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New phase boundary and high pressure thermoelasticity of ZnO

Frédéric Decremps (*) and Jianzhong Zhang
Mineral Physics Institute
SUNY at Stony Brook, Stony Brook, NY 11794-2100 USA

Robert C. Liebermann
Department of Geosciences
SUNY at Stony Brook, Stony Brook, NY 11794-2100 USA

(*) **Now at :** *Laboratoire de Physique des Milieux Condensés,*
Université Pierre & Marie Curie, Tour 13, B77,
4, place Jussieu, 75252 Paris CEDEX 05, France

e.mail : fad@pmc.jussieu.fr
fax : +33 1 44 27 44 69

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Abstract

The phase transition of zinc oxide from B4 (hexagonal wurtzite structure) to B1 (cubic rocksalt structure) has been studied by energy dispersive powder diffraction technique up to 11 GPa and 1273 K. Analysis of equation-of-state (PVT) data for the rocksalt phase yields precise values of the bulk modulus and its temperature derivative. The previously accepted P-T phase diagram is shown to be incorrect. It is established that the B1 phase is not recoverable. The equilibrium transition pressure of the B4-to-B1 transformation is near 6 GPa (at ambient temperature) and the $d\mathrm{P}/d\mathrm{T}$ slope close to zero. These new results are confirmed by using simultaneously three other different types of experiment (imaging, ultrasonic and X-ray diffraction studies on single crystal specimens).

Introduction. - Since the work of Bates *et al* [1], it has been known that ZnO transforms from zincite (with the wurtzite or B4 structure) to a rock-salt (B1) phase at high pressure; the transition was observed at temperatures above 700 K, with a positive dP/dT slope that extrapolates to $P_T \sim 9.5$ GPa at 300 K. Based on *post-mortem* analysis by X-ray powder diffraction, Bates *et al* claimed that the rocksalt phase of ZnO was recoverable at ambient conditions (in the presence of NH_4Cl mineralizer as a catalyst). A decade later, using *in-situ* X-ray diffraction, Jamieson [2] found the transition wurtzite-rocksalt (in the neighborhood of 9 GPa at 300 K) to be reversible. We have confirmed Jamieson's conclusion that the high pressure rocksalt phase is not recoverable at ambient conditions [3]. Inoue [4] explored the phase diagram of ZnO from 600 to 1000 K in the pressure range 3-9 GPa using *in-situ* X-ray diffraction and observed a negative slope $dP/dT = -5.10^{-3}$ GPa/K of the phase boundary and $P_T \sim$6 GPa at 300 K. In view of recent high-pressure experiments at room temperature [5, 7, 8, 9] which confirm the value of P_T(300 K)=9 GPa, the validity of Inoue's extrapolation must be questioned. In addition, from solution calorimetric studies, Davies and Navrotsky [10] estimated a slope dP/dT$\sim$0. However, in spite of these several ambiguities, the Bates *et al* phase diagram still prevails in the literature.

Since the LDA+U calculation method seems to be well adapted to ZnO [6], these theoretical calculations need to be tested and validated with robust and accurate experimental data for the pressure of the phase transition, the dP/dT slope and the compressibilities. Furthermore, despite the publication of numerous theoretical studies to understand more about bulk rocksalt ZnO [7, 8, 11], experimental data on its thermoelastic properties are still missing.

In this letter, we report the results of experiments to 11 GPa and 1273 K which provide new information on the phase diagram of ZnO and on the thermoelastic properties of its rocksalt phase.

Experiment. - The experiments were performed using a DIA-type cubic anvil apparatus (SAM-85) with the white synchrotron radiation from the superconducting wiggler magnet X-17B at the National Synchrotron Light Source of the Brookhaven National Laboratory. The diffraction patterns were collected for up to 300s using energy dispersive techniques with a fixed Bragg angle $2\theta = 7.48934°$. The details of the beam-line setup and the procedure of patterns acquisition have been previously published [12]. Two experiments were conducted on polycrystalline zinc oxide (with a nominal purity of 99.9995%, purchased from Alfa AESAR) which was loaded next to NaCl powder in a boron nitride capsule. Sodium chloride was used in order

