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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 using Equilibrium time of total energy in isobaric and isothermal ensemble. The calculations ran on the RAVEN supercomputer of Cardiff University employing Molecular Dynamics simulation and DL_POL_4 software, the short and long-range interatomic interactions modeled by Buckingham-

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Coulomb potential. In this work we used low and high range of pressure and temperature of 0-30 GPa and 40-200 GPa, and 300-500 K and 1500-3000 K respectively. Although no data about confirming phase transition using equilibrium time of total energy as our knowledge, our results are in agreement with the classical method but are still a prediction which needs experimental confirmation. This work has great importance in nanotechnology and many industrial and academic sectors.

1.Introduction

Among Zinc Oxide structures, the Wurtzite structure (B4) is the most stable one, with hexagonal unit cell parameters $a = b = 3.242 \text{ \AA}$ and $c = 5.188 \text{ \AA}$ at ambient conditions. These parameters, however, depend on the free electrons concentration, concentration of foreign atoms, and defects, external strain, pressure, and temperature³. Their values vary from 3.2475 \AA , to 3.2501 \AA and from 5.2042 to 5.2075 \AA , for a , and c -parameters respectively⁴, while, μ value varies from 0.383 \AA to 0.3856 \AA . The main cause of structure deviation from ideal wurtzite is probably due to lattice stability and ionicity⁵.

For ZnO Zinc blend structure, the parameter value of unit cell varies from 4.60 \AA to 4.619 \AA ; the Zinc blend type is metastable in nature, but it can be stabilized by heteroepitaxial growth on cubic substrates^{6, 7, 8}. While Rocksalt type is metastable, at zero pressure^{9, 10}. Wurtzite and Zinc blend types have tetrahedral coordinates; four nearest neighbors (each atom of Zn is surrounded by four atoms of O and vice versa) and 12 next-nearest neighbors. Due to the long-range Colombian interactions, the four tetrahedral lengths remain almost fixed with a distortion of tetrahedral angles; the ratio of c/a drops and the μ value rises.

At ambient temperature, a phase transition from Wurtzite to Rocksalt has been reported in different works, which takes place between around 5 GPa and 15 GPa ^{9, 11, 12}. However the Rocksalt structure anticipated to turn into Zinc blend at 260 GPa ^{13, 14, 15}, the total energy of Wurtzite structure is in the vicinity of the experiment data -7.52 eV^5 ,

In our work presented here, we analyzed the effect of extended pressures (0-200 GPa) and temperatures (300-3000 K), on the time dependence of the total energy. We analyzed the evolution of the equilibrium time of total

energy for isobaric and isothermal ensembles to show evidence of phase transitions.

2. Methods

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 Zn^{+2} and 1458 O^{-2}), we used a Buckingham-Coulomb Potential for short and long-range interactions, with a cut-off of 12 Å; while Ewald Summation¹⁷ calculated long-range interactions¹⁸. The total time for system equilibrium and measurement is set to 300 ps, with a time step Δt of 0.001 ps, respecting the Periodic Boundary Conditions. A thermodynamic ensemble NVT is employed to relax temperature and pressure by 10 ps for each one, 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; $a = b = 3.242$ Å, and $c = 5.188$ Å. The crystallographic component vectors of Wurtzite according X , Y and Z axis are respectively $a(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$, $a(\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0)$, and $a(0, 0, \frac{c}{a})$. The bases of atoms in Cartesian coordinates are (0,0,0), (0,0, μc), $a(\frac{1}{2}, \frac{\sqrt{3}}{6}, \frac{c}{a})$, and $a(\frac{1}{2}, \frac{\sqrt{3}}{6}, (\mu + \frac{1}{2})\frac{c}{a})$ ⁵, where the dimensions of the simulation box are $(9a) \times (9b) \times (9c)$.

3. Results and Discussion

Parallel Molecular dynamics technique is a powerful computational method for studying condensed matter; to find macroscopic properties from microscopic calculations using statistical physics. In this work we search to find the equilibrium time of total energy from its evolution in time under the range of temperature 300-3000(K) and low and high pressure(0-30 GPa)and 4.-200 GPa respectively), in isothermal and isobaric ensemble, to confirm phase transition.

