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Simulated Equations of State of ZnO with Rocksalt Phase at High Temperature and High Pressure

Yu-xiao Liu^a, Xiao-wei Sun^b, Ting Song^a, Cheng-wei Wang^{a,c*}

a. College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China;

b. School of Mathematics and Physics, Lanzhou Jiaotong University, Lanzhou 730070, China; c.

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China

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The equation of state of ZnO with rocksalt phase under high pressure and high temperature was calculated by using the molecular dynamics method with effective pair potentials which consist of the Coulomb, dispersion, and repulsion interaction. It was shown that molecular dynamics simulation is very successful in accurately reproducing the measured molar volumes of the rocksalt phase of ZnO over a wide range of temperatures and pressures. The simulated P - V - T data matched experimental results up to 10.4 GPa and 1273 K. In addition, the linear thermal expansion coefficient, isothermal bulk modulus and its pressure derivative were also calculated and compared with available experimental data and the latest theoretical results at ambient condition. At extended temperature and pressure ranges, the P - V - T relationship, linear thermal expansion coefficient, and isothermal bulk modulus were predicted up to 2273 K and 50 GPa. The detailed knowledge of thermodynamic behavior and equations of state at extreme conditions are of fundamental importance to the understanding of the physical properties of ZnO.

Key words: Equation of state, ZnO, Molecular dynamics simulation, Pair potentials

I. INTRODUCTION

ZnO is an interesting solid as it is a wide-band-gap semiconductor with a range of technological applications including electronic and electro-optic devices, catalysis, chemical sensors, and conductive solar cell window layers [1-3]. If most of the covalent II-VI compounds crystallize at normal conditions of temperature and pressure in a zinc-blende or cinnabar structure, ZnO possesses a hexagonal wurtzite structure. This phase transforms to the rocksalt phase in the range of 10 GPa, as reported by Bates, White, and Roy [4]. On the other hand, ZnO is one of the candidate constituents of the Earth's lower mantle [5]. Investigation of its thermodynamic properties at high temperature and high pressure is important for understanding mantle structure [6-8]. Among these thermodynamic properties, the way that expansion coefficient and isothermal bulk modulus vary with pressure and temperature plays a very important role in the Earth and material science. Reliable predictions of the thermal expansion coefficient and isothermal bulk modulus are significant in describing many other important properties of solids at the conditions of the lower and upper mantle of the Earth. Temperatures and pressures present in the lower mantle are difficult to achieve in the laboratory. Complement to experiment, molecular dynamics simulation has been

used as a powerful tool to tackle this issue. Molecular dynamics simulation based on interatomic interactions have been used extensively to investigate microscopic structures of a wide variety of chemical and physical systems, and their macroscopic thermodynamic and physical properties.

New computational techniques have led to calculations of the thermodynamic properties of ZnO. To date, several theoretical studies of both wurtzite and rocksalt phases using the linear combination of Gaussian-type orbital Hartree-Fock method [9], the full potential linear muffin-tin orbital approach to density functional theory [10], linearized augmented plane wave [11], local-density approximation (LDA), and generalized gradient approximation (GGA) [12] methods have been reported. However, these studies have focused mainly on calculating the equilibrium transition pressure from wurtzite to rocksalt phases and not to investigate the equation of state of the rocksalt phase of ZnO at extreme temperature and pressure conditions. An accurate equation of state for crystalline materials is very important in many applications involving high pressure and elevated temperature [13-15]. In past several years, some significant advances have been made in high-pressure experimental techniques. However, the information on material properties at high pressures is still limited, especially for the investigation of equation of state of ZnO with rocksalt phase under the conditions of both high temperature and high pressure.

In this research, we first accurately simulated and predicted the P - V - T relationship of the rocksalt phase of ZnO at pressure and temperature up to 50 GPa and

*Author to whom correspondence should be addressed. E-mail: cwwang@nwnu.edu.cn, sunxxww@126.com, Tel.: +86-931-3879297, Fax: +86-931-4938401.

2273 K, respectively, using effective pair potential by the molecular dynamics method. In addition, the linear thermal expansion coefficient, isothermal bulk modulus and its pressure derivative in normal conditions are calculated and compared with the available experimental and theoretical data. At extended temperature and pressure ranges, the P - V - T relationship, linear thermal expansion coefficient, and isothermal bulk modulus have been predicted up to 2273 K and 50 GPa. The simulated results are of fundamental importance in material science and geophysics.

