Physica B 426 (2013) 13–19

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Phase transition and thermodynamic properties of CaF_2 via first principles

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ARTICLE INFO

Article history:
Received 23 April 2013
Received in revised form
28 May 2013
Accepted 31 May 2013
Available online 7 June 2013

Keywords:
Density functional theory
QHA
Phase transition
CaF_2

ABSTRACT

The structural stabilities, phase transitions and thermodynamic properties of CaF_2 under high pressure and temperature are investigated by first-principles calculations based on the plane-wave pseudopotential density functional theory method within the generalized gradient approximation (GGA). The calculated lattice parameters of CaF_2 under zero pressure and zero temperature are in good agreement with the existing experimental data and other theoretical data. Our results demonstrate that the sequence of the pressure-induced phase transition of CaF_2 is the fluorite structure (Fm3m), $PbCl_2$-type structure (Pnma) and Ni_2In-type structure ($P6_3/mmc$), and the transition pressures are obtained. The temperature-dependent volume and thermodynamic properties of Fm3m phase CaF_2 at 0 GPa are presented. The thermodynamic properties of CaF_2 in Fm3m, Pnma and $P6_3/mmc$ phases at 300 K are predicted using the corrected and uncorrected quasi-harmonic approximation model. The variations of the thermal expansion α and heat capacity C_V with pressure P and temperature T of CaF_2 in the three phases are systematically obtained.

1. Introduction

CaF_2, a well-known face-centered cubic (FCC) ionic crystal, is an important alkaline-earth fluoride. Due to its excellent transmission properties over a wide wavelength range from UV to IR, it has many valuable optical properties for industrial applications [1–4], for example, it has been designated as the lens material for photolithography at wavelengths in the deep ultraviolet region [1,3]. The adsorption of CaF_2 on a semiconductor surface has been the topic of interest due to their possible use in electronic devices [5]. CaF_2 is also proposed as an excellent internal pressure calibration in moderate high-pressure and high-temperature x-ray diffraction experiments [6,7]. The reason why CaF_2 could be chosen as an optical material and pressure calibrant is that it has a cubic crystal structure with perfect optical isotropy [8], and has a good chemical durability [9] and mechanical properties [10–13]. In addition, CaF_2 occurs naturally as a mineral and its high-pressure phase may be geologically important as a component of the lower mantle [14]. Therefore, the structural stabilities and thermodynamic properties of CaF_2 under high pressures and high temperatures are of much theoretical and experimental interest, especially the pressure-induced phase transformations of CaF_2 are widely investigated from experiment to theory [15–25].

At ambient pressure, CaF_2 has a cubic fluorite structure with Fm3m space group. Seifert and Bunsenges [15] reported that CaF_2 can transform from fluorite structure to $PbCl_2$-type structure (Pnma) under pressure ranging from 8 GPa to 10 GPa, and $PbCl_2$-type structure becomes quenchable when CaF_2 is heated to moderate temperatures (about 573 K). Dandekar and Jamieson [16] confirmed experimentally this result by powder diffraction, and found that the high pressure phase revert to fluorite structure under decompression. Afterward, Gerward et al. [17] encountered the transition at about 9.5 GPa by synchrotron radiation, and the high pressure phase was shown to be stable up to 45 GPa at 300 K. Speziale and Duffy [18] found that single crystal of CaF_2 in the $PbCl_2$-type structure, grown at 8.6 GPa and 1100 K in a molten Ca $(OH)_2$ flux [19], is stable up to 49 GPa at room temperature. El'kin et al. [20] also investigated the initial stages of phase transformations in CaF_2 in an ideal hydrostatic pressure at room temperature by means of the strain gauge technique, finding that the phase transition pressure is 8.01 ± 0.01 GPa. Recently, Dorfman et al. [21] researched the behavior of CaF_2 at extreme pressure by angle-dispersive x-ray diffraction experiments, and obtained that CaF_2 transform from $PbCl_2$-type structure (Pnma) to Ni_2In-type structure ($P6_3/mmc$) at pressure range of 63–79 GPa. For nanocrystalline CaF_2, Wang et al. [22] reported that the pressure-induced

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0921-4526/$ - see front matter
http://dx.doi.org/10.1016/j.physb.2013.05.033

Fm3m–Pnma phase transition starts at 14.0 GPa and the orthorhombic phase is stable up to 46.5 GPa.

In theories, many research groups [23–26] studied on the phase transition of CaF_2 under high pressures. For the first Fm3m–Pnma phase transition, their results are consistent with each others. However, the second Pnma–$P6_3/mmc$ phase transition of CaF_2 under pressure is disputed. For examples, Wu et al. [23] reported firstly the phase transition of CaF_2 from $PbCl_2$-type structure (Pnma) to Ni_2In-type structure ($P6_3/mmc$) in the pressure range of 68–72 GPa by using full-potential linearized augmented plane wave (FP-LAPW) method. Cui et al. [25] and Shi et al. [26] predicted that the Pnma–$P6_3/mmc$ phase transition pressures of CaF_2 are 278 GPa and 105 GPa, respectively. Up to date, the temperature dependence of pressure-induced phase transition has not been deliberated.

In this work, we investigate the structural stabilities, phase transitions and thermodynamic properties of CaF_2 under high pressures and high temperatures via the quasi-harmonic approximation, by which we have successfully obtained the structural and thermodynamic properties of BeO [27]. The rest of the paper is organized as follows: The theoretical method is introduced and the computation details are given in Section 2. Some results and discussion are presented in Section 3. Finally, the summary of our main results and conclusions are given in Section 4.