3.1 Under low pressure

Figures1-6 show the evolution in time of total energy under 0-30 GPa and at 300-3000 K, later we will extract the equilibrium time of total energy from these curves, in order to study the relationship between total energy variation and the phase transition of ZnO Wurtzite type,

comparing with available theoretical and experimental data.

Figure1 shows that; under 0-30 GPa and at 300 K, the total energy is approximately linear; there are appearing of fluctuations with rising temperature, especially at 3000 K see figure 6, where there is a dramatic growing of fluctuations, due to liquid state²¹. We can see from Figures1-6, 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 the pressure reduces the fluctuations.

However, the effect of pressure on fluctuations and equilibrium time is more than the effect of temperature.

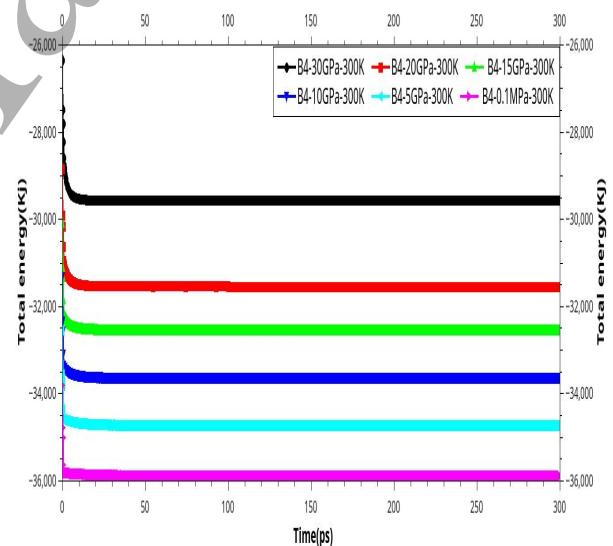


Figure1: Total energy of ZnO-wurtzite phase under the range of 0.1MPa-30 GPa and at 300 K.

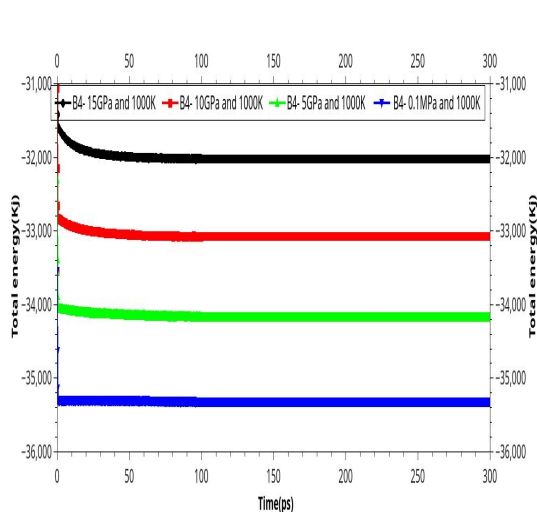


Figure 2: Total energy of ZnO-wurtzite phase under the range of 0.1 MPa-30GPa *GPa* and at 1000 K.

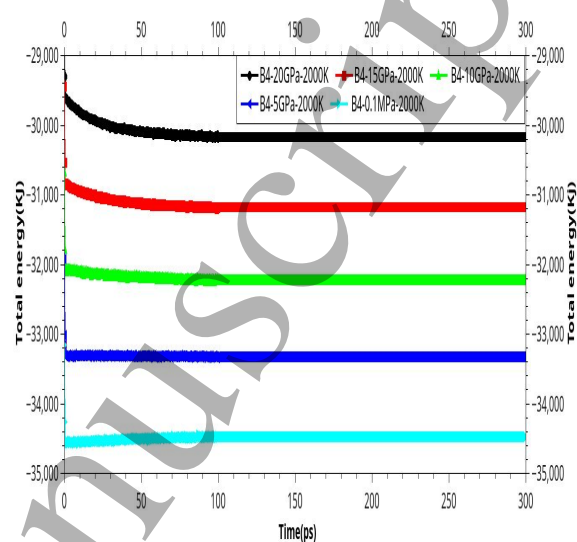


Figure 4: Total energy of ZnO-wurtzite phase under the range of 0.1MPa-30GPa (*GPa*) and at 2000K.

