

Stability of rocksalt phase of zinc oxide under strong compression: Synchrotron x-ray diffraction experiments and first-principles calculation studies

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The stability of rocksalt (*B1*) phase of ZnO under high pressure up to 2 Mbars was studied using angular dispersive x-ray diffraction at room temperature and compared to the structurally analogous CdO where both theoretical and experimental results are available. First-principles total energy calculations predict the *B1*-to-*B2* (CsCl-type) phase transition in ZnO and CdO to occur at 261 and 83 GPa, respectively. The bulk moduli, K_0 , of the *B1* structure of ZnO were measured and the possible high pressure CsCl-type (*B2*) structure was looked for. The potential application of ZnO as an internal pressure marker in x-ray diffraction study at the megabar range is proposed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357644]

I. INTRODUCTION

Zinc oxide (mineral name: zincite) has many industrial applications such as in the production of adhesive tapes, automobile tires, ceramics, glass, varistors, etc. As a result of its advantageous electronic properties, it is rapidly gaining the credibility for applications in optoelectronic devices, such as UV light emitters, chemical and gas sensors, and spin functional devices.¹⁻³ At ambient conditions, ZnO has the wurtzite-type (*B4*) structure (space group $P6_3mc$), in which the Zn (or O) atoms are tetrahedrally coordinated to four O (or Zn) atoms. Upon compression above 9.0 GPa, a phase transition to rocksalt-type (*B1*) structure (space group $Fm\bar{3}m$), with an increase in coordination number from 4 to 6, was found in 1962.⁴ Many *in situ* high pressure techniques, such as energy dispersive x-ray diffraction,⁵⁻⁹ extended x-ray-absorption fine structure (EXAFS) and x-ray-absorption near-edge structure (XANES) (Ref. 9) at various synchrotron sources,^{6,7} Zn-Mössbauer spectroscopy,¹⁰ Raman scattering,^{11,12} electrical resistance,¹³ optical absorption edge,¹⁴ and photoluminescence¹⁵ measurements have been applied to characterize this phase transition in the last decade. Very recently, a least energy transition pathway for the *B4*-*B1* transformation has been proposed from two independent first-principles investigations.^{16,17} On the other hand, the change of the internal structural parameter u of the *B4* phase with high pressure has been obtained from structural refine-

ments using high resolution angle dispersive x-ray diffraction (ADXRD) up to 12 GPa in a helium pressure medium.¹⁸

The stability of the *B1* phase is the fundamental issue concerned in the present study. The motivation being that the wide indirect band gap of the rocksalt *B1* structure is favorable for *p*-type doping which is difficult for the *B4* structure.^{2,19} Therefore, if the *B1* structure could be quenched at ambient condition, it might broaden the potential applications of ZnO. Several reports showed that *B1* phase reverted to *B4* phase with pronounced hysteresis during decompression.^{6,9,10} However, others including our recent study found that the *B1* phase can be partially quenched to ambient conditions.^{4,5,7,18} It was found that nanoscale grain size can delay the *B4*-to-*B1* phase transition under pressure.²⁰ The manipulation of the grain size to nanoscale may help to fully quench the *B1* phase after pressure is released.¹⁹ Very recently, transmission electron micrograph (TEM) revealed that quenched nanoscale sample was predominantly in *B4* phase while some particles were in the *B1* phase after the compact sample was pulverized for the TEM study.²¹ Furthermore, electron irradiation was found to promote the *B1*-*B4* transformation.²¹

A recent high pressure x-ray diffraction study found that the *B1* phase of ZnO is stable at least up to 202 GPa.²² First-principles total energy calculations predicted that the *B1* phase should transform to CsCl-type (*B2*) structure (space group $Pm\bar{3}m$) at 260 GPa [local-density approximation (LDA)] or 256 GPa [generalized gradient approximation (GGA)].²³ So far no experimental validation of this prediction is reported. The remarkable optical properties, such as

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TABLE I. Equation of state parameters for ZnO and CdO from first-principles calculations and high pressure XRD experiments. K_0 is bulk modulus at ambient conditions, K'_0 pressure derivative of K_0 , and V_0 molar volume at ambient conditions.