II. THEORETICAL METHOD

Molecular dynamics simulation is a well-established technique in mineralogy, especially for studying the effects of high pressure and high temperature on the properties of a solid [16-20]. A detailed description of the molecular dynamics method has been provided elsewhere [21-23]. In short, the molecular dynamics method consists of solving numerical equations for atomic motion, assuming initial coordinates and velocities of atoms and a model of interaction between them. It is often the case in molecular dynamics calculations that periodic boundary conditions are applied. The technique consists of solving a set of differential equations obtained by applying Newton's laws over all particles of the system. It requires the calculation of the force on each atom in any given configuration. This calculation involves forces between all pairs of interacting atoms. For a macro cell or cluster of about 1000 atoms or more, there would be millions of such pairs depending on the range of interatomic interaction. Most of the computation time is used in the force calculation, which is repetitive at each time step of the simulation. We carried out a molecular dynamics simulation at high pressures and temperatures with effective pair potential on a system of 256 particles (128 Zn and 128 O) in the NTP (constant N is the number of particles, T is the temperature, and P the pressure) ensemble. The system was allowed to evolve for 4 ps, of which first 2 ps are used for equilibration and not included in calculation of thermodynamic averages. A time-step of 1 fs was used for integrating equations of motion and the number of time-steps was $n=2000$. The equations of motion were integrated using a modified form of the Beeman algorithm [24]. The cut-off radius taken for the short-range potential was about 10 Å. Coulombic interaction was calculated using Ewald method [25]. Typically, the actual temperature differed from the required temperature by less than 1 K, the actual pressure differed from the required pressure by less than 1 MPa, and the standard discrepancy in the volume was less than 0.002 cm³/mol. All the simulations were performed using the GULP program that is based upon the Mott-Littleton methodology for accurate modeling of perfect and defect lattices [26].

We have applied the constant-pressure and constant-

temperature molecular dynamics simulations with the empirical pair potential given in the following form:

$$V_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where the right terms represent Coulomb, repulsive interactions, and van der Waals, respectively; Z_i or Z_j is an effective charge of the i th atom, e the electronic unit charge, A_{ij} the magnitude of repulsion force, B_{ij} the softness parameter, and C_{ij} the van der Waals coefficient of ionization. Here r_{ij} is the interionic distance between atoms i and j . Values of the parameters of ZnO [27] used in simulations are listed in Table I. The parameters of the short-range pair potentials were obtained by empirical fitting to the properties of the wurtzite structure of ZnO. These properties include the lattice constant, elastic and dielectric constants. Following Sun's previous study, the performance of these potential parameters is rather good for describing properties of ZnO with rocksalt structure at high pressures and temperatures [7,8].

TABLE I Short-range potential parameters of ZnO used in simulations

	A/eV	$B/\text{Å}$	$C/\text{eVÅ}^6$
Zn-Zn	0.00	0.1000	0.00
Zn-O	700.30	2.9586	0.00
O-O	22764.00	6.7114	27.88

III. RESULTS AND DISCUSSION

In a recent study, Decremps *et al.* have obtained the P - V - T data for the rocksalt phase of ZnO over the range 300-1273 K and 3.2-10.4 GPa by X-ray diffraction experiment [28]. The experimental and simulated data of molar volumes versus P and T over the wide temperature and pressure range for the rocksalt phase of ZnO is displayed in Table II. When the temperature is not high, there is a difference between the present work and experiment, but the difference is not more than 1.84% at 300 K and 0.13% at 1273 K. This is because the data collected on compression at low temperature from the X-ray diffraction experiment may be influenced by nonhydrostatic stresses in the cell assembly, so includes only data collected on cooling at constant ram load. Note that the obtained results are in excellent agreement with experiment at high temperature and pressure. At 1273 K and 9.25 GPa, the simulated molar volume calculated to be 11.668 cm³/mol is only larger by 0.07% than the corresponding measured value. It is obvious that the discrepancy between the experimental and molecular dynamics simulation is decreased with increased temperature and pressure. Due to this fact, we can conclude that our interatomic potential model and empirical fitting potential parameters work well at high temperature and high pressure.

TABLE II The experimental and simulated data of molar volumes versus P and T for the rocksalt phase of ZnO

