Behavior of phase transition of ZnO in nanoscale of time a molecular dynamics computation

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Abstract

The phase transition of Zinc Oxide Wurtzite structure is investigated at the Nanoscale of time and space using Equilibrium Parallel Molecular Dynamics simulation. We extend existing results to higher pressure and temperature. The calculations ran on the RAVEN supercomputer of Cardiff University with DL_POL_4 software. The interatomic interaction modeled by Buckingham-Coulomb potential for short and long-range interactions. We study the evolution in time of the total energy in isothermal and isobaric ensemble, to find the equilibrium time of the system, under the ranges of pressure 0–200(GPa) and temperature 300–3000(K). This is a new method to investigate the phase transition. Our results are closed to available theoretical and experimental data.

1. Introduction

Zinc Oxide is stable, with a wurtzite structure, with unit cell parameters a = b = 3.2496(Å) and c = 5.2042(Å) [1, 2]. The volume of unit cell depends on the free electrons concentration, concentration of foreign atoms, and defects, external strains, and temperatures [3]. These parameters values vary from 3.2475, to 3.2501(Å) and from 5.2042 to 5.2075(Å), for a and c-parameters respectively [4]. While, the ratio of c/a vary from 1.593 to 1.6035(Å), and μ value vary from 0.383 to 0.3856(Å). The main cause, of structure deviation from ideal wurtzite is probably, because the lattice stability and iconicity [5]. For ZnO cubic zincblend structure, the parameter value of unit cell varies from 4.60 to 4.619(Å); the Zinc blend type is metastable and can be stabilized, only by heteroepitaxial growth on cubic substrates [6–8]. While, rocksalt type is metastable, at zero pressure [9, 10]. There are tetrahedral coordinates for both Wurtzite and Zinc blend types, which makes four nearest neighbors and 12 next-nearest neighbors of both ZnO structures respectively, they have the same bond length. Due to the long-range Colombain interactions, the four tetrahedral lengths remain almost fixed, through the distortion of tetrahedral angles, where the ratio of c/a drops and the μ value rises. The c/a value shows the biggest deviation from the ideal value, because the relationship with the variation of the electronegativity of the two components, since the c/a values are less than the ideal value. There is a phase transition from wurtzite to rocksalt, which started at around 10(GPa) and finished at 15(GPa) [9, 11]. This result is more than that established by Karzel et al [12]. ZnO returned to wurtzite type at 1.9 ± 0.2 (GPa), however rocksalt anticipated to turn into zinc blend at 260(GPa) [13, 14]. Whereas, under 15(GPa) and 55(GPa); a nanocrystal yields a single metastable cubic phase of ZnO, but this is distinct than bulk dimension [15]. The total energy (nearly the cohesive energy per bond) is −9.769 eV, −9.754(eV), −9.611(eV) for wurtzite, zinc blend, and rocksalt respectively, while the experiment result is −7.52(eV) [5]. This work analyzed the effect of extended pressures 0–200(GPa) and temperatures 300–3000(K), on the evolution in time of the total energy; Consequently, we used the equilibrium time of total energy for isobaric and isothermal ensembles, to show the phase transition. This work presents a new technique, for confirming phase transition. There are no other studies of ZnO wurtzite under these conditions of temperature and pressure. This computational prediction requires experimental confirmation.
2. Methods

Today, Parallel Molecular dynamics predictions are a powerful computational technique, for studying large systems; to find macroscopic properties, from microscopic calculations, using statistical physics. This work used dlpoly_4 software, where calculations ran on the RAVEN supercomputer in Cardiff University (UK). To model the interatomic interactions of 2916 ZnO Wurtzite atoms ($1458 \text{ Zn}^+ + 1458 \text{ O}^-$), we used a Buckingham-Coulomb potential, for short and long-range interactions, with a cut-off of 12 Å; Outside this radius, the
potential is insignificant [16], while Ewald summation [17] calculated long-range interactions [18]. The total time for system equilibrium and measurement is 300000 ps, and time step $\Delta t$ is 0.001 (ps), respecting the periodic conditions. A thermodynamic ensemble nST employed, for relaxation value of 10 (ps), for each temperature and pressure in the range of 300–3000 (K) and 0–200 (GPa) respectively [19, 20]. The lattice parameters of hexagonal wurtzite type extracted from experimental results are $a = b = 3.2496$ (Å), and $c = 5.2042$ (Å) [1, 2]. The crystallographic component vectors of wurtzite according X, Y and Z axis are respectively $a \left(\frac{1}{2}, \frac{-\sqrt{3}}{2}, 0\right)$, $a \left(\frac{1}{2}, \frac{-\sqrt{3}}{2}, 0\right)$, and $a \left(0, 0, \frac{c}{a}\right)$. The bases of atoms in Cartesian coordinates are
(0,0,0), (0,0,μc), a$(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$, and a$(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$ ($\mu$ + $\frac{1}{2}$)$\frac{c}{2}$) [5], where the dimensions of the simulation box are $(9a)x(9b)x(9c)$. The error bar of total energy calculations is between 0.0027 and 0.0064 Å.

