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Structural stability of Zn_3N_2 under high pressure

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ABSTRACT

In situ high-pressure energy dispersive X-ray diffraction experiment on Zn_3N_2 has been performed by using a diamond anvil cell instrument with synchrotron radiation at room temperature. The results showed that the structure of Zn_3N_2 is stable in the experimental pressure range up to 25.2 GPa. According to the Birch – Murnaghan equation of state determined from the relationship of unit cell volume and pressure, assuming $B'_0=4$, the bulk modulus $B_0=228(2)$ GPa has been obtained.

1. Introduction

Zn_3N_2, which is black in color, was first synthesized by Juza and Hahn in 1940 [1]. In 1993, Kuriyama et al. obtained the polycrystalline Zn_3N_2 films through the direct reaction between Zn and NH_3 which were evaporated onto quartz substrates [2]. At room temperature, Zn_3N_2 film shows a high electron mobility of about $100\,cm^2/(V\,s)$ [3]. It was determined to be an n-type semiconductor, with a direct gap of 1.23 eV. Zn_3N_2 film can be used to produce p-type ZnO:N [4]. Due to the possible application prospect, Zn_3N_2 has attracted more and more attention since 2000. Recently, several groups obtained Zn_3N_2 films through different methods, including shielded reactive vacuum arc deposition [5,6], molecular-beam epitaxy [7], reactive radio-frequency (rf) magnetron sputtering [8–11], etc.

Zn_3N_2 is isostructural with Mg_3N_2, Ca_3N_2, and Cd_3N_2, which adopt the anti-bixbyite structure [12]. The space group is *Ia*-3, and lattice parameter a is equal to 9.7691(1) Å. Zn_3N_2 is a derivative of the CaF_2 structure, where N and Zn atoms occupy the Ca positions and three-fourth of the F positions, respectively. In this cubic structure, Zn atoms occupy the tetrahedral sites of an approximately cubic close packed array of N atoms. The close-grained structure indicates the possible small compress coefficient of Zn_3N_2. Generally, the lattice mismatch as well as the different thermal expansion coefficients between thin film and substrate always lead to strain. Many nitrides undergo the crystal structure phase transition under high pressure, such as Li_3N, Cu_3N, Mg_3N_2, Al_3N [13–16]. Considering the application prospect of film materials, it is important to learn the pressure effect on the structure and consequently physical behaviors of Zn_3N_2. In this paper, we report the study of high-pressure structural stability of Zn_3N_2 based on the diamond anvil cell (DAC) technique by using *in situ* high-pressure energy dispersive X-ray diffraction with synchrotron radiation.

2. Experiments

The *in situ* high-pressure X-ray energy dispersive diffraction experiment on Zn_3N_2 was carried out at room temperature in a diamond anvil cell at Beijing Synchrotron Radiation Facility (BSRF). The culet of diamond is 500 μm in diameter and the hole in a T301 stainless steel gasket is 250 μm in diameter. The powder sample is loaded into the hole in the gasket. The pressure on the sample was measured by using the ruby fluorescence method. The spot size of the focused X-ray beam was $25\times30\,\mu m$ and the storage ring was operated at 2.2 GeV and 60–100 mA. In this experiment, the relation of energy of photon and channel was $E=0.5444+0.00885\,chn$. The diffraction angle θ is fixed to 10°.

3. Results and discussions

Fig. 1 shows the spectra of X-ray energy dispersive diffraction results of Zn_3N_2 under various pressures. The diffraction data are collected in the pressure range of 0–25.2 GPa. There are the diffraction peaks of Zn_3N_2 and fluorescence peaks of Zn in the X-ray diffraction patterns. There also is an escaping peak