T/K	P/GPa	$V/(cm^3/mol)$		T/K	P/GPa	$V/(cm^3/mol)$	
		Experiment	Calculation			Experiment	Calculation
300	3.2	11.501	11.713	873	4.75	11.749	11.809
300	3.5	11.511	11.694	873	6.1	11.641	11.720
300	4.9	11.427	11.610	873	7.5	11.556	11.641
300	6.25	11.376	11.533	873	8.4	11.514	11.587
300	6.25	11.363	11.533	873	10.15	11.437	11.489
300	7.2	11.304	11.480	973	8.6	11.545	11.612
473	5.25	11.489	11.648	973	10.05	11.484	11.527
473	6.65	11.433	11.565	1073	5.2	11.833	11.809
473	7.6	11.380	11.510	1073	6.5	11.751	11.769
473	7.75	11.418	11.501	1073	7.95	11.644	11.641
473	10.4	11.306	11.358	1073	8.8	11.589	11.631
473	10.4	11.259	11.358	1073	9.8	11.538	11.566
673	5.65	11.564	11.125	1173	9.0	11.629	11.644
673	7.05	11.496	10.893	1173	9.45	11.598	11.619
673	7.95	11.447	10.688	1273	5.65	11.916	11.900
673	10.2	11.352	10.494	1273	7.05	11.801	11.793
773	8.20	11.477	11.565	1273	8.45	11.716	11.714
773	10.15	11.398	11.455	1273	9.25	11.659	11.668

TABLE III The predicted molar volumes for the rocksalt phase of ZnO in the temperature range from 300 to 1273 K and pressure up to 50 GPa

T/K	15 GPa	20 GPa	25 GPa	30 GPa	35 GPa	40 GPa	45 GPa	50 GPa
	$V/(cm^3/mol)$							
300	11.080	10.856	10.653	10.464	10.287	10.124	9.970	9.827
473	11.125	10.893	10.688	10.494	10.314	10.149	9.994	9.851
673	11.177	10.943	10.726	10.529	10.348	10.181	10.022	9.878
773	11.203	10.964	10.751	10.549	10.366	10.198	10.040	9.889
873	11.224	10.982	10.766	10.566	10.384	10.210	10.052	9.903
973	11.250	11.009	10.786	10.591	10.402	10.231	10.071	9.918
1073	11.280	11.036	10.810	10.608	10.419	10.243	10.084	9.931
1173	11.298	11.060	10.833	10.625	10.438	10.261	10.096	9.941
1273	11.342	11.090	10.850	10.644	10.451	10.277	10.113	9.962

The determination of the P - V - T relationship of solid materials is a problem of considerable importance in basic and applied science. Accurate P - V - T equations of state for crystalline materials are very important in many applications involving high pressure and elevated temperature. The investigation of the thermodynamic properties such as thermal expansivity and bulk modulus is based on the P - V - T relationship referred to as an equation of state. Based on the reliability of the interatomic potential set at high temperature and pressure, we attempt to predict the molar volumes at extended pressure up to 50 GPa and temperature between 300 and 1273 K. The predicted results are shown in Table III. In addition, we have also predicted P - V - T relationships of the rocksalt phase of ZnO at the extended temperature range of 1373 K to 2273 K, in the pres-

sure range of 0 to 50 GPa, which are listed in Table IV. Note that the molar volume increases with increasing temperatures and decreases with increasing pressure.

Thermal expansivity and bulk modulus are very important parameters for understanding the thermodynamic and thermoelastic behaviour of solids at high pressures and temperatures. Reliable predictions of the thermodynamic parameters, including thermal expansion coefficient α_P , isothermal bulk modulus K_T , and its pressure derivative K'_T , are important in the study of the lower and upper mantle of the Earth [23]. A precise knowledge of these parameters is therefore essential in devising a reliable equation of state of materials that is applicable over an extended range of temperature and pressure. The linear thermal expansion coefficient, isothermal bulk modulus and its pressure derivative of

TABLE IV The predicted data of molar volumes versus P and T for the rocksalt phase of ZnO

P/GPa	1373 K	1473 K	1573 K	1673 K	1773 K	1873 K	1973 K	2073 K	2173 K	2273 K
	$V/(\text{cm}^3/\text{mol})$									
0	12.366	12.430	12.483	12.516	12.574	12.604	12.690	12.720	12.755	12.879
5	11.981	12.018	12.055	12.097	12.142	12.176	12.215	12.271	12.327	12.349
10	11.652	11.691	11.702	11.746	11.778	11.813	11.842	11.877	11.903	11.957
15	11.365	11.395	11.408	11.441	11.472	11.490	11.531	11.557	11.588	11.624
20	11.095	11.132	11.147	11.178	11.210	11.230	11.248	11.279	11.292	11.344
25	10.867	10.890	10.915	10.942	10.956	10.981	11.001	11.032	11.061	11.073
30	10.665	10.683	10.701	10.723	10.746	10.759	10.775	10.806	10.826	10.848
35	10.471	10.489	10.504	10.519	10.538	10.554	10.580	10.594	10.621	10.632
40	10.293	10.310	10.326	10.346	10.361	10.376	10.391	10.405	10.423	10.438
45	10.125	10.145	10.157	10.166	10.182	10.198	10.216	10.232	10.251	10.263
50	9.969	9.987	10.005	10.013	10.032	10.038	10.057	10.075	10.083	10.093

TABLE V Simulated thermodynamic parameters for the rocksalt phase of ZnO

Method	$\alpha_P/10^{-5}\text{K}^{-1}$	K_0/GPa	K'_0	Reference
This work	1.01	178.3	3.57	
MD ^a	0.16	198.0	2.60	[29]
HF-PI		132.0	3.80	[30]
CHF-PI		170.0	3.37	[31]
GGA		180.0	4.69	[31]
X-ray		228.0	4.00	[11]
X-ray		194.0	4.70	[31]

^a MD: Molecular dynamics.