Phase	Method	ZnO			CdO		
		K_0 (GPa)	K'_0	V_0 (\AA^3)	K_0 (GPa)	K'_0	V_0 (\AA^3)
B1	Expt.	177 ± 4^a (helium medium)	4	19.60 ± 0.02^a	150 ± 1^c (methanol-ethanol)	4	25.95 ± 0.06^c
		194 ± 11^a (silicone oil medium)	4	$19.67 \pm 0.07^{a,b}$	147 ± 4^c (no medium)	4.2 ± 0.1^c	26.05 ± 0.09^c
		194 ± 20^d (no medium)	4	21^d			
	Calc.	172.7^e	3.68^e	20.502^e	130^f	4.13^f	27.15^f
		168^a	4.46^a	20.366^a	129^a	4.71^a	27.255^a
B2	Expt.	169 ± 7^c (no medium)	4.66^c	23.31 ± 0.18^c
	Calc.	156.9^e	3.77^e	19.785^e	114^f	4.66^f	25.41^f
		161^a	4.54^a	19.478^a	128^a	4.98^a	25.302^a

^aThis work.^bReference 18.^cReference 31.^dReference 22.^eReference 23.^fReference 30.

dielectric function, refractive index, absorption, and electron energy-loss spectrum, predicted for the ultrahigh pressure *B2* phase of ZnO,²⁴ motivated us to investigate the stability of *B1* structure of ZnO under strong compression.

II. EXPERIMENTAL DETAILS

In situ high pressure ADXRD experiments were carried out at the 16-ID-B station of HPCAT, Advanced Photon Source, Argonne National Laboratory. Polycrystalline ZnO with a nominal purity of 99.9995% (Puratronic®, Alfa Aesar) was used as samples. Synchrotron radiation monochromatized with a Si (220) to 0.4008 Å was focused to about 15 μm in diameter on the sample by Kirkpatrick-Baez (KB) mirrors. Diffraction patterns were recorded on a MAR345 image plate or a MAR charge-coupled device (MAR-CCD). Diffraction patterns were obtained from integrated intensities using the program FIT2D.²⁵ Three separate runs were performed. In runs 1 and 2, T301 stainless steel gasket with a hole diameter of about 100 μm was used as the sample chamber in a symmetric diamond anvil cell (DAC). Helium and silicone oil were used as pressure-transmitting media,¹⁸ respectively. The pressure was determined by the ruby luminescence method.²⁶ In run 3, a pair of beveled diamond anvils with culet size of 40 μm-10°-400 μm and a rhenium gasket with a sample hole of diameter about 15 μm was used. In this run, no pressure medium was used. A typical exposure time for the collection of the diffraction patterns was 30 s.

III. RESULTS AND DISCUSSIONS

The volume and pressure data on the *B4* and *B1* phases of ZnO were fitted to the Birch equation of state (EOS).^{18,27} The experimentally derived bulk modulus at ambient conditions, K_0 , of the *B1* phase is compared with the calculated

values in Table I. A “softer” K_0 , of 177.7 ± 4.6 GPa, for the *B1* phase was obtained with helium as the pressure medium. This value is to be compared with a K_0 of 194 ± 11 GPa when silicone oil was used as pressure medium. This observation is rather common where nonhydrostatic conditions often result in an overestimation the value of K_0 compared to that under hydrostatic or quasihydrostatic conditions.²⁸ It is interesting to note that the K_0 value of the *B1* phase of ZnO obtained here using silicone oil is in surprisingly good agreement with a previous report (for pressure up to 202 GPa) where no pressure medium was used.²² This indicates that the compressibility curves with and without pressure-transmitting medium may merge at pressures in the megabar range. Thus, within experimental errors, the K_0 derived from data obtained under nonhydrostatic conditions and quasihydrostatic conditions may be very close. This raises the possibility of using ZnO as a pressure marker for high pressure experiments using the EOS in run 3 which was designed to reach pressure above 2 Mbars.

