13A, 18C/2003G194

Equation of State of the High-pressure phase of ZnO

Yoshihisa MORI[1], Naoto NIIYA[1], Takafumi MIZUNO[1] and Tadashi NISHII[1]
[1]Department of Applied Science, Okayama University of Science
1-1 Ridai, Okayama 700-0005, Japan

Introduction

ZnO is a wide band gap semiconductor and the crystal structure at ambient pressure is the fourfold-coordinated wurzite structure (B4). In this material, a theoretical report described that the B4 phase transforms to the sixfold-coordinated NaCl structure (B1) and the B1 phase transforms to the eightfold-coordinated CsCl structure (B2) and the transition-pressure of the second phase transition was calculated to be at 256 GPa [1]. On the other hand, the high pressure synchrotron X-ray diffraction study was performed up to 56 GPa by Desgreniers[2], and he reported that the transition pressure from the B4 to the B1 phase was 9.1 GPa and the bulk moduli of the B4 and B1 phases were 142.6 and 202.5 GPa, respectively and the B1 phase was stable up to this pressure. In this paper, we carried out X-ray study of ZnO to obtain an accurate equation of state of the B1 phase and to find the second phase transition to the B2 phase.

Experimental

The high-pressure synchrotron X-ray diffraction studies were carried out using the Angle Dispersive X-ray diffraction at BL13A and BL18C beam lines at Photon Factory. The energies of the X-ray source at BL13A and BL18C were 30 and 20 KeV, respectively. Pressure was generated by using a diamond anvil cell (DAC) and bevelled diamonds with 100, 150 μm culet were used. A Re-W alloy was used as a gasket. The typical size of the sample chamber was 60 μm in diameter and the X-ray source collimated to 40 μm in diameter. The pressure was determined by the ruby fluorescence method A 16:3:1 mixture of ethanol and methanol and water was used as a pressure-transmitting medium. The X-ray diffraction data was detected on the imaging plate and analyzed by the Rietveld refinement (RIETAN-2000)[3].

Results and discussions

With increasing pressure, the B4 structure transformed to the B1 phase around 9 GPa, which is good agreement with the previous experimental reports [2]. The lattice parameters of *a* and *c* for the B3 structure decreased smoothly with increasing pressure. The *c*/*a* ratio also decreased with increasing pressure and the pressure coefficient was -5.61×10^{-4} GPa^{-1} which is almost the same value as previously reported. The bulk modulus of the B4 phase was determined by the Birch-Murnaghan's equation (B_0'=4.0) to be 139.9 ± 2.2 GPa which is similar to the experimental values of 142.6 GPa by Desgreniers [2] and the theoretical values of 133.7 GPa (the generalized gradient approximation:GGA) and smaller than 162.3 GPa (the local-density approximation:LDA) by Jaffe [1]. The pressure dependence of the volume during the phase transition from the B4 to the B1 phase is shown in Fig.1 with the previous experimental data. The volume reduction with the phase transition is –16.8% in the unit cell. The evaluation of the bulk modulus of the B1 high-pressure phase is sensitive to the value of the initial volume, however it is not easy to determine the value with accuracy. The initial volume was estimated by interpolation to be 0.0196 nm^3. The bulk modulus and its pressure derivative of the B1 were determined by the Birch-Murnaghan's equation to be 199.2 ± 6.0 GPa and 4.08 ± 0.13, respectively. The value of bulk modulus are good agreement with the experimental result (202.5 GPa) by Desgreniers and the LDA calculation (205.7 GPa) and larger than GGA calculation (172.7 GPa) by Jaffe.

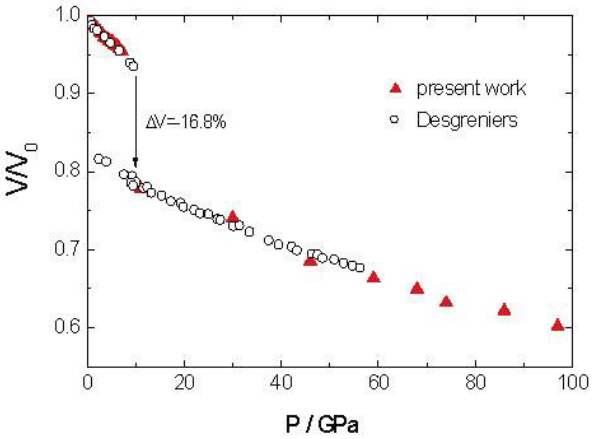

Fig. 1. Pressure dependence of volume through the phase transition. The phase transition occurred with the volume reduction of -16.8 % in the unit cell.

Summary

An X-ray diffraction study of ZnO was carried out. ZnO transformed from the B4 structure to the B1 structure around 9 GPa and the B1 phase was stable up to 100 GPa and there was no phase transition up to this pressure. The bulk moduli for both phases were 139.9 ± 2.2 and 199.2 ± 6.0 GPa, respectively.

References

[1] J. E. Jaffe, J. A. Synder, Z. Lin, A. C. Hess, Phys. Rev. B, 62, 1660 (2000).
[2] S.Desgreniers, Phys Rev B **58,** 14102 (1998).
[3] F. Izumi, in The Rietveld Method, edited by R. A. Young(Oxford University Press,Oxford, 1995), chap. 13

* mori@das.ous.ac.jp