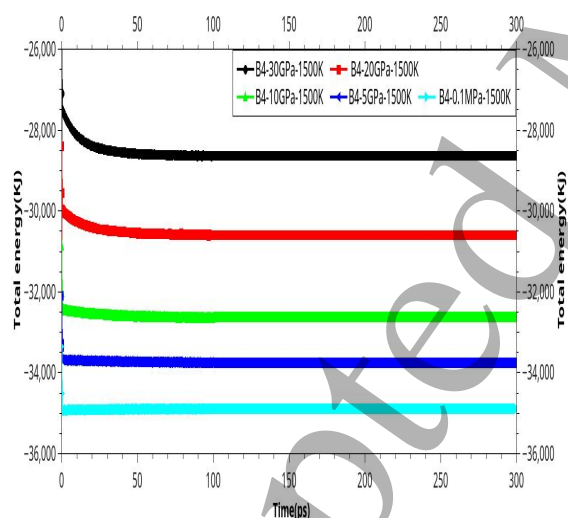


Figure 3: total energy of ZnO-wurtzite phase under the range of 0.1 MPa-30 *GPa* and at 1500 K

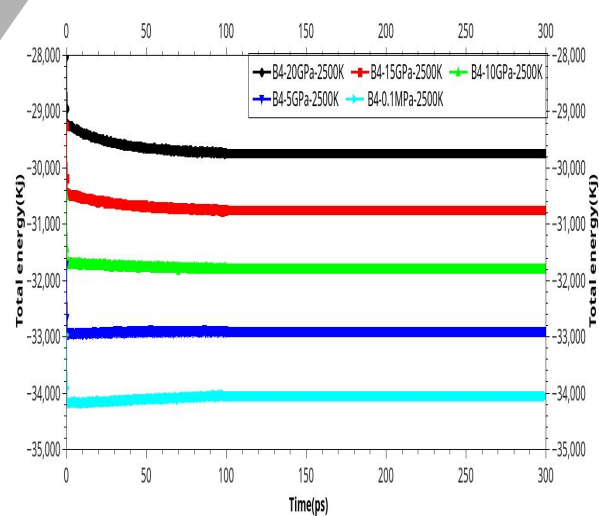


Figure 5: Total energy of ZnO-wurtzite phase under the range of 0.1 MPa-20 *GPa* and at 2500 K

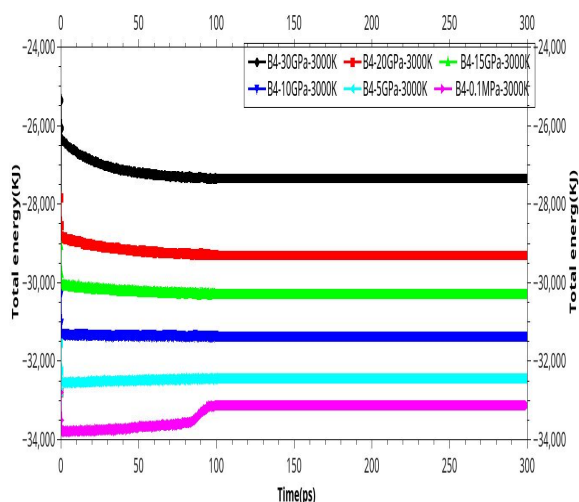


Figure 6: Total energy of ZnO-wurtzite phase under the range of 0.1 MPa-20 GPa and at 3000 K

In order to extract the equilibrium time of total energy, we use the method as shown in Figure 7.