Figure 1 shows selected diffraction patterns for pressures at and higher than 185 GPa in run 3. Since the focused beam size is close to the size of sample hole which was distorted slightly above 1 Mbar, the diffraction peaks from the rhenium gasket could be observed. The diffraction peaks from *B1* phase ZnO and rhenium gasket were represented by markers labeled as *Z* (*hkl*) and *R* (*hkl*) in Fig. 1, respectively. From the estimated phase ratio between the sample and gasket in the diffraction patterns, the diffraction from the gasket is caused by the scattering with the tail of the focused beam. The results clearly indicate that the *B1* phase of ZnO remains stable up to 209 GPa—the highest measured static pressure for ZnO. When the pressure was increased beyond 209 GPa, one of the diamond anvil developed a ring crack. The corresponding XRD pattern consisted of the contributions from the sample (and gasket) under about 215 GPa conditions and

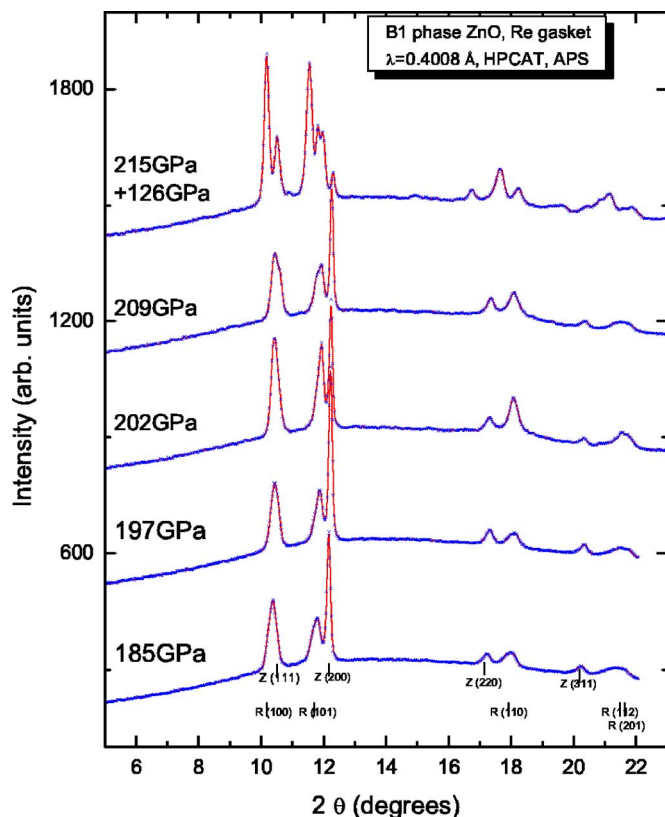


FIG. 1. (Color online) The selected ADXRD patterns of ZnO under high pressure from 185 GPa.

about 126 GPa conditions since this anvil failure event just happened within the 30 s of the diffraction collection period. An immediate follow-up XRD measurement confirmed the pressure dropping and no phase transition from the *B1* structure was observed. Figure 2 shows the unit cell volume ($Z=4$) of *B1* phase of ZnO as a function of pressure obtained in runs 2 and 3.

