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ScienceDirect
Current Applied Physics 7 (2007) 135–138
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

Structure of nanocrystalline ZnO up to 85 GPa ☆

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Received 4 January 2005; accepted 22 February 2006
Available online 11 May 2006

Abstract

The structure of nanocrystalline and bulk polycrystalline ZnO were examined up to 85 GPa and 50 GPa, respectively using synchrotron X-rays and diamond anvil cells at ambient conditions. The transition from the wurtzite to the rock salt phase in the nano-ZnO takes place at 10.5 GPa; this transition pressure is 1.5 GPa higher than in bulk ZnO. A large volume collapse of about 17.5% is observed during the transition in both systems. The rocksalt phase is stable and no structural transitions are observed for both compounds at higher pressures up to the experimental limit. On decompression the rocksalt phase is found to co-exist with the wurtzite phase at ambient conditions for the nano-ZnO.

PACS: 81.40.Vw; 64.70.Nd; 61.50.Ks

Keywords: High pressure; X-ray diffraction; Structural phase transition; Equation of state; ZnO

1. Introduction

ZnO is an important material widely used in various applications ranging from electronic to medical, such as optoelectronic devices, piezoelectronic transducers, chemical sensors, thyristors, cosmetics and pharmaceutical lotions [1–4]. Because of quantum confinement effects in the semiconducting nanocrystals, one may expect superior optical properties for nanocrystals than bulk. ZnO nanocrystals or quantum dots (QD) have potential applications in UV lasers, solid state spinel batteries and fabricating nanolasers [5–7]. Nano-ZnO has a thermal stabilizing effect on low density polyethylene [8]. Further, ZnO nanowires have high hydrogen storage capacity under pressure [9].

The growing importance of this material has opened up several synthetic procedures for fabricating size specific nanostructures such as nanowires, needles and rods. Grain size in these structures significantly influences their physical and chemical properties; for example, the sensitivities of ZnO-gas sensors increases with reduction in grain size. The structures of nanocrystals also depend on grain size, and the properties are reported to be very different from the bulk [10,11]. In order to understand the structural behaviour of nano-ZnO under pressure and the stability of different high pressure phases, we performed X-ray diffraction experiments using diamond anvil cell and synchrotron radiation up to 85 GPa. To compare the bulk properties, we performed high pressure experiments on bulk ZnO simultaneously up to 50 GPa.

2. Experimental details

High purity nanocrystalline ZnO (99.99%) with a grain size 50 nm and bulk polycrystalline ZnO (4 N purity) supplied by Sigma–Aldrich were used in these high pressure experiments. Rhenium gaskets of 200-μm thickness were pre-indented to 25–30 μm in a Mao-Bell type diamond anvil cell, and a gasket hole of 135-μm diameter was drilled

☆ Based on presentation at the Optical Probes of Conjugated Polymers and Biosystems (OP2005), Bangalore India, January 4–8, 2005.

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doi:10.1016/j.cap.2006.02.009

in the indentations. The diamonds typically had 350-μm culets. The samples were loaded with a silicone oil (Polydimethyl-siloxane) pressure transmitting medium with small ruby grains [12]. X-ray diffraction (XRD) experiments were performed using synchrotron X-rays at the HPCAT high resolution powder diffraction beam line, ID-16-B, at the advanced photon source. The incident wavelength was 0.36798 Å, and the typical beam size at the sample was 20×20 μm. The XRD patterns were collected using a MAR image plate camera at 100×100 μm^2 pixel resolution for 10–20 s. Pressures were measured using the conventional ruby fluorescence method. The images were integrated using the FIT2D program [13], and structural refinements were carried out by the Rietveld method using the RIETICA (LHPM) package [14].

3. Results and discussion

3.1. Bulk ZnO

Under normal conditions, ZnO crystallizes in the wurtzite structure with $P6_3mc$ space group. The Zn atoms are crystallographically located at 1/3, 2/3, 0, and O atoms are at 1/3, 2/3, z. A number of diffraction patterns were collected by increasing the pressure gradually up to 50 GPa, and the wurtzite phase was found to transform to the rocksalt phase at 8.9 GPa. Both the wurtzite and rocksalt phases co-existed up to 11.5 GPa. The wurtzite–rocksalt transition pressure obtained in our experiment closely agrees with the previously reported values in the literature [15–17]. The rocksalt phase was found to be stable up to 50 GPa, and no further structural transitions were observed. The variation of d values with pressure for bulk ZnO is shown in Fig. 1.