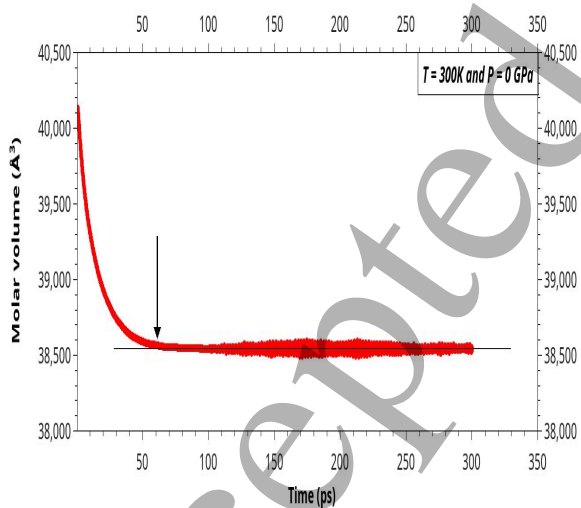


Figure 7: total energy of ZnO-w versus time and the method to extract equilibrium time value of total energy, where we plot a horizontal line on equilibrium area, the last contact point between this curve and the horizontal line will be the value of equilibrium time of total energy.

The total energy per atom is summarized in Table 1; these values are closed to other work⁵; the total energy of ZnO-w rises with increasing temperature and pressure, except under 20 GPa and at 300 K, wherever it decreased to -10.81 KJ per atom, due to the phase transition and the new structure of rocksalt^{9,11,22}. These values are relative to the literature data⁵.

| P(GPa) | 0 | 5 | 10 | 15 | 20 | 25 |
|--------|--------|--------|--------|--------|--------|--------------|
| T(K) | 30 | | | | | |
| 300K | -12.30 | -11.91 | -11.53 | -11.57 | -10.81 | -10.47-10.14 |
| 500K | -12.25 | -11.86 | -11.48 | -11.12 | -10.76 | |

Table 1: total energy values under 0.30 GPa and at 300 K and 500 K

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, see Figure 8.

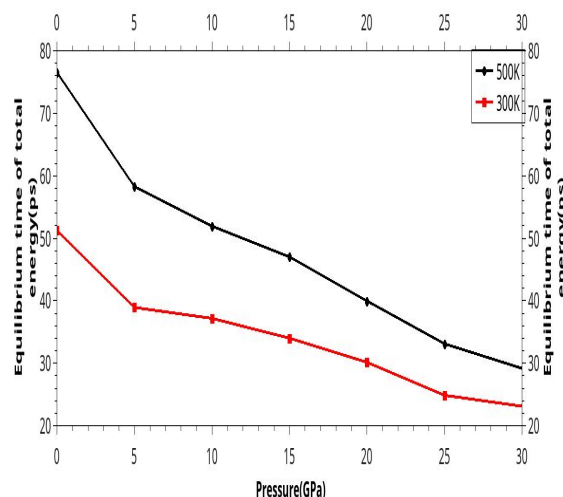


Figure 8: the equilibrium time of total energy versus pressure, in isothermal ensemble under low pressure 0-30 GPa and at low temperatures 300 K and 500 K).

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^{22, 14}. In our work the phase transition is between 5 GPa and 15 GPa. Unfortunately, there is no data under the rest ranges of pressure and temperature for comparison; this prediction needs experimental confirmation in future. For isobaric ensemble, under low pressure and temperature, the equilibrium time of total energy versus temperature is shown in Figure 9, converged curves means the same structure, while diverged curves means not the same one; that is a sign of phase transition. 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, the cavity between 5 GPa and 15 GPa displayed the interval of phase transition,

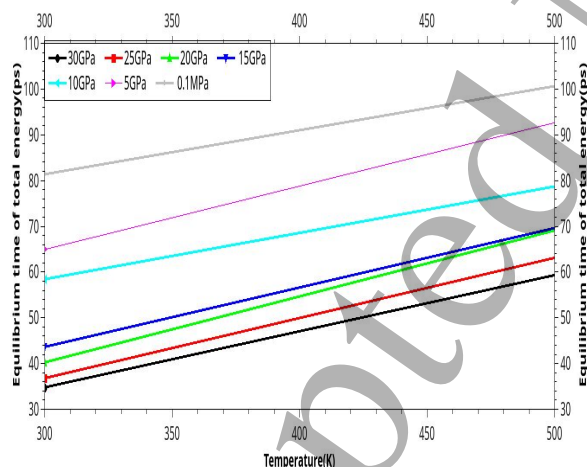


Figure 9: equilibrium time of total energy versus temperature under low pressure (0-30 GPa) and temperature (300 K and 500 K).