It is unfortunate that the predicted *B1*-to-*B2* phase transition in ZnO at 260 GPa cannot be verified directly by the

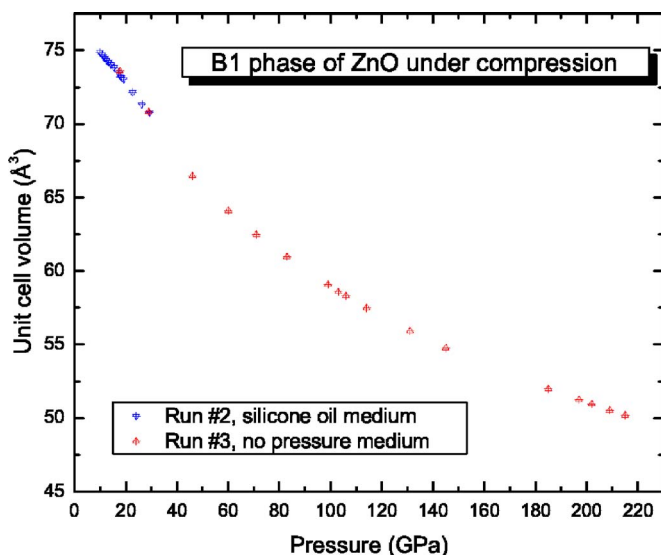


FIG. 2. (Color online) The unit cell volume ($Z=4$) of the *B1* phase of ZnO as a function of pressure in runs 2 and 3.

present experiment. Since Zn and Cd belong to the same group in the periodic table,^{23,29} the already known pressure induced phase transition in CdO could be used to help us evaluate the theoretical prediction. Total energy calculations for CdO predicted a *B1*-to-*B2* phase transition at around 89 GPa.³⁰ This is in very good accord with a recent experimental report that the phase transition started at around 90 GPa.³¹ However, if the calculated and measured K_0 of CdO for both *B1* phase and *B2* phase are compared as shown in Table I, it is found that the K_0 were significantly underestimated by the calculations. The predicted K_0 of the *B2* phase of CdO is 10% smaller than that of *B1* phase. This observation is in *apparent* contradiction with the effect of higher coordination number of 8 in the *B2* phase and therefore is expected to result in higher incompressible than the *B1* phase with a coordination number of 6. It should be noted that the K_0 of *B2* phase was derived from the high pressure data in the range of 102–176 GPa. As will be explained later, the discrepancy between theory and experiment is misleading and is due to the lack of low pressure data points in the experimental measurements.

In the first-principles calculations for ZnO,²³ the K_0 value for *B2* phase, predicted to be stable above 250 GPa, is lower than that of *B1* phase when the full range of computed results was used in the EOS fit. However, a different K_0 is obtained using only energy-volume $E(V)$ data corresponding to the experimental pressure range in fitting the EOS. This clearly highlights the inconsistency on a direct comparison between the “experimental” and theoretical K_0 . By definition, K_0 is the bulk modulus at the “equilibrium” volume. Since both the *B1* and *B2* do not exist at zero pressure, only a subset of experimental data at high pressure was available in the fitting of the EOS. This led to the apparent discrepancy between theory and experiment.

Total energy calculations for the *B1* and *B2* phases of ZnO, as well as for CdO, were performed to compare with previous calculations and experimental results. The total energy versus molar volume for the *B1* and *B2* phases of ZnO and CdO shown in Figs. 3(a) and 3(b), respectively. The bulk moduli were calculated by fitting the $E(V)$ data to the Birch-Murnaghan third-order EOS.³² A smaller K_0 for the *B2* phase of ZnO than that of *B1* phase was also found. The result is consistent with that reported previously.²³

The *B2* phase is unstable at ambient conditions; therefore, there is no experimental equilibrium structure. The comparison of the bulk modulus derived from high pressure data, strictly speaking, makes no practical sense at all. To this end, bulk moduli for *B1* and *B2* phases of ZnO as a function of pressure were derived and shown in Fig. 4(a). The insets in Fig. 4(a) highlight the difference between *B1* and *B2* phases at the low pressure and high pressure ranges. It is clear that at low pressure near ambient, the calculated K_0 of the *B1* phase is slightly larger than that of the *B2* phase. However, the $K(P)$ curves of these two phases cross as pressure increases with the bulk moduli of *B2* phase becoming larger than those of *B1* phase when the pressure is above 120 GPa. This indeed confirms the general perspective that the highly packed *B2* phase should be more incompressible than the *B1* phase at high pressure.