to provide a pseudo-hydrostatic pressure environment for the sample as well as an internal pressure standard. Pressure was calculated from the Decker's equation of state with an accuracy better than 0.2 GPa in the study range. The temperature was measured with a W/Re24%-W/Re6% thermocouple in contact with the sample and the NaCl layer. In these experiments the sample was first compressed at ambient temperature up to about 11 GPa, followed by heating to the maximum temperature of 1273K. Data were collected on cooling at constant ram load. This procedure was repeated seven times at different ram loads in order to obtain data points at many different P-T conditions. In two other different experiments, the behavior and properties of a single-crystal specimen of ZnO were examined at 873 K (on both compression and decompression between 0 and 7 GPa) using direct imaging of its length [13], Laüe X-ray diffraction, and ultrasonic interferometry [14].

Phase boundary. - During cold compression, toward 9.8 GPa, the appearance of two new diffraction peaks (with an energy of 22.51 keV and 31.89 keV, related to the cubic d-spacing (200) and (220) respectively) reflects the onset of the wurtzite-rocksalt structural transformation, in excellent agreement with the previous high-pressure studies (except Inoue, see above). At 300 K and 11 GPa, before heating the sample, the transition was not yet

complete and diffraction lines from the two (cubic and hexagonal) coexisting phases were observed.

Figure 1 represents a typical change of the diffraction patterns during one of the seven different cooling cycles (the pressure decreases due to the loss of thermal pressure). At 873 K and 4.77 GPa, there is no evidence of the B4 phase; however, at 4.36 GPa and 673 K, the occurrence of five new peaks in the X-ray pattern clearly reveals the onset of the B1 to B4 transition. Similar data for the B1→B4 transition were obtained along six other cooling cycles, as well as: *i*) one decompression at 300 K, during which the B4 phase has been detected in the x-ray pattern to be recoverable at 2.0 ± 0.5 GPa; and *ii*) two isothermal compressions at 873 K during which we detected the B4 $\rightleftharpoons$ B1 transitions.

In the experiment with a single-crystal specimen of wurtzite ZnO, three distinct diagnostic techniques were utilized simultaneously to detect the phase transition (Fig. 2): *(i)* Direct imaging reveals a large reduction of the specimen length (hence, volume) on compression between 4.36 GPa and 6.13 GPa at 873 K; *(ii)* Laüe X-ray diffraction spectra indicate the appearance of the B4 phase at 4.31 GPa on decompression at 873 K; and *(iii)* Ultrasonic travel times of the C_{44} shear mode abruptly decrease at 5.6±0.8 GPa on

compression and increase again at 4.3±0.5 GPa on decompression at 873 K.

On the basis of our new experimental data, we present a phase diagram for ZnO (Fig. 3) which differs significantly from previous studies [1, 4]. The wurtzite phase is recovered following experiments throughout the entire P-T space investigated, with a large hysteresis of the transition at low temperature, consistent with previous room temperature studies. This considerable hysteresis is singular in the II-VI semiconductor family and may be related to the conclusion of Karzel *et al* [8] from *ab-initio* calculations: the wurtzite phase of ZnO is highly unstable. Two different reasons may contribute to this result. First, as discussed by Ubbelohde [15], the transition may not occur at the exact point (P,T) where the free energies of the two different phases are equal because of the possible existence of a zinc oxide hybrid crystal. In that case, the interface and the strain energy stored in this hybrid compound have to be taken into account : they enlarge the region where the free energies match and, consequently, lead to a P-T region in which the two phases coexist. Secondly, the occurrence of this hysteresis could also be explained as the existence of a kinetic barrier, which delays the nucleation of the new phase (rocksalt when increasing pressure, wurtzite when decreasing pressure). Therefore, because of this hysteresis below 600 K, the determination of the

dP/dT slope has only been undertaken for higher temperatures, leading to a constant value very close to zero and unexpectedly small considering the large transition volume change $\Delta V(20\%)$. From the Clausius-Clapeyron relation, $(dP/dT)_{equil} = \Delta S/\Delta V$, this leads to an entropy change of the phase transition also close to zero, in very good agreement with the extrapolation of the calorimetric studies [10]. The strong sp^3 covalent bonding of the wurtzite phase implies a high Debye temperature and low entropy (commonly observed for tetrahedral coordinate related structure, like diamond). Thus, only a low vibrational entropy of the rocksalt phase may explain the observed limited entropy change. High pressure phonon density of state measurements by inelastic neutron scattering may elucidate this point.