ZnO with rocksalt phase at ambient condition were investigated first. The results obtained are shown with experimental and other computational results [11,29-32] in Table V. The linear thermal expansion coefficient α_P was obtained by fitting the computed T - V results to the equation $\alpha_P=1/a(\partial a/\partial T)_P$, where a represents the lattice parameter. The molecular dynamics simulated result for the rocksalt structure is $1.01\times 10^{-5}\text{K}^{-1}$ and it has a large discrepancy with the value of Aoumeur's [29]. The main reason lies in the different potentials adopted that were applied in simulation. Aoumeur *et al.* used molecular dynamics simulation based on Tersoff's potential to calculate the linear thermal expansion coefficient, and the Tersoff's potential simply considered the interaction of Zn-Zn and O-O and neglected the interaction of the Zn-O. The isothermal bulk modulus K_0 and its pressure derivative K'_0 at standard condition were obtained by fitting the P - V results to the equation $K_T=-V(\partial P/\partial V)_T$ and the Birch-Murnaghan third-order equation of state [32], respectively. The isothermal bulk modulus for rocksalt structure is well described by our simulation and the results agree well with generalized gradient approximation (GGA) calculations [31], however, it was found that the Coulomb-

Hartree-Fork method of Clementi about the *ab initio* perturbed ion model (CHF-PI) result [31] underestimates the bulk modulus by 4.7%. In addition, the K'_0 is more in agreement with the CHF-PI results [30,31], but it was found that the experimental data [11,31] overestimate the value. Any discrepancy might be due to the sample quality and the accuracy of each experimental method. Each calculation method also has its own limitations related to the basic material parameters, basis sets, and the precisions used, in addition to the approximations of the method itself, leading to variations in the calculated parameters. All in all, the overall good agreement with the experiment and previous theoretical work is a good validation of the reliability of the interatomic potential set and its transferability under high pressures.

In order to study further the influences of pressure and temperature on thermal expansivity and isothermal bulk modulus of ZnO with rocksalt phase, simulations over a wide range of pressures and temperatures (300-2273 K and 15-50 GPa) were performed and the results are shown in Table VI and VII. It is well-known that there are certain difficulties associated with the measurement of thermal expansion coefficient at high temperatures which lead to considerable uncertainties in the experimental values [33]. It has been emphasized that most of the serious errors in the calculations of thermodynamic functions arise due to the uncertainty of thermal expansivity at high temperatures [34]. It is, therefore, desirable to develop a model that is semi-empirical or semi-phenomenological for evaluating and predicting thermal expansivity. We think that application of molecular dynamics tools for the calculation of thermal expansivity and bulk modulus properties is a viable strategy for obtaining some of the available information [35]. From Table VI we can see that the linear thermal expansion coefficient increases with increasing temperature and decreases with increasing pressure. Note that the influence of temperature on thermal expansion at high pressures is very small and may be

TABLE VI The predicted data of the linear thermal expansivity coefficient $10^{-6}\alpha_P$ versus P and T for the rocksalt phase of ZnO

T/K	15 GPa	20 GPa	25 GPa	30 GPa	35 GPa	40 GPa	45 GPa	50 GPa
	$10^{-6}\alpha_P$							
300	7.335	6.783	5.866	5.662	5.313	5.240	4.740	4.591
473	7.449	6.862	5.988	5.732	5.361	5.237	4.764	4.592
673	7.581	6.952	6.130	5.812	5.416	5.233	4.791	4.594
773	7.646	6.997	6.200	5.851	5.444	5.231	4.804	4.595
873	7.713	7.044	6.271	5.891	5.471	5.229	4.818	4.596
973	7.779	7.088	6.342	5.930	5.499	5.227	4.830	4.597
1073	7.843	7.132	6.411	5.970	5.526	5.225	4.844	4.598
1173	7.911	7.176	6.481	6.009	5.553	5.223	4.858	4.599
1273	7.972	7.220	6.552	6.049	5.582	5.221	4.871	4.599
1373	8.038	7.268	6.622	6.088	5.608	5.219	4.885	4.600
1473	8.102	7.310	6.692	6.127	5.636	5.217	4.897	4.601
1573	8.170	7.356	6.761	6.167	5.664	5.215	4.911	4.601
1673	8.233	7.399	6.829	6.206	5.691	5.213	4.926	4.603
1773	8.297	7.442	6.900	6.244	5.718	5.211	4.937	4.603
1873	8.366	7.487	6.969	6.284	5.746	5.209	4.952	4.605
1973	8.425	7.533	7.038	6.324	5.771	5.208	4.965	4.605
2073	8.489	7.575	7.105	6.361	5.799	5.206	4.978	4.605
2173	8.552	7.622	7.173	6.400	5.825	5.204	4.990	4.607
2273	8.614	7.659	7.244	6.438	5.853	5.202	5.004	4.608