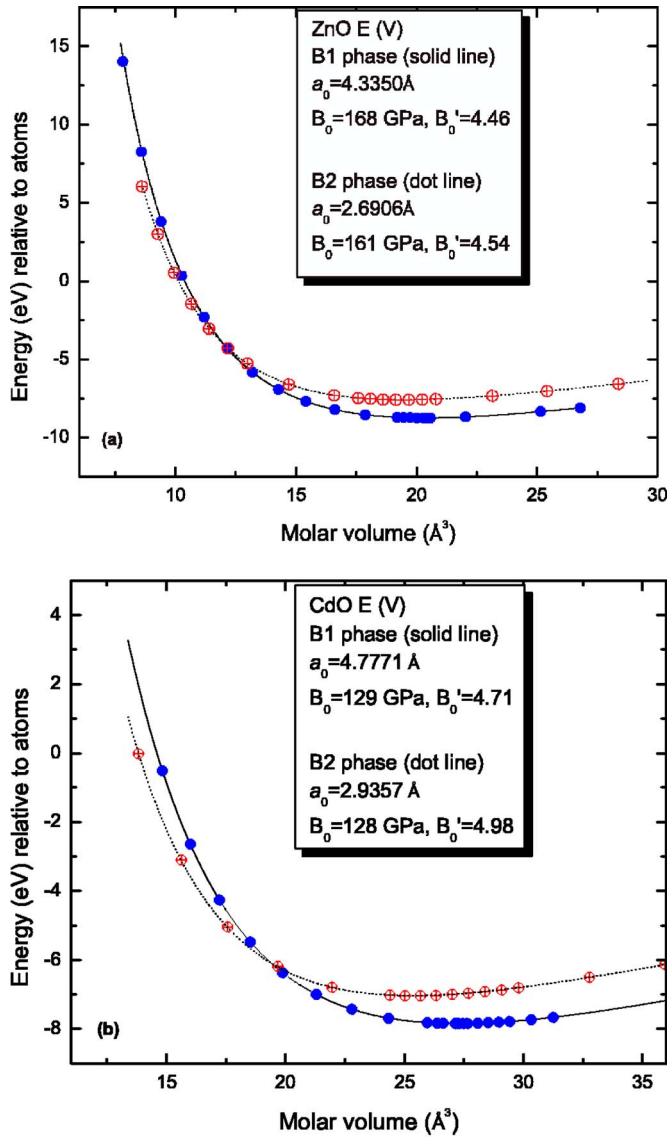


FIG. 3. (Color online) The first-principles total energy calculation results $E(V)$ for B1 phase (solid line) and B2 phase (dash line): (a) ZnO and (b) CdO.

A similar trend of $K(P)$ for CdO is shown in Fig. 4(b). The data derived from experimental results are represented by symbols.³¹ The theoretical results from Ref. 30 were shown as dotted lines. The previous results underestimated the $K(P)$ for both phases. The present results, however, are in very good agreement with the experimental data. Once again, the $K(P)$ for B1 and B2 phases change with pressure with B1 larger than B2 at low pressure and the reverse trend is observed in the high pressure range. The negative slope of the common tangent between the B1 and B2 phase's $E(V)$ curves in Figs. 3(a) and 3(b) gives the pressure for the phase transition. Alternatively, the intersecting point of the enthalpy $H(P)=E+PV$ can be used to calculate the transition pressure P_T . The calculated P_T are 261 GPa for ZnO and 83 GPa for CdO. These values are in substantial agreement with previous calculations.^{23,30} The large activation barrier associated with the B1 and B2 transformations gives rise to the large hysteresis effect observed in the experiment at room