Whereas the space between 15 GPa and 30 GPa is neglected, it indicates the Rocksalt structure^{9, 11, 22}. Figure 10 shows that there is a phase transition at 2000 K, while

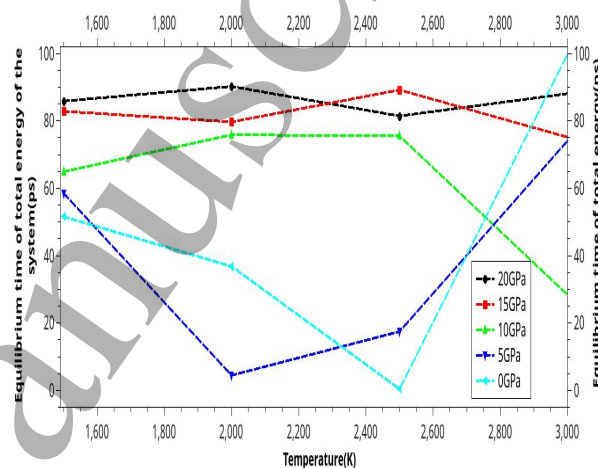


Figure 10: equilibrium time of total energy versus temperature under low pressure (0-20 GPa) and temperature (1500 K-3000 K) in an isobaric ensemble

Under the effect of 3000(K), this is a sign of other structure. Under 10 GPa the equilibrium time is still bit linear under the range 300-2500 K, while drops between 2500-3000 K due to another structure²² as shown in Figure 10. These data are in agreement with available information of ZnO phase transition^{9, 11, 22}. In an isobaric ensemble under 0.20 GPa and at 300-3000 K the phase transition is clear comparing with available results as mentioned in Figure 11. Under 1500 K and all pressures the curve is bit linear (the same structure), while at 2000 K and in the range of 0.5 GPa the equilibrium time decreases but at 2500 K and under the same range of pressure, there is rising of equilibrium time due to the impact of temperature is more than the effect of pressure (not the same type of ZnO), later under the range of pressure 5-20 GPa and at both temperature we have

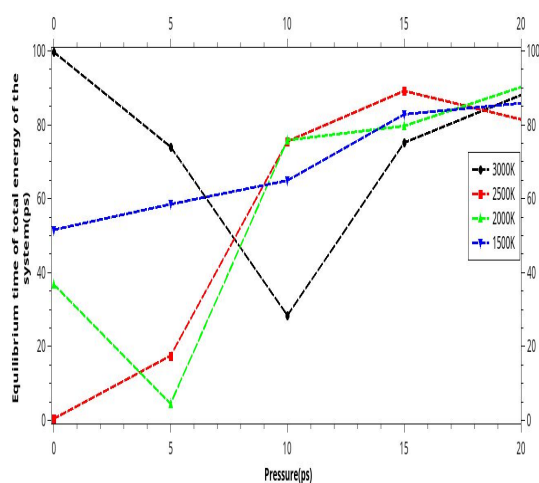


Figure 11: equilibrium time of total energy versus temperature under low pressure (0-20 GPa) and temperature (1500 K-3000 K)

the same variation of equilibrium time (the same structure). At 3000 K and between 0 GPa and 5 GPa there is bit decreasing of equilibrium time, while between 5 GPa and 10 GPa dropped and increasing till 15 GPa; it is the interval of phase transition according theoretical and experimental data^{9,10}. Later in the range of 15-20 GPa, all the curves are converged to the same value (the Rocksalt one)^{9, 11, 2}.