Thermoelasticity. - In the case of our X-ray diffraction experiments on ZnO, we obtained 36 P-V-T data points for the rocksalt phase over the range 300-1273 K and 3.2-10.1 GPa (TABLE 1). Since data collected on compression at room temperature may be contaminated by non-hydrostatic stresses in the cell assembly, we include only data collected on cooling at constant ram load; thus our data set may be contrasted with those in previous work in which only data obtained on cold compression were analyzed.

The volume V(P,T)=$V_{T,P}$ of rocksalt ZnO at high pressures and high

temperatures is shown in Table 1. The lattice parameters were determined from pure B1 patterns using five diffraction peaks (namely (111), (200), (220), (311) and (222)). Pressure-volume measurements from ambient to high temperatures were analyzed with a simultaneous fit of the whole data set to the high-temperature Birch-Murnaghan equation of state [16]: $P = \frac{3}{2}B_{T,0}[(V_{T,0}/V_{T,P})^{\frac{7}{3}} - (V_{T,0}/V_{T,P})^{\frac{5}{3}}]\{1 + \frac{3}{4} * (B_0' - 4) * [(V_{T,0}/V_{T,P})^{\frac{2}{3}} - 1]\}$, where B_0' is the pressure derivative of the bulk modulus, $B_{0,T}$ corresponds to the isothermal bulk modulus (or incompressibility) at the temperature T: $B_{0,T} = B_{0,300} + (\partial B_{0,T}/\partial T)_P * (T - 300)$, and $V_{T,0}$ is the volume at high temperature and ambient pressure: $V_{T,0} = V_{300,0} * \exp \int_{300}^{T} \alpha \, dT$, (in this range of P-V-T data, the thermal expansion at zero pressure was assumed to be *(i)* linearly temperature dependent: $\alpha = \alpha_0 + \alpha_1 * T$ and *(ii)* constant: $\alpha = \alpha_0$). From the high pressure measurements performed by S. Desgreniers [5] up to 56 GPa, the pressure derivative B_0' was fixed to 3.54 and the best fitting solution (with $\alpha = \alpha_0 + \alpha_1 * T$) yields $B_{0,300} = 201 \pm 5$ GPa, $V_{0,300} = 19.66 \pm 0.02$ Å^3, $\alpha_0 = 4.7 \pm 0.3 * 10^{-5} K^{-1}$ and $\alpha_1 = 2.2 \pm 0.8 * 10^{-8}$, but also a somewhat high value of $(\partial B_{0,T}/\partial T)_P = -0.082 \pm 0.015$ GPa/K. If we hold $\alpha = \alpha_0$ constant, we obtain $B_{0,300} = 191 \pm 3$ GPa, $V_{0,300} = 19.70 \pm 0.02$ Å^3, $\alpha_0 = 5.2 \pm 0.2 * 10^{-5} K^{-1}$ and $(\partial B_{0,T}/\partial T)_P = -0.048 \pm 0.010$ GPa/K. How-

ever, in a recent paper [17], the bulk modulus of $3d$ transition-metal monoxides has been observed to be linearly dependent on the unit-cell volume like $B_0 = 524 - 17V_0$ (B_0 in GPa and V_0 in Å^3). The value of the bulk modulus for ZnO obtained with a constant thermal expansivity seems to be in better agreement with these systematics considerations. Previous X-ray diffraction studies of the equation of state of rocksalt ZnO had yield values of $B_{0,300}$ from 170 to 228 GPa [5, 7, 8, 9] as shown in Table 2. Our new results are in excellent agreement with the experimental data from S. Desgreniers [5] and with those obtained from theoretical Hartree-Fock calculations ([8, 11]).