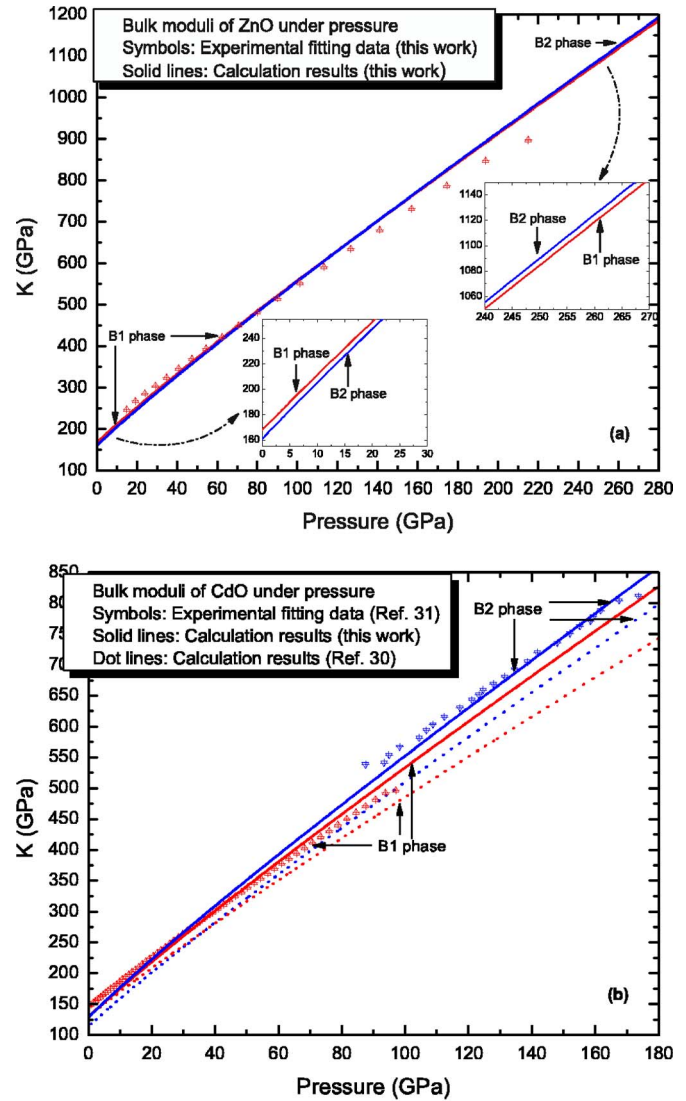


FIG. 4. (Color online) The measured and calculated bulk moduli K of B1 and B2 phases as a function of pressure: (a) ZnO and (b) CdO.

temperature. For example, the B1-to-B2 phase transition in CdO was observed over a pressure range from 91 to 102 GPa.³¹

The B1 phase of ZnO is found to be stable at least up to 209 GPa from the present experiment. This observation prompts the possibility of using the derived EOS of B1 ZnO as an internal pressure marker for pressure higher than the well-known B4-to-B1 phase transition at 9 GPa. ZnO is one of the four oxide powders used as internal standards for quantitative x-ray diffraction analysis, and as external standards for checking the intensity response of x-ray diffraction instruments certified by the National Institute of Standards and Technology (NIST).³³ For high pressure diffraction beamlines in synchrotron sources, it is possible to use the B4 phase to calibrate the wavelength or the distance between the sample and detector at ambient conditions. The simple B1 phase with a fine grain size could extend this NIST calibration standard to high pressure conditions from 10 GPa to multimegabar (>200 GPa) range.

IV. CONCLUSION

Angular dispersive x-ray diffraction studies have shown that the *B1* phase of ZnO remains stable under high pressure up to 209 GPa at room temperature. First-principles total energy calculations were performed for the pressure induced *B1*-to-*B2* phase transition in ZnO and CdO, and transition pressures were estimated at about 261 and 83 GPa, respectively. The pressure dependences of the measured and calculated bulk moduli of the *B1* and *B2* structures of ZnO and CdO have been analyzed. The stability of its *B1* structure upon strong compression makes the ZnO meriting its use as an internal pressure standard up to megabar range in x-ray diffraction research.

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