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Abstract
An *in situ* energy dispersive x-ray diffraction study on nanocrystalline ZnS was
carried out under high pressure up to 30.8 GPa by using a diamond anvil cell.
The phase transition from the wurtzite to the zinc-blende structure occurred
at 11.5 GPa, and another obvious transition to a new phase with rock-salt
structure also appeared at 16.0 GPa—which was higher than the value for the
bulk material. The bulk modulus and the pressure derivative of nanocrystalline
ZnS were derived by fitting the Birch–Murnaghan equation. The resulting
modulus was higher than that of the corresponding bulk material, indicating
that the nanomaterial has higher hardness than the bulk material.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Compared with conventional bulk materials, nanomaterials exhibit many promising
characteristics as regards strength, and thermal, electronic and magnetic properties, especially
surface features and energy band structure. Many characteristics of nanomaterials are related
to surface and volume effects. The property of structural transition under pressure of
nanomaterials has become a subject of intense interest and has been widely investigated in
the high-pressure research field.

ZnS is a semiconductor with a wide energy band gap among II–VI compound materials,
and has an important application in preparing film components for illumination. The phase
transition under high pressure of bulk ZnS has been studied systematically in recent years [1–
10]. According to the results, ZnS possesses two structures: wurtzite ($P6_3mc$; $Z = 2$) and
zinc-blende ($F\bar{4}3m$; $Z = 2$) structure at ambient conditions. They can transform into rock-salt
structure under high pressure and, furthermore, into a distorted version of rock-salt structure.

Up to now, less research on phase transitions of nanocrystalline ZnS has been carried out, especially under higher pressure.

In this work, in order to compare with bulk material, the pressure-induced structure transition of nanocrystalline ZnS was investigated by using *in situ* synchrotron radiation energy dispersive x-ray diffraction (EDXD) via a diamond anvil cell under high pressure (up to 30.8 GPa) at room temperature.

2. Experimental details

With an average size of 6 nm determined by high-resolution transmission electron microscopy (HRTEM)—see figure 2—sol–gel nanocrystalline ZnS, which was doped with 1 wt% Eu, was employed in the present study. With the storage ring operating at 2.2 GeV and the current intensity being 95–70 mA, the EDXD experiment was carried out in Beijing Synchrotron Radiation Laboratory (BSRL). A mixture of methanol/ethanol 4:1 was used as the pressure medium, and fine Ag powder mixed with the sample served as the internal pressure calibrant; the sample was confined in the gasket hole (L605 stainless steel) between the opposing anvils of a diamond cell. The spectra were recorded at room temperature with the diffraction angle θ between the direct beam and the detector set as $9.3251°$. The pressure was determined from the (111) and (200) peaks of Ag along with the established equation of state, and the interplanar spacing d was determined via

$$Ed = 6.199\,27/\sin\theta \ (\text{keV Å}).$$

3. Results and discussion

Typical EDXD patterns under different pressures are illustrated in figure 1, including two peaks of Ag(111) and Ag(200). With pressure increasing, all peaks behave normally below 11.5 GPa and shift to the higher-energy region. At 11.5 GPa, an abnormal change that corresponded to the (110) diffraction peak was observed, i.e., the peak (110) of the wurtzite phase vanished and a new one appeared, suggesting that a transition from wurtzite to zinc-blende structure had occurred at this pressure. With the pressure increasing to 16.0 GPa, the (002) diffraction peak of wurtzite disappeared, and simultaneously a new one appeared, indicating the presence of another structural transition. According to the indexing results indicating that the new diffraction peak corresponds to the (200) line of rock-salt structure, we considered this new structure to be the rock-salt phase.