3. Results and discussion

To confirm the validity of Buckingham-Coulomb potential, to find the equilibrium time of total energy in isothermal and isobaric ensemble, and to exhibit phase transition; we analyzed the evolution in time of total energy under the range of temperature 300–3000(K) and pressure 0–200(GPa), as shown in figures 1–11.
Later, equilibrium time of total energy is employed, to study the relationship between total energy variation and the phase transition of ZnO wurtzite type, comparing with available theoretical and experimental data.

Figure 1 shows that, under 0 (GPa) and the range of temperature 300–3000 (K), the total energy is approximately linear; there are a noteworthy reproducible of fluctuations with rising temperature especially at 3000 (K). There is a dramatic growing of fluctuations, due to solid-liquid state [21]. We can see from figures 1–11, the evolution of total energy versus time; increasing of equilibrium time of total energy, with increasing the
temperature and its reducing with increasing pressure, also increasing pressure reduces the fluctuations. However, the effect of high pressure on fluctuations and equilibrium time is more than the effect of high temperature.

To extract the equilibrium time of total energy from its evolution in time, we used the following technique as expressed in figure 12.

Under low pressure (0–30(GPa)) and at low temperatures (300(K) and 500(K)), after extracting the equilibrium time of total energy, in isothermal ensemble, the curve of equilibrium time of total energy, versus pressure is shown in figure 13. Whereas, both curves under 300 K and 500 K are in the vicinity of available results.

The equilibrium time of total energy of ZnO wurtzite, at both temperatures dropped below 5(GPa) and tends to be almost smooth till 15(GPa), later it converged to the same value. The available theoretical and experimental results displayed a phase transition, from wurtzite type, to rocksalt structure starting at around 10(GPa) and ending at 15(GPa) [9, 10], while LDA calculations found that the phase transition happened under 6(GPa) [14, 22]. In our work, the phase transition is between 5(GPa) and 15(GPa), see figure 13; our data are in the vicinity of available experimental and theoretical information.

| Table 1. Total energy (KJ per atom) of ZnO wurtzite structure, under the ranges of pressure 0–20(GPa) and temperature of 300(K) and 500(K). |
|---|---|---|---|---|---|---|---|
| T(K) | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| 300 | −12.30 | −11.91 | −11.53 | −11.57 | −10.81 | −10.47 | −10.14 |
| 500 | −12.25 | −11.86 | −11.48 | −11.12 | −10.76 | — | — |
The total energy per atom is summarized in table 1; these values are close to other work [5]. The total energy of ZnO-w rises with increasing temperature and pressure, except under 20 (GPa), wherever it decreased to $-10.81$ (KJ) per atom, due to the phase transition and the new structure of rocksalt [9, 11, 22], see table 1. These values are relative to the literature data [5]. Unfortunately, there is no data under the rest ranges of pressure and temperature for comparison; this prediction needs experimental confirmation in future. For

Figure 15. Equilibrium time of total energy versus temperature under low pressure (0–20(GPa)) and temperature (1500(K)–3000(K)) in an isobaric ensemble.

Figure 16. Equilibrium time of total energy versus temperature under low pressure (0–30(GPa)) and temperature (300(K)) and 500(K)) in an isothermal ensemble.

Figure 17. Equilibrium time of total energy versus Temperature under low pressure (0–200(GPa)) and temperature (1500 K–3000(K)).
isobaric ensemble, under low pressure and temperature, the equilibrium time of total energy versus temperature is shown in figure 14. From previous curve, the variation of equilibrium time of total energy versus temperature is completely linear; there is proportionality between the equilibrium time of total energy and temperature. Converging of curves transcribed selfsame ZnO structure; while, the presence of a gap between curves indicated a phase transition. So the cavity between 5 (GPa) and 15 (GPa) displayed the interval of phase transition, whereas the space between 15 (GPa) and 30 (GPa) is neglected, it indicates the rocksalt structure [9, 11, 22]. Figure 15 exhibits shows that melting takes place around 2228 K for ZnO. At 2500 (K) and under 10, 15, and 20 (GPa), the curves converged to the selfsame value of equilibrium time of total energy, that one means ZnO rocksalt type. Nevertheless after melting degree; under 10 (GPa), there is another ZnO type [22], due to dropping of equilibrium time of total energy. Under 0 (GPa) and lower than melting degree around 2000 (K), the curve maintains steady, because there is one ZnO wurtzite type, after melting degree the equilibrium time of total energy decreases, due to phase transition till 2500(K), where it increases to those under 10, 15, and 20 (GPa) of rocksalt. However under 5 (GPa), the equilibrium time of total energy decreases till 2000(K) (no wurtzite