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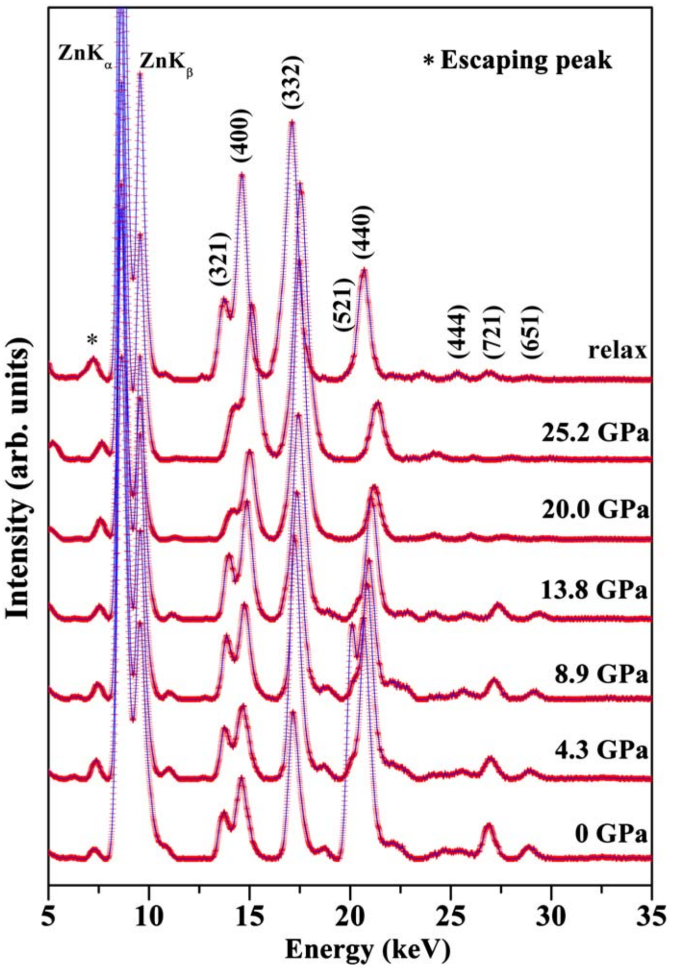

Fig. 1. Spectra of energy dispersive X-ray diffraction pattern of Zn_3N_2 under various pressures.

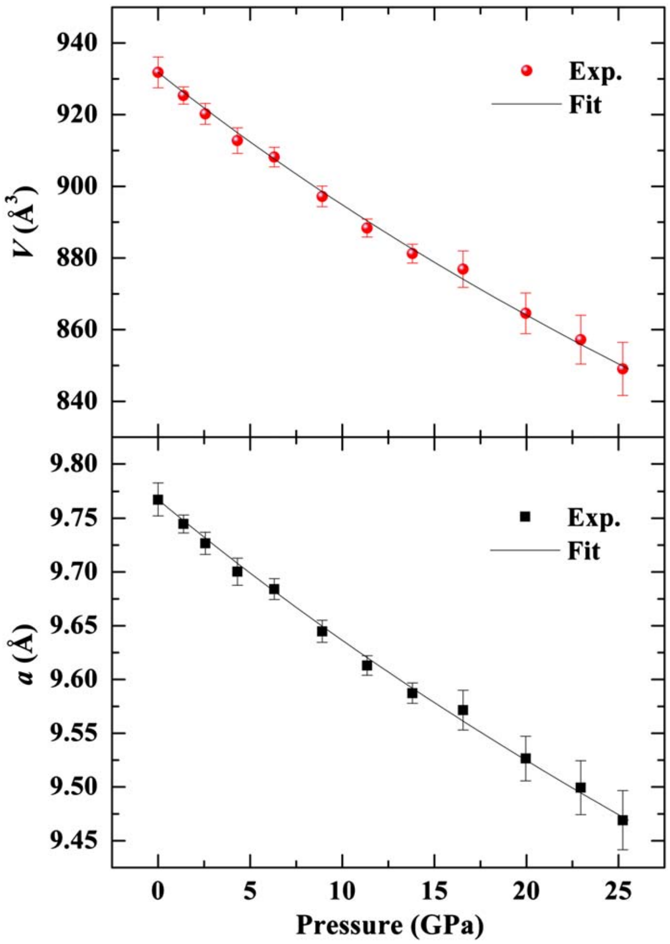

Fig. 2. Pressure dependences of (a) unit cell volume and (b) lattice parameter of Zn_3N_2 at room temperature.

indicated with asterisk, due to the high rank of the peak (3 3 2) of the sample. The indexes of sample peaks are denoted in the XRD patterns. All the Gaussian-type diffraction peaks shift towards the high-energy direction with increasing pressure and return to the original sites when the pressure releases to ambient. From the XRD patterns, the structural phase transition cannot be found in this experimental pressure range because no splitting or merging peaks are observed. Thus the peak fitting, indexing, and cell parameter refining are based on the primal structure of Zn_3N_2 with the space group I*a*-3.