The volume evolution was deduced according to the crystal face spacing measured over the whole pressure range. Figure 3 shows the compaction ratio of the sample at different pressures. The appearance of the turning point at 11.5 GPa shows a change of volume, which indicates a phase transition from wurtzite to zinc-blende structure. The abrupt change of volume compaction ratio indicates a new structural transition when the pressure is 16.0 GPa. Previous study on bulk ZnS showed that the pressure of the transition to the rock-salt phase is about 12 GPa. However, the transition pressure is higher in our case. We think that this is due to the high surface energy of the nanocrystalline form. Compared to bulk materials, nanoparticles are characterized by small particle size, high surface energy, and considerable number of surface atoms. With the grain size decreasing, the surface tension depresses too. In the present study, samples with an average particle size of 4 nm were used; a higher pressure is necessary to overcome the extra surface energy. Thus the pressure for the structural transition is raised. According to the volume–pressure experimental data, the Birch–Murnaghan equation
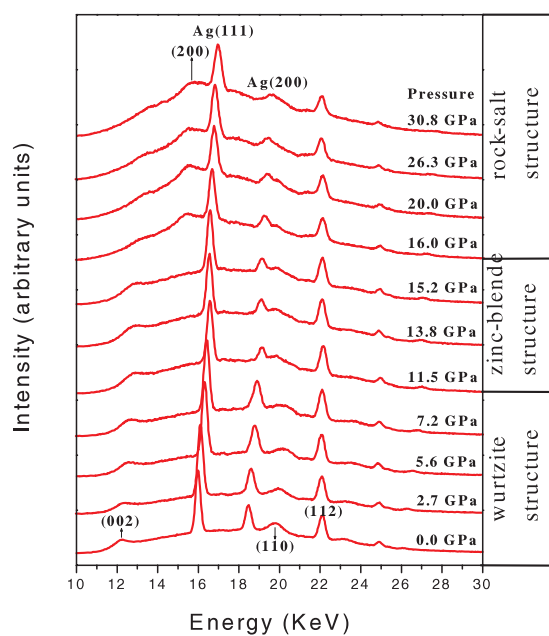
Figure 1. The EDXD pattern of nanocrystalline zinc sulphide under different pressure.
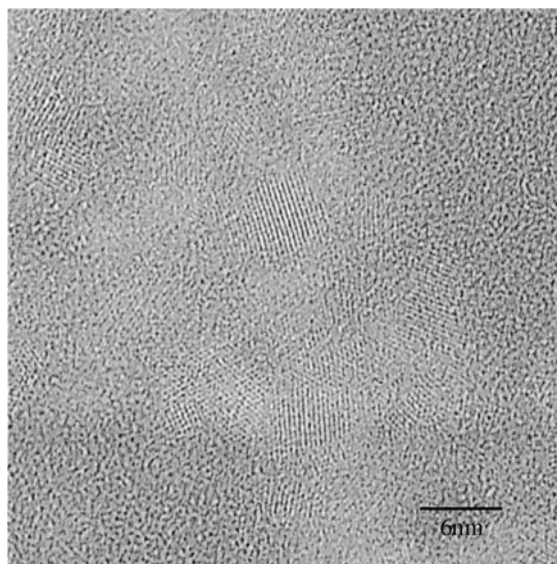

Figure 2. A HRTEM image of ZnS.

of state for ZnS is fitted as follows:

$$P \text{ (GPa)} = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{7/3} - \left(\frac{V}{V_0} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4}(B_0' - 4) \left[\left(\frac{V}{V_0} \right)^{2/3} - 1 \right] \right\}.$$

The values of the zero-pressure bulk modules (B_0) and its pressure derivative (B_0') were also determined as 96 and 4.86 GPa respectively. Compared with values for bulk ZnS ($B_0 = 80.1$ GPa [1], $B_0 = 75.8$ GPa [4]), the bulk modulus that we obtained is large.
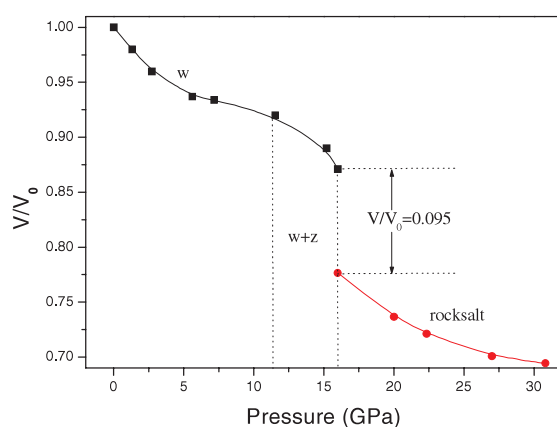
Figure 3. Comparison of the calculated states of ZnS over the pressure range of 0–30.8 GPa.

4. Conclusions

A phase transition from wurtzite to zinc-blende structure occurs at 11.5 GPa. With pressure increasing to 16.0 GPa, another phase transition appears at a higher pressure of 16.0 GPa, indicating a phase transition to the rock-salt structure. The higher phase transition pressure is related to the characteristics of the nanocrystalline form.

By fitting the Birch–Murnaghan equation, the bulk modulus B_0 (96 GPa) and the pressure derivative B_0' (4.86)—which are higher than those of the corresponding bulk material—are derived; this should also be correlated with the characteristics of the nanocrystalline form.

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