Conclusion. - In this study, we have confirmed that the rocksalt structure is not recoverable at ambient temperature. The phase transition of ZnO between the wurtzite and the rocksalt structures is reversible, with transformation kinetics or hysteresis being sensitive to temperature, as expected for an Arrhenius-type behavior. Previous studies of ZnO have been influenced by significant uncertainties in the phase diagram and inaccurate thermoelastic data. Our data demonstrate that the wurtzite-rocksalt transition occurs with a slope $d\mathrm{P}/d\mathrm{T}$ close to zero and an equilibrium transition pressure of about 6 GPa (the kinetic pressure transition of the B4→B1 was observed at 9.8 GPa). Analysis of the equation of state data P-V-T for the rocksalt phase

yields $B_{0,300}$=191-201 GPa and $V_{0,300} = 19.70 - 19.66$ Å^3. In addition, the consistent mapping out of the P-T phase diagram by four different experiments reveals the potentiality of making the ZnO cubic phase accessible at ambient pressure: an extrapolation of the B1→B4 phase boudaries indicates an irreversibility at low temperature ($T \sim 200K$). In this respect, further studies on cubic ZnO (electronic transitions, e.g. insulator to metal) and new related technological applications should be fascinating.

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References

[1] C.H. Bates, W.B. White and R. Roy, *Science*, **137**, (1962), 993.

[2] J. C. Jamieson, *Phys. Earth planet. Interiors*, **3**, (1970), 201.

[3] We recently reproduced the experiment from Bates *et al* by subjecting powder ZnO (*without* NH_4Cl) to pressures greater than 12 GPa at about 1300 K. We found an identical X-ray spectrum for the same sample before and after the hot pressing, with a pattern perfectly matching the wurtzite single-phase fingerprint.

[4] K. Inoue, *Ph. D. thesis*, University of Tokyo, (1975).

[5] S. Desgreniers, *Phys. Rev. B*, **58**, (1998) 14102.

[6] V.I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B*, **44**, (1991) 943.

[7] J.M. Recio, M.A. Blanco, V. Luaña, R. Pandey, L. Gerward and J. Staun Olsen, *Phys. Rev. B*, **58**,(1998) 8949.

[8] H. Karzel, W. Potzel, M. Köferlein, W. Schiessl, U. Hiller, G.M. Kalvius, D.W. Mitchell, T.P. Das, P. Blaha, K. Schwartz and M.P. Pasternak, *Phys. Rev. B*, **53**, (1996) 11425.

[9] L. Gerward and J. Staun Olsen, *J. Synchrotron Radiat.*, **2**, (1995) 233.

[10] P.K. Davies and A. Navrotsky, *J. Solid State Chem.*, **38**, (1981) 264.

[11] J. E. Jaffe and A. C. Hess, *Phys. Rev. B*, **48**,(1993) 7903.

[12] D.J. Weidner, M.T. Vaughan, J. Ko, Y. Wang, X. Liu, A. Yeganeh-haeri, R.E. Pacalo and Y. Zhao, *Geophysics Monograph Series*, **67**, (1992) 13.

[13] M.T. Vaughan, J. Chen, L. Li, D.J. Weidner and B. Li, in *Science and Technology of High-Pressure Research*, edited by M. H. Manghnani, W. J. Nellis and M. F. Nicol, (AIRAPT-17) to be published.

[14] R.C. Liebermann and B. Li, *Review in Mineralogy. Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, edited by R. J. Hemley, Vol. **37** (Washington DC) 1998 pp 459-492.

[15] A.R. Ubbelohde, *Quart. Rev.*, **11**, (1957) 246.

[16] S.K. Saxena and J. Zhang, *Phys. Chem. Minerals*, **17**, (1990) 45.

[17] J. Zhang, *Phys. Rev. Lett.*, **84**, (2000) 507.

Table caption

Table 1. Pressure (P)- Volume (V) measurements of cubic-ZnO at high temperatures (T). Numbers in parentheses are standard variation and refer to the last digits.

Table 2. Birch-Murnaghan equation of state parameters for the B1 phase of ZnO. Volumes, V, are per chemical formula unit. $P_{T\uparrow}$ and $P_{T\downarrow}$ indicate the kinetic transition pressure at ambient temperature upon compression and decompression respectively. Uncertainties (numbers in parentheses) refer to the last digits. "N.R." ("R.") refers to the non-reversibility (reversibility) of the B4-B1 transition. Superscripts "F" indicate a fixed value of $B_0^{'}$ in the Birch-Murnaghan fitting.