3.2 High pressure

Figures 12-20 shows the evolution of total energy in time under high pressure and high temperature; we will extract from these curves the equilibrium time to confirm the phase transition comparing with available information.

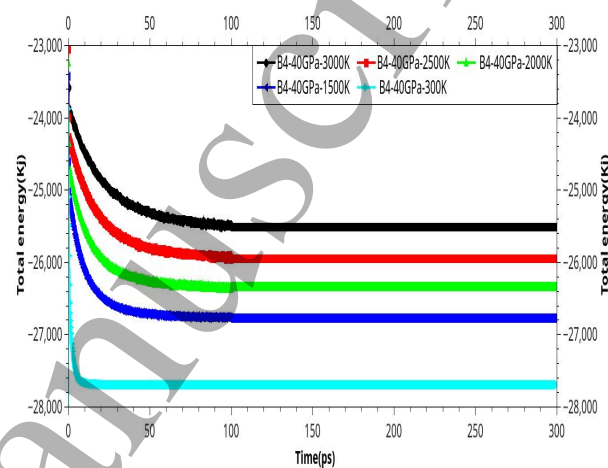


Figure12: evolution in time of total energy under 40 GPa and at 300-3000 K

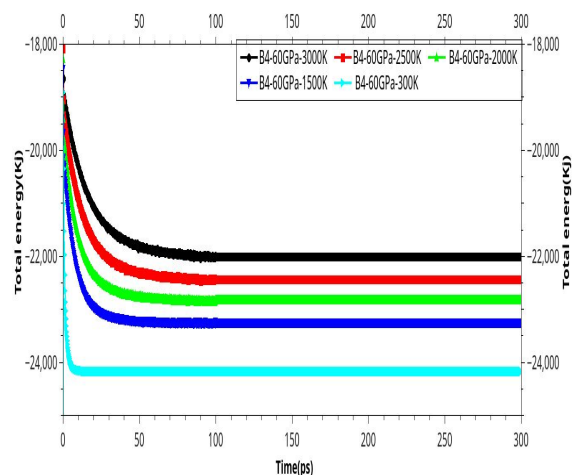


Figure 13: evolution in time of total energy under 60(GPa) and at 300-3000(K).

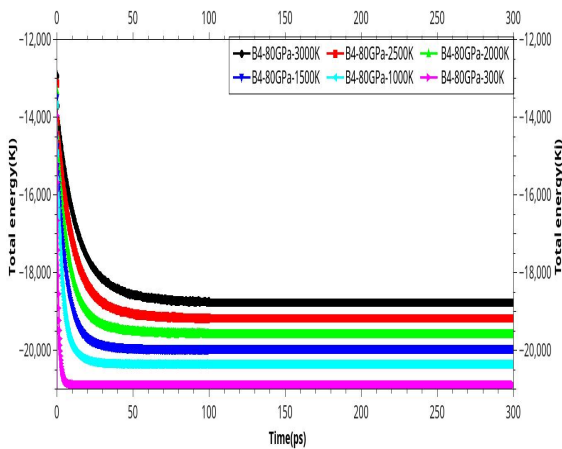


Figure 14: evolution in time of total energy under 80 GPa and at 300-3000 K.

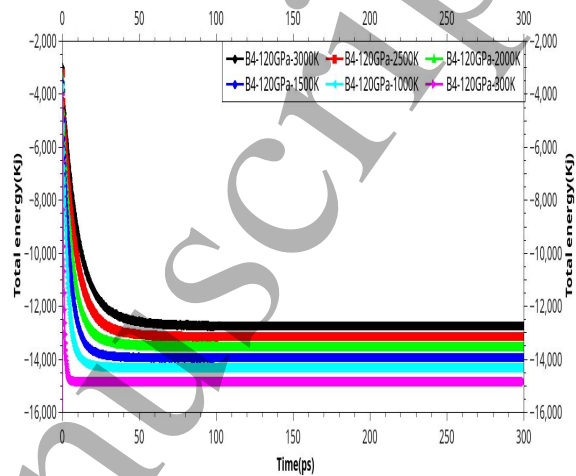


Figure 16: evolution in time of total energy under 120 GPa and at 300-3000 K.

