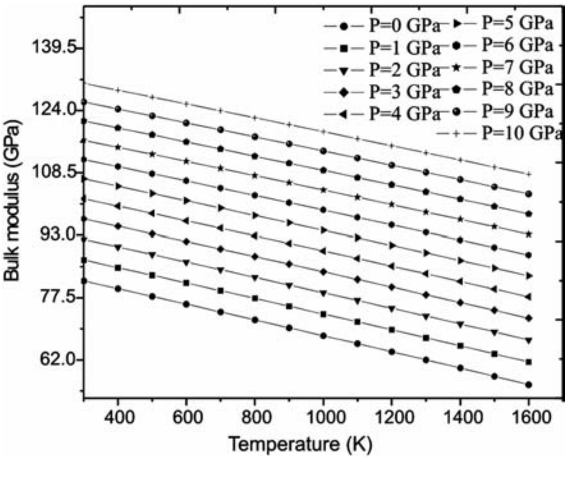

Fig. 17 — Temperature dependence of bulk modulus at different pressure for CaF_2 using Eq. (8)

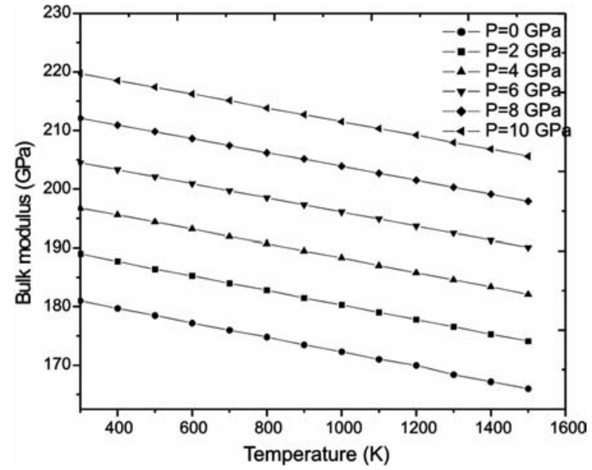

Fig. 18 — Temperature dependence of bulk modulus at different pressure ZnO (wurtzite structure) using Eq. (8)

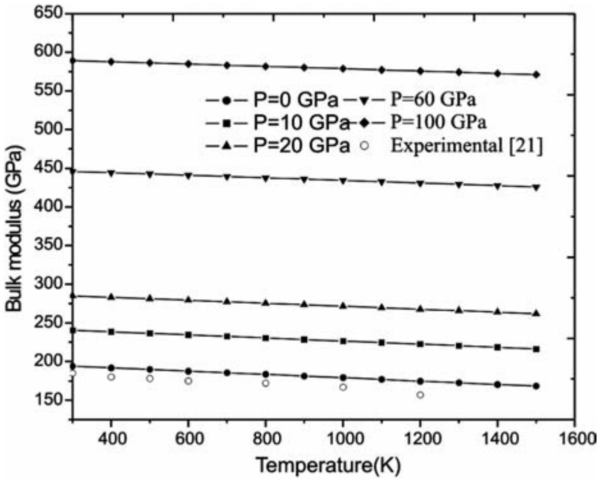

Fig. 19 — Temperature dependence of bulk modulus at different pressure ZnO (rocksalt structure) using Eq. (8)

agreement between theory and experiment[21].This supports the validity of the model used in the present paper. We found that these materials gradually soften with the increase of temperature while they harden with the increase of pressure.

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