2. Theoretical methods and calculation details

2.1. Total energy electronic structure calculations

In the electronic structure calculations, we employ the plane-wave pseudo-potential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) code [28,29], the generalized gradient approximation (GGA) proposed by Perdew et al. [30] was adopted as the exchange-correlation potentials. The norm-conserving pseudopentials introduced by Hamann et al. [31] is employed for the interactions of the electrons with the ion cores. A plane-wave basis set with energy cutoff of 780 eV is applied. For the Brillouin-zone sampling, we use the Monkhorst-Pack meshs [32] $4\times4\times4$, $2\times4\times2$ and $4\times4\times2$ for Fm3m, Pnma, and $P6_3/mmc$, respectively. These parameters were carefully tested. The convergences of the energy, the maximum ionic force, the maximum ionic displacement, and the maximum stress are 2.0×10^{-5} eV/atom, 0.05 eV/Å, 0.002 Å, and 0.1 GPa.

The calculated total energies as a function of the primitive cell volume for CaF_2 are used to determine the bulk modulus of CaF_2 and its pressure derivative through a third order Birch–Murnaghan equation of states (EOS) [33], in which the total energy and pressure as a function of volume are given as

$$E(V)=E_0+\frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^3B^{'}+\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^2\left[6-4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \tag{1}$$

where E_0 is the total energy, V_0 is the equilibrium volume, B is the bulk modulus at $P=0$ GPa, and B' is the first order derivative of the bulk modulus with respect to pressure.

2.2. Thermodynamic properties of CaF_2

The thermodynamic properties of CaF_2 are investigated by the quasi-harmonic approximation (QHA) with GIBBS2 code [34] described in details below. The non-equilibrium Gibbs function $G^*(V,p,T)$ under a given pressure p and temperature T in the quasi-harmonic approximation takes the form of

$$G^*(V,p,T)=E_{sta}(V)+pV+F^*_{vib}(V,T), \tag{2}$$

where the static energy E_{sta} is the direct result of the electronic structure calculation, in the QHA approach, the vibrational contribution to the Helmholtz energy is given by

$$F^*_{vib}=\int_0^\infty\left[\frac{\hbar\omega}{2}+k_BT\ln(1-e^{-\hbar\omega/k_BT})\right]g(\omega,x)d\omega \tag{3}$$

where $g(\omega, x)$ is the phonon density of state (PDOS), depends on the crystal geometry. Other trivial contributions to the free energy can be ignored for ideal CaF_2 crystal.

The equilibrium entropy (S), Helmholtz free energy (F), Gibbs free energy (G), internal energy (U), constant-volume heat capacity (C_V), and isothermal bulk modulus (B_T) are expressed as

$$S=S(V(p,T),T)=-\left(\frac{\partial F}{\partial T}\right)_V=\sum_j\left[-k_B\ln(1-e^{-\omega_j/k_BT})+\frac{\omega_j}{T}\frac{1}{e^{\omega_j/k_BT}-1}\right] \tag{4}$$

$$C_V=C_V(V(p,T),T)=\left(\frac{\partial U}{\partial T}\right)_V=\sum_j C_{V,j}=\sum_j k_B\left(\frac{\omega_j}{k_BT}\right)^2\frac{e^{-\omega_j/k_BT}}{(e^{-\omega_j/k_BT}-1)^2} \tag{5}$$

$$B_T=-V\left(\frac{\partial p}{\partial V}\right)_T=V\left(\frac{\partial^2F}{\partial V^2}\right)_T \tag{6}$$

Another set of thermal properties depend on the thermodynamic Grüneisen ratio $\gamma_{th}=\alpha B_TV/C_V$, where α is the volumetric thermal expansion coefficient. In the quasi-harmonic approximation, the volume derivative of $-TS$ is used to compute γ_{th}

$$\gamma_{th}=-\frac{V}{C_VT}\left(\frac{\partial(-TS)}{\partial V}\right)_T \tag{7}$$

Once the Grüneisen ratio is known, the thermal expansion coefficient (α), constant-heat capacity (C_p) and adiabatic bulk modulus (B_S) are given as follows:

$$\alpha=-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p=\frac{\gamma_{th}C_V}{VB_T} \tag{8}$$

$$C_p=\left(\frac{\partial H}{\partial T}\right)_p=C_V(1+\gamma_{th}\alpha T) \tag{9}$$

$$B_S=-V\left(\frac{\partial p}{\partial V}\right)_S=V\left(\frac{\partial^2U}{\partial V^2}\right)_S=B_T(1+\gamma_{th}\alpha T) \tag{10}$$

2.3. The empirical energy correction method

The accuracy of the thermodynamic properties calculated by this method is determined by the quality of the underlying energy and vibration-relevant data. In most cases, these data are obtained as a result of first principles calculations, and the main source of uncertainty originated from the exchange-correlation functional. The accuracy of the calculated thermodynamic properties is greatly improved if the empirical energy corrections (EEC) [35] is applied to shift the static $E(V)$ curve in a way that the model reproduces the experimental volume and the bulk modulus at ambient conditions.

In this work, the BPSCAL correction method is used to correct the static energy $E_{sta}(V)$. The BPSCAL correction modifies the static energy according to

$$\widetilde{E}_{sta}(V)=E_{sta}(V_0)+\frac{B_{exp}V_{exp}}{B_0V_0}\left[E_{sta}\left(\frac{VV_0}{V_{exp}}\right)-E_{sta}(V_0)\right] \tag{11}$$

where (V_0, B_0) are calculated static equilibrium properties, (V^0_{exp}, B^0_{exp}) are experimental properties at room conditions, and