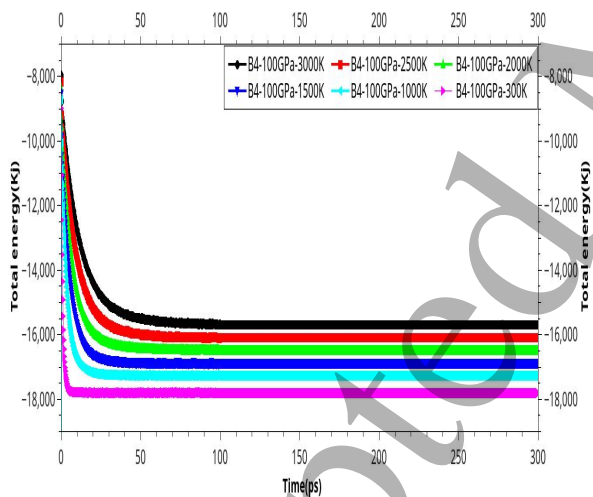


Figure 15: evolution in time of total energy under 100 GPa and at 300-3000 K

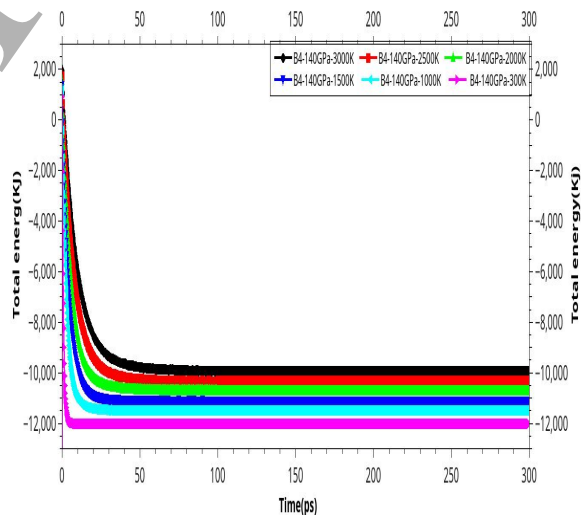


Figure 17: evolution in time of total energy under 140GPA and 300-3000K

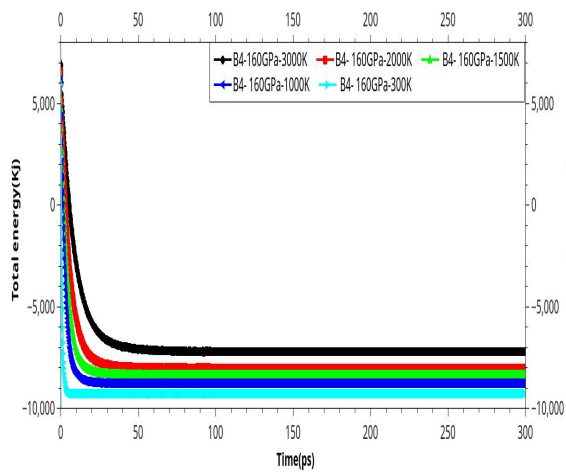


Figure 18: evolution in time of total energy under 160 GPa and at 300-3000 K

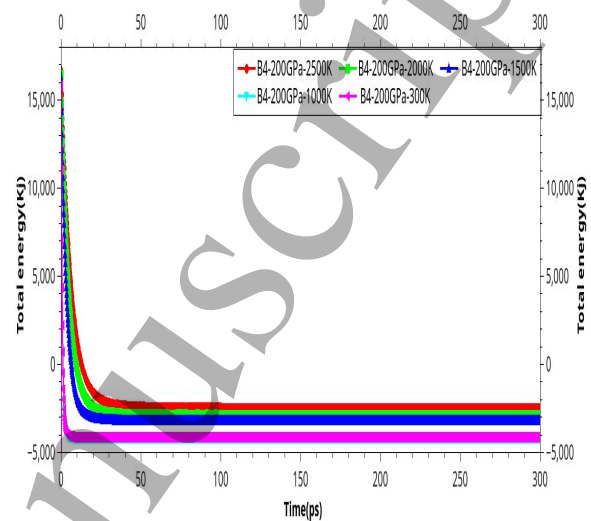


Figure 20: evolution in time of total energy under 200 GPa and at 300-3000 K

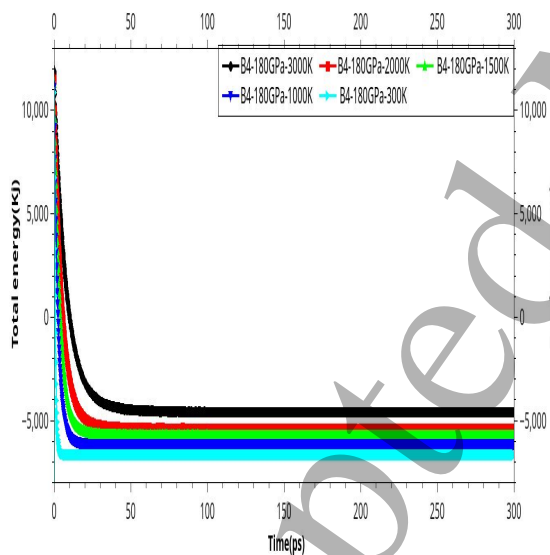


Figure 19: evolution in time of total energy under 180 GPa and at 300-3000 K

Our data are in agreement with available results⁵. The total energy increases with increasing the temperature and pressure, see Table 2.

| P(GPa) | 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 | -4.5 | -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 |

Table2: total energy of ZnO wurtzite structure under 40-200 GPa and 1500-3000 K

Figure 21 shows the equilibrium time versus pressure under the range of pressure 40-200 GPa and temperature of 1500-3000 K; under all temperatures, the curves converged under 40 GPa and 200 GPa approximately to the same values; 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 have the same variation due to the solid-liquid state. 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), which elucidated a phase transition^{5, 9, 11, 22}.