The pressure volume data were fitted with the third order Birch–Murnaghan equation of state with $B_0' = 4$. The compressive parameters are given Table 1.

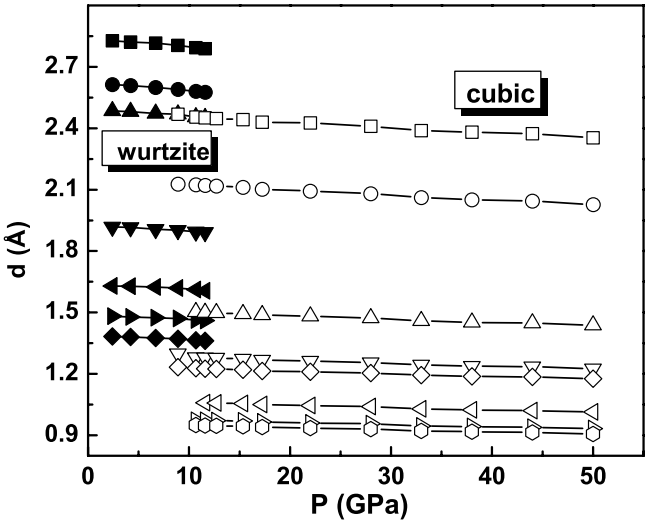

Fig. 1. Variation of d values for the wurzite and cubic phases with pressure for bulk ZnO.

Table 1
Experimental compressive parameters for ZnO

	ZnO (nano)		ZnO (bulk)	
	Wurtzite	Rocksalt	Wurtzite	Rocksalt
B_0 (GPa)	151(6)	221(12)	154(8)	229(8)
V_0 (Å^3)	24.009(6)	19.565(1)	24.009(5)	19.117(2)
P_T (GPa)	–	10.5	–	8.9

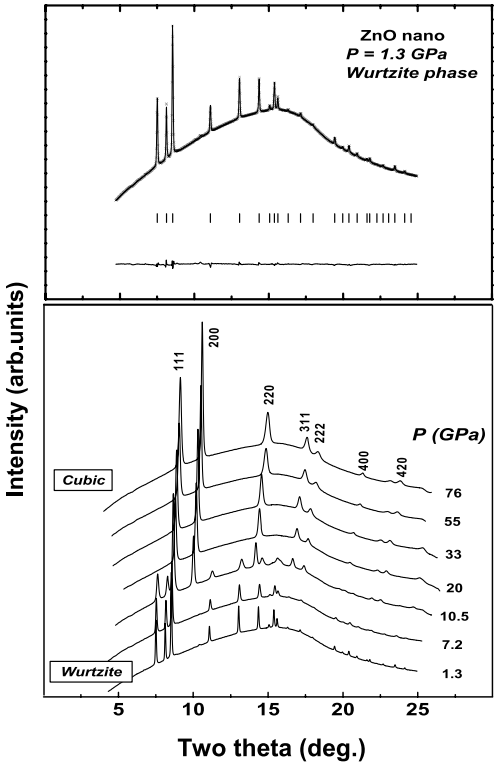

Fig. 2. X-ray diffraction patterns collected at different pressures for the nano-ZnO. The top panel shows the Rietveld refinement at 1.3 GPa for the wurtzite phase. The solid line is the calculated spectrum, and the symbols represent the observed data. The difference and phase markers are shown below.

3.2. Nano-ZnO

Representative X-ray diffraction patterns at different pressures for the nano-ZnO are shown in the Fig. 2. The transformation from the wurtzite phase to the rocksalt phase began around 10.5 GPa with both phases co-existing up to 13 GPa. While the bulk modulii obtained for the wurtzite and rocksalt phases by fitting the PV data (Fig. 3) were similar to those of bulk ZnO as in Table 1, the transition pressure were 1.6 GPa higher than for bulk ZnO.

The difference of transition pressure is attributed to micro strains associated with the small grains. A similar grain size effect has been reported in 12-nm, 18-nm and 30-nm ZnO. The transition pressure for 12-nm ZnO is as much as 5.6 GPa greater than that of bulk ZnO. Our results for 50-nm nano-ZnO indicate clearly the inverse relation of the transition pressure to grain size.