



Phase transition of cadmium fluoride under high pressure

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ARTICLE INFO

Article history:

Received 6 July 2011

Accepted 28 September 2011

by Y.E. Lozovik

Available online 2 October 2011

Keywords:

A. Semiconductors

C. Crystal structure and symmetry

D. Phase transitions

E. Synchrotron radiation

ABSTRACT

We investigated the high pressure phases of CdF₂ by a joint theoretical and experimental study. The structural and electronic properties of CdF₂ were extensively explored to high pressure by *ab initio* calculations based on the density functional theory. A structural phase transition from the fluorite-type (*Fm-3m*, $Z = 4$) structure to the cotunnite-type (*Pnma*, $Z = 4$) structure was estimated below 8 GPa, and this phase transition was examined by the high pressure experiments up to 35 GPa at room temperature. Both high pressure angle dispersive X-ray diffraction and Raman spectroscopy experiments provided convincing evidence to verify the phase transition. Our work makes clear pressure-induced phase transitions and structural information of CdF₂ under high pressure.

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1. Introduction

Cadmium fluoride (CdF₂), a highly ionic crystal, has been seriously considered as an optical window, due to its excellent transmission properties without absorption bands over a wide wavelength range from visible to ultraviolet light [1]. In addition, it becomes a semiconductor after doping and heat treatment and is always used as a water insoluble cadmium source in oxygen-sensitive applications, such as metal production. At ambient conditions, CdF₂ crystallizes in the fluorite-type structure (*Fm-3m*, $Z = 4$) [2–4], a common highly coordinated polymorph of binary metal fluorides. Many properties of metal fluorides sharing the fluorite-type structure, such as CaF₂ [5], BaF₂ [6,7], and PbF₂ [8], have been well characterized. There is substantial interest to explore possible metastable high pressure polymorphs with novel structures and properties that may be quenched to ambient conditions for practical applications. For instance, single crystals of fluorite in a cotunnite-type structure (*Pnma*, $Z = 4$) has been experimentally synthesized under high pressure [9], and also theoretically predicted to be a potential optical crystal with a very large energy gap (9 eV) [10]. Actually, the fluoride → cotunnite phase transition is one of the most studied solid–solid phase transitions in the divalent metal fluorides, both from experimental and theoretical points of view. That phase transition has already been predicted for CdF₂ by first-principle calculations [11], but not yet observed experimentally. The main objective of this study is to investigate the possibility of the existence of an orthorhombic cotunnite-type structure at moderate pressure.

Besides, we note that the cotunnite-type structure is known from other fluorides. Therefore, it is not meaningless to first check the predicted phase transition sequence of CdF₂ systematically by the newly developed particle swarm optimization (PSO) technique on crystal structure prediction, which requires only chemical compositions for a given compound to predict stable or metastable structures at given external conditions (e.g., pressure). The relative simplicity of this metal fluoride also makes it well suited for evaluating the differences between theoretical and experimental studies of the structural properties.

In this paper, results on synchrotron X-ray diffraction, Raman spectroscopy and theoretical investigations on the high pressure stability of CdF₂ are reported. A high pressure phase with an orthorhombic cotunnite-type structure was observed at pressures higher than 7 GPa in transition metal fluoride for the first time.

2. Experimental and theoretical details

Studies on powdered CdF₂ (Alfa Products, purity 99.99%) were performed using symmetric diamond anvil cells utilizing 500 μm anvil culets. A T301 stainless steel gasket of 250 μm was preindented to a thickness of about 80 μm by the diamonds. The sample was placed in the 150 μm diameter cavity, and a 4:1 mixture of methanol–ethanol was used as pressure transmitting medium to keep hydrostatic stress. Synchrotron X-ray diffraction measurements were carried out at 4W2 High Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). Pressure was determined by ruby fluorescence [12]. A monochromatic beam (wavelength of 0.6199 Å) was focused on the sample, and data were recorded on a MAR image plate. Diffraction data were processed using the FIT2D data analysis program [13]. Raman spectra were recorded using a Renishaw inVia Raman system.

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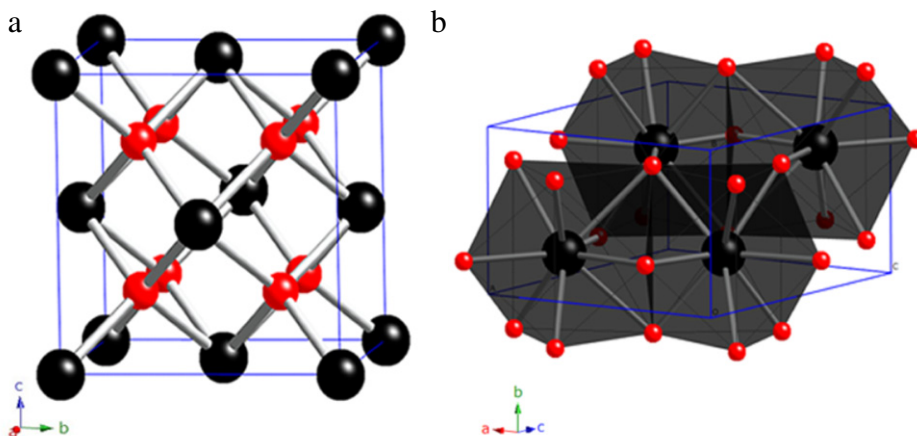


Fig. 1. (Color online). Crystal structures of CdF_2 : (a) Fluorite-type phase at 5 GPa. (b) Cotunnite-type structure at 20 GPa.