| T(K) | 40   | 60   | 80   | 100  | 120  | 140  | 160  | 180  | 200  |
|------|------|------|------|------|------|------|------|------|------|
| 1500 | -9.18| -7.97| -6.84| -5.79| -4.78| -2.87| -1.97| -1.1 |
| 2000 | -9.03| -7.83| -6.72| -5.66| -4.61| -3.67| -2.74| -1.84| -0.96|
| 2500 | -8.9 | -7.69| -6.57| -5.11| -4.35| -3.53| -2.74| -4.57| -0.87|
| 3000 | -7.75| -7.55| -6.44| -5.38| -4.36| -3.4 | -1.57| -0.51| |
structure, and still constant till 2500 (phase transition), where it rises to that of rocksalt; our data are in agreement with available information of ZnO phase transition [9, 11, 22].

To demonstrate and analyze the phase transition, using equilibrium time of total energy; we used low pressure 0–20 (GPa) and high temperature 300–3000 (K), as mentioned in figure 16.

Between 5 and 15 (GPa), under all temperatures, the equilibrium time of total energy tends to converge to one value, which means the structure of ZnO rocksalt type. The phase transition starts at 5 (GPa) and finishes at 15 (GPa) under all temperatures, that is closed to theoretical and experimental information [2, 9, 11]. In the range of pressure 0–200 (GPa) and temperature 1500–3000 (K), see figure 17; under all temperatures, the curves converged under 40 (GPa) and 200 (GPa); this justifies the existence of the same structure of rocksalt [9, 11, 22]. Under both temperatures of 2000 (K) and 2500 (K) (around melting degree of ZnO), the curves are converged to the same value of equilibrium time of total energy at 40–200 (GPa) ranges of pressure. Under 180 (GPa) and at 1500 (K) and 3000 (K), there are two beaks; one is upward (3000 (K)) and the second is downward (1500 (K)).

Figure 20. Evolution in time of total energy under 200 GPa and at 300–3000 K.

Figure 21. Equilibrium time of total energy versus Temperature under low pressure (0–200 GPa) and temperature (1500 K–3000 K).

Table 3. Comparison between phase transition values and those found by LDA, GGA [22] and other LDA/GGA [14, 22].

| P (GPa) | our work | LDA [22] | GGA [22] | other LDA/GGA [22] | exp [22] |
|--------|----------|----------|----------|--------------------|---------|
| B4 to B1 | 5 to 15 | 9.08(9.20) | 11.59(11.51) | 6.6 | 9.1, 8.7 |
| B4 to Bk | 25 | 27.66(27.75) | 24.35(24.65) | | |
| Bk to Bk | 30.6(30.2) | 32.36(32.85) | | | |
| Bk to Bk | 12.19(12.13) | 15.56(16.53) | | | |
| Bk to Bk | 180 | 196.03(195.70) | 183.4(183.25) | | |
| Bk to Bk | 80, 100, 140 | 156.05 | 144.40 | | |
which elucidated a phase transition \[9, 11, 22\]. Our data are in the vicinity of theoretical and experimental work \[5\], see table 2; where the total energy increases with increasing the temperature and pressure, however we have no available results, under previous conditions of temperature and pressure to compare with, the evolution of total energy in time under the range of pressure 160–200GPa is shown in figure 18–20, while the equilibrium time is in figure 21.

Table 3 shows a comparison between our results and ZnO wurzite phase studied by common tangent method, and Enthalpy curves crossings (shown in parentheses) \[22\].

4. Conclusion

Equilibrium parallel molecular dynamics simulation, and dply_4 software are used to predict the effect of isothermal and isobaric ensembles, on equilibrium time of total energy of ZnO, in the range of pressures 0–200(GPa), and temperatures 300–3000(K); in order to confirm the phase transition. These calculations ran on the RAVEN supercomputer, of Cardiff University, in United Kingdom. Jumping or dropping of peak of equilibrium time of total energy versus pressure or temperature, gap existence between curves denotes a phase transition of ZnO structure; according comparison with pressure transition of available data; this work confirmed firstly the validity of this new method, which used the time as the main ingredient of equilibrium molecular dynamics, to predict the existence of phase transition. This new method has an agreement existing results of pressure transition.; However, this new method makes predictions, which needs more confirmation in future. In order, to find the required time of phase transition under specific temperature and pressure, for other materials, we need more computational, theoretical, and experimental work to achieve that time. This work will be more practical, because it used the nanoscale of time, and will permit to know other structures during that phase transition, beside that, it will permit to know the behavior of each phase at both temperature and pressure.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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