TABLE VII The predicted data of isothermal bulk modulus K_T versus P and T for the rocksalt phase of ZnO

T/K	15 GPa	20 GPa	25 GPa	30 GPa	35 GPa	40 GPa	45 GPa	50 GPa
	K_T							
300	240.21	255.58	271.47	287.82	304.38	320.61	336.74	352.35
473	234.09	249.39	265.46	282.73	300.40	317.89	335.36	352.30
673	227.46	243.17	260.50	278.35	296.39	314.31	332.44	349.68
773	223.77	242.02	259.67	277.53	294.53	310.75	326.50	341.94
873	222.10	240.65	258.62	276.33	293.25	310.07	325.83	341.07
973	219.27	239.24	258.30	275.35	292.16	307.56	322.09	336.08
1073	217.70	235.80	253.14	270.45	288.07	305.60	322.30	339.07
1173	215.75	234.77	253.31	270.55	286.23	301.16	315.13	328.28
1273	209.49	226.60	246.17	265.30	285.02	304.17	323.31	341.80
1373	208.24	229.07	247.94	265.52	283.08	299.71	315.80	331.04
1473	204.92	225.36	245.61	263.91	281.78	298.87	314.93	330.67
1573	204.90	226.10	245.77	264.50	282.17	298.42	314.07	328.27
1673	202.32	222.30	241.24	259.57	277.19	292.50	308.72	322.72
1773	198.73	218.79	239.58	257.66	276.24	292.53	309.38	323.74
1873	197.76	217.17	237.04	255.67	273.56	289.55	305.90	320.87
1973	194.14	216.12	236.35	255.57	272.64	289.53	305.43	320.05
2073	191.77	212.60	232.52	251.78	270.62	287.96	304.24	319.30
2173	190.76	212.52	230.59	249.83	267.22	284.48	299.78	314.97
2273	187.63	208.26	228.94	246.53	263.71	279.32	293.51	307.36

neglected at above 50 GPa pressure. This is mainly because the anharmonic effects become less important at high pressure. Thus, the linear thermal expansivity of the rocksalt phase ZnO at high pressures is a weak

function of temperature.

Table VII shows the isothermal bulk modulus K_T as a function of pressure up to 50 GPa at temperatures from 300 K to 2273 K. It is obvious that the isothermal

bulk modulus of the rocksalt phase ZnO increases with the increase of pressure, and decreases with increasing temperature.

IV. CONCLUSION

Molecular dynamics simulations of the rocksalt phase of ZnO were presented using effective pair potentials in order to investigate the behavior of the equation of state under elevated pressures and temperatures. The P - V relationship under different isotherms at selected temperatures was obtained and compared with the X-ray diffraction experimental data. It was shown that the molecular dynamics simulation is very successful in accurately reproducing the measured volumes of ZnO with rocksalt phase over a wide range of temperature and pressure. Also, the isothermal and isobaric properties are discussed from the corresponding P - V - T relationship, and the properties are summarized in the pressure 0-50 GPa ranges and the temperature up to 2273 K. In addition, the linear thermal expansion coefficient, isothermal bulk modulus and its pressure derivative of ZnO with rocksalt phase at ambient condition were investigated. At extended temperature and pressure ranges, the linear thermal expansion coefficient and isothermal bulk modulus were predicted up to 2273 K and 50 GPa. It can be determined that the linear thermal expansion coefficient of ZnO with rocksalt phase is increased with increasing temperature. The influence of temperature on thermal expansivity is very small and may be neglected at above 50 GPa pressure. Therefore, the thermal expansivity of ZnO with rocksalt phase at high pressures is a weak function of temperature. The isothermal bulk modulus of ZnO with rocksalt phase decreases with increasing temperature and increases with increasing pressure.

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