According to the Bragg formula

$$E(\mathrm{keV}) \times d(\AA) = 6.19925/\sin\theta, \tag{1}$$

we got the *d* spacings of Zn_3N_2 under various pressures. The lattice parameter and unit cell volume (V) under different pressures are obtained through the *d* spacings. Fig. 2 shows the pressure dependences of unit cell volume and lattice parameter for Zn_3N_2, where the bold line is the fit to data. In the experimental error range, V is decreasing with the increasing pressure. Using the Birch – Murnaghan equation of state (EOS) [17]

$$P(\mathrm{GPa}) = \frac{3}{2} \times B_0 \times \left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right] \times \left\{1 - \left(3 - \frac{3}{4} \times B'_0\right) \times \left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\} \tag{2}$$

we obtained, assuming the first-order derivative to be $B'_0=4$, the ambient pressure bulk modulus $B_0=228(2)$ GPa for Zn_3N_2. The value of B_0 is larger than those of most nitrides, so Zn_3N_2 is a stiff material.

The schematic view of Zn_3N_2, with the anti-bixbyite structure, is shown in Fig. 3(a). There are four N atoms around one Zn atom, which forms a ZnN_4 tetrahedron. For the N atom, the surrounding six Zn atoms combine to one ''NZn_6 octahedron'', which is not a strict octahedron due to the smaller ion radius of Zn ion than that of N ion. The details of ZnN_4 tetrahedron and ''NZn_6 octahedron'' are shown in Fig. 3(b). According to Shannon Table [18], the ratio of the radius of Zn^{2+} ion to that of N^{3-} ion is equal to 0.411, being close to the ratio limit of 0.414 to form tetrahedron. So it is difficult to compress the ZnN_4 tetrahedron, which induces that Zn_3N_2 has a large ambient pressure bulk modulus.

4. Conclusions

In summary, the structural stability of Zn_3N_2 under high pressure has been investigated through *in situ* high-pressure X-ray energy dispersive diffraction experiments. There is no structural transition in the experimental pressure range. The big bulk modulus B_0 of 228(2) GPa indicates that Zn_3N_2 is a stiff nitride.

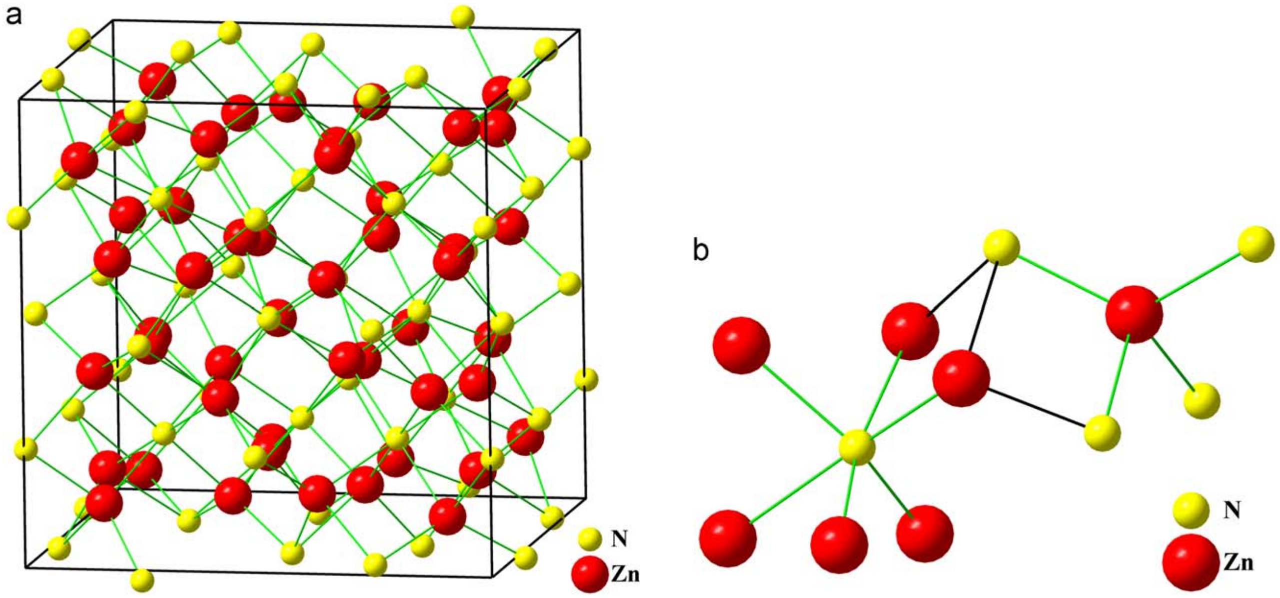

Fig. 3. (a) The schematic views of Zn_3N_2. The unit cells are outlined. (b) The details of ZnN_4 tetrahedron and "NZn_6 octahedron".

Acknowledgments

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