Table 1

Calculated equilibrium lattice parameter a_0 , bulk modulus B_0 , and the derivative of bulk modulus B'_0 compared with the experiment data.

	a_0 (Å)	B_0 (GPa)	B'_0
Present GGA	5.493	95	4.04
Present LDA	5.313	127	4.43
Our experiment	5.381	120	
Former experiment ^a	5.364 – 5.395		

^a Ref. [1,4].

The excitation source was the 514.5 nm line of an argon ion laser. The standard silicon line was applied to calibrate the Raman system before the experiment.

We explored the high-pressure phases of CdF_2 by using our newly developed PSO algorithm for crystal structure prediction as implemented in the CALYPSO code [14]. This method has been successful in the prediction of high pressure phases for solids [15–17]. The underlying *ab initio* structural optimizations and the electronic properties are based on the density functional theory (DFT) within both the generalized gradient approximation (GGA) [18] and local density approximation (LDA) as implemented in the VASP code [19]. The all-electron projector-augmented wave (PAW) [20,21] method was adopted with the PAW potentials taken from the VASP library where $5s^24d^{10}$ and $2s^22p^5$ states were used as valence electrons for Cd and F, respectively. The cutoff energy (800 eV) and Monkhorst–Pack meshes were chosen, which gave the sufficient convergence of total energy (within 1 meV/atom). Raman spectra and XRD spectra simulations were performed by Quantum Espresso [22] and Reflex Module of Materials Studio Program, respectively. The phonon calculations were carried out by using a supercell approach [23] as implemented in the PHONOPY code [24].

3. Results and discussion

First, we checked the predicted fluoride \rightarrow cotunnite phase transition of CdF_2 through the PSO algorithm for crystal structure prediction combined with first-principles calculation. Structure evolution with up to six formula units (f.u.) per simulating cell were carried out at 0, 20, and 60 GPa. At ambient pressure, the experimentally observed fluorite-type structure (see Fig. 1(a)) was successfully found immediately in 1 PSO steps. The simulated lattice parameters are in good agreement with previous experimental and theoretical results (see Table 1), indicating the reliability of our calculations. At both 20 and 60 GPa, the cotunnite-type structure is predicted to be the most stable modification. Moreover, we

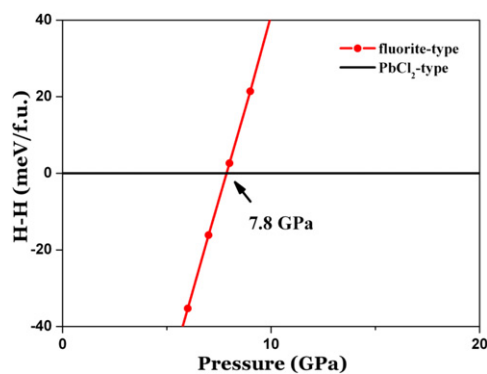


Fig. 2. (Color online). Enthalpy curves (relative to the cotunnite-type structure) as a function of pressure. The exchange–correlation function is used with GGA.

performed the phonon dispersion calculations for the cotunnite-type structure at 20 and 40 GPa. No imaginary phonon frequencies were found in Brillouin Zones to confirm the structural stability of the new structure. In the cotunnite-type structure (Fig. 1(b)), Cd is nine-fold coordinated by F atoms. The $\{\text{CdF}_9\}$ polyhedra are tricapped trigonal prisms. The fact that the coordination number of Cd changes from eight to nine in fluoride \rightarrow cotunnite transition is consistent with the expected general trend of increasing coordination number with pressure. As shown in Fig. 2, detailed calculations of enthalpies within GGA reveal that the phase transition occurs at 7.8 GPa, which is in good agreement with the previous study (9 GPa). The theoretical results strongly indicate the existence of cotunnite modification in CdF_2 at a moderate pressure.

To explore the phase transition, Raman spectra has been measured from ambient pressure to high pressure of approximate 14 GPa. In agreement with previous reports, we find a strong Raman active mode (T_{2g}) at 315 cm^{-1} at ambient condition. The T_{2g} mode shifts to high frequency with the increase of pressure. Then the T_{2g} mode disappears and the new Raman modes appear at 7.2 GPa, revealing a pressure-induced phase transition. We compared the experimental and theoretical Raman spectra at both ambient pressure and high-pressure of 10 GPa, as shown in Fig. 3. Our theoretical result from the fluorite-type structure agrees well with the experimental one [25] at ambient pressure, however, the experimental spectrum at 10 GPa is not good enough to identify the high-pressure phase as the cotunnite-type structure. The relatively poor experimental spectrum is attributed to the laser passing through the diamonds under high-pressure. In the process of decompression, the T_{2g} mode in the fluorite-type structure does not appear until 0.6 GPa.

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