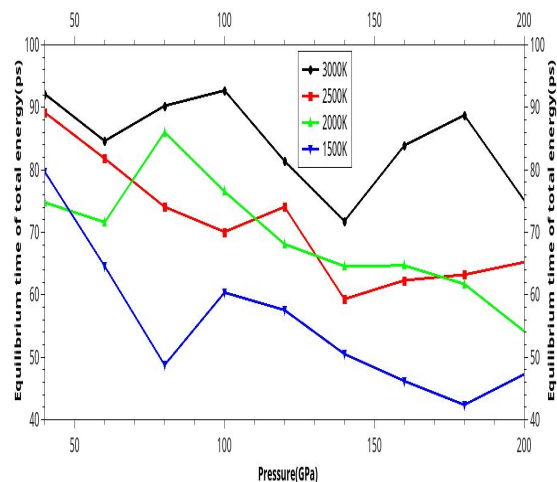


Figure 21: equilibrium time of total energy versus Temperature under low pressure (0-200 GPa) and temperature (1500 K) - 3000 K).

Table3 shows a comparison between our results and ZnO Wurtzite phase studied by common tangent method, and Enthalpy curves crossings (shown in parentheses)²²

| P_t | 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 B _k | 25 | 27.66(27.75) | | 24.35(24.65) | |
| B _k to B _h | -- | 30.6(30.2) | | 32.36(32.85) | |
| B _k to B _i | 17 | 12.19(12.13) | | 15.56(16.53) | |
| B ₈₁ to B ₂ | 180 | 196.05(195.70) | | 183.4(183.25) | |
| B _h to B ₂ | 80, 100, 140 | 156.05 | | 144.40 | |

Table3: Comparison between phase transition values and those found by LDA, GGA^[22] and other LDA/GGA^[14].

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-w, 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 method has an agreement with existing results of pressure transition; however, this 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.

Acknowledgments

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