Table 1

P(GPa)	T(K)	V($\AA^3$)	P(GPa)	T(K)	V($\AA^3$)	P(GPa)	T(K)	V($\AA^3$)
7.20	300	18.768(30)	10.2	673	18.848(13)	8.60	973	19.168(10)
6.25	300	18.866(11)	7.95	673	19.005(19)	9.80	1073	19.156(12)
6.25	300	18.888(07)	7.05	673	19.087(11)	8.80	1073	19.242(11)
4.90	300	18.972(08)	5.65	673	19.199(11)	7.95	1073	19.332(10)
3.50	300	19.111(17)	10.15	773	18.924(13)	6.50	1073	19.511(13)
3.20	300	19.095(18)	8.20	773	19.056(23)	5.20	1073	19.647(10)
10.40	473	18.693(13)	10.15	873	18.989(17)	9.45	1173	19.257(12)
7.60	473	18.895(19)	8.40	873	19.117(20)	9.00	1173	19.307(11)
6.65	473	18.982(09)	7.50	873	19.187(15)	9.25	1273	19.358(10)
5.25	473	19.076(10)	6.10	873	19.328(15)	8.45	1273	19.453(09)
10.40	473	18.771(13)	4.75	873	19.507(09)	7.05	1273	19.593(16)
7.75	473	18.957(20)	10.05	973	19.067(13)	5.65	1273	19.784(16)

Table 2

Refs	Method	$V_{0,300}$	$B_{0,300}$	B'_0	$P_{T\uparrow}$	$P_{T\downarrow}$
This work	X-ray ($\alpha = \alpha_0 + \alpha_1 T$)	19.66(2)	201(5)	3.54^F	9.8(4)	2.0(5)
This work	X-ray ($\alpha = \alpha_0$)	19.70(2)	191(3)	3.54^F	9.8(4)	2.0(5)
[1]	Quench+X-ray	19.60			9.5	N.R.
[5]	X-ray	19.60(6)	202.5(2)	3.54(4)	9.1(2)	1.9(2)
[7]	X-ray	19.53	194	4.8	10	R.
[8]	X-ray+Mössbauer	19.484	228	4^F	8.7	~ 2
[9]	X-ray	19.60	170(10)	9.5(9)	~ 10	R.
[11]	Calc. (Hartree-Fock)	19.799	203.3	3.6	8.57	
[7]	Calc. (CGA)	20.099	176	5.39		N.R.
[8]	Calc. (Hartree-Fock)		205	4.88	14.5	

Figure captions

Figure 1. X-ray energy dispersive spectra for ZnO from one cooling cycle (from T=1273K down to 300K). At 673 K and 4.36 GPa, five new diffraction peaks reflect the occurrence of a phase transition from a pure rocksalt structure to a wurtzite+rocksalt mixture. At the top, a single B4 phase spectrum has been dot-ploted to emphasize the corresponding peaks in the B1+B4 mixture.

Figure 2. Phase transformation highlights at 873 K by simultaneously performing three different type of single-crystal experiments in SAM85 apparatus. We conducted two independent runs; in both cases, the hexagonal ZnO single crystal was cut as a cylinder of 2mm of length and 2mm of diameter. The first study has been carried out with a cylinder axis along (001), and along (100) for the second one. (a) Imaging technique. This original X-ray "shadowing" method consists in lighting the entire single crystal with a broad X-ray beam. The transmitted light is incident on a fluorescent crystal; the resulting image is viewed by a CCD camera and recorded on computer. (b) Laüe x-ray diffraction technique. Six patterns outline the shift from the rocksalt to the wurtzite structure fingerprint. (c) Ultrasonic technique. This

method has been recently developed in our laboratory for performing sound velocity measurements up to 20 GPa and 1500 K [14]. The present figure features the marked travel time decrease for shear waves (propagating along the wurtzite c hexagonal axis) when ZnO undergoes a transformation to the cubic phase.

Figure 3. Phase diagram of ZnO. Solid (open) symbols identify the B4→B1 (B1→B4) phase transition. The squares at 873 K enhance the remarkable and consistent determinations of the phase boundaries by four different experiments (X-ray powder diffraction, Laüe diffraction, imaging and ultrasonic studies, see Fig 2).

Figure 1

Figure 2(a)

Figure 2(b)

Figure 2(c)

Figure 3