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# Permanent densification of amorphous zinc oxide under pressure: A first principles study

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## ABSTRACT

Ab initio simulations within a generalized gradient approximation are carried out to investigate the densification mechanism of amorphous zinc oxide (a-ZnO) under hydrostatic pressure. In contrast to the crystalline ZnO, the densification of a-ZnO is found to proceed gradually and is associated with a structural modification from a low density amorphous state to a high density amorphous state. Accompanied by the phase transformation, the mean coordination number increases from  $\sim 4.0$  to  $\sim 5.5$ . The high-density amorphous form of ZnO has a local structure, partially comparable with that of the rocksalt type ZnO crystal and presents a semiconducting behavior. The phase change is irreversible because upon pressure release, an amorphous model largely consisting of fivefold coordination is recovered. The decompressed model can be, therefore, classified as an intermediate phase between the wurtzite-like and the rocksalt-like amorphous configurations.

## 1. Introduction

Zinc oxide (ZnO) has been drawing the attention of researchers for decades, particularly as a semiconductor material due to its low cost, high abundance and non-toxic nature [1] besides its wide direct bandgap ( $\sim 3.37$  eV at room temperature) makes this material a good alternative for the optoelectronic devices of short-wavelength [2]. Its piezoelectricity, good chemical properties in terms of stability and catalytic activity, optical and electrical properties also make ZnO a convenient candidate for other application areas such as micro sensors, transparent conductive oxides, catalytic use, and space applications [3,4]. In virtue of all these features, ZnO is an extensively studied material for the last decades, with a history going back to 1920s. Major part of all these studies involves the investigation of its physical, mechanical and electronic properties.

ZnO, a member of II–VI group of semiconductors, has a tendency to crystallize in the wurtzite (WZ) structure. Under hydrostatic compression, a structural phase transformation from the WZ crystal to a rocksalt (RS) structure occurs at around 10 GPa [5].

Some advantageous features of amorphous materials such as permitting economic manufacturing in large dimensions and having competitive characteristics with the crystalline ones bring a new point of view to the oxide semiconductor materials market [1]. Even though high quality ZnO crystals can be obtained in bulk form [6], the growth process of the crystalline ZnO films requires high temperatures around 500–800 °C, which is an important drawback against the amorphous

ZnO (a-ZnO) [2]. Higher cost to produce crystalline materials is also another factor to direct interest of the researchers on amorphous materials [6].

Although the properties, manufacturing methods and application fields of the crystalline form of the ZnO have been studied comprehensively, there are limited studies on the synthesis and characterization of a-ZnO [2,7,8] and thus there is a little known and a great unexplored space for a-ZnO in terms of its structure and properties.

In this study, the effects of high pressure treatment on the structure of a-ZnO are for the first time investigated using a constant pressure ab initio approach and a gradual irreversible amorphous-to-amorphous phase change is proposed for it.

## 2. Computational method

The initial a-ZnO model was generated by Drabold's group from the liquid state using a first principles molecular dynamics technique [9]. The amorphous model consists of 128 atoms (64 Zn atoms and 64 O atoms). For the crystalline ZnO, a supercell having 108 atoms was constructed. Both structures at zero pressure were optimized using the ab initio code SIESTA [10] within the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [11]. The Troullier and Martins scheme was used to contract pseudopotentials [12]. The double zeta plus polarized orbitals were chosen for the calculations. The simulations were executed within the isoenthalpic-isobaric (NPH) ensemble. The pressure optimization was achieved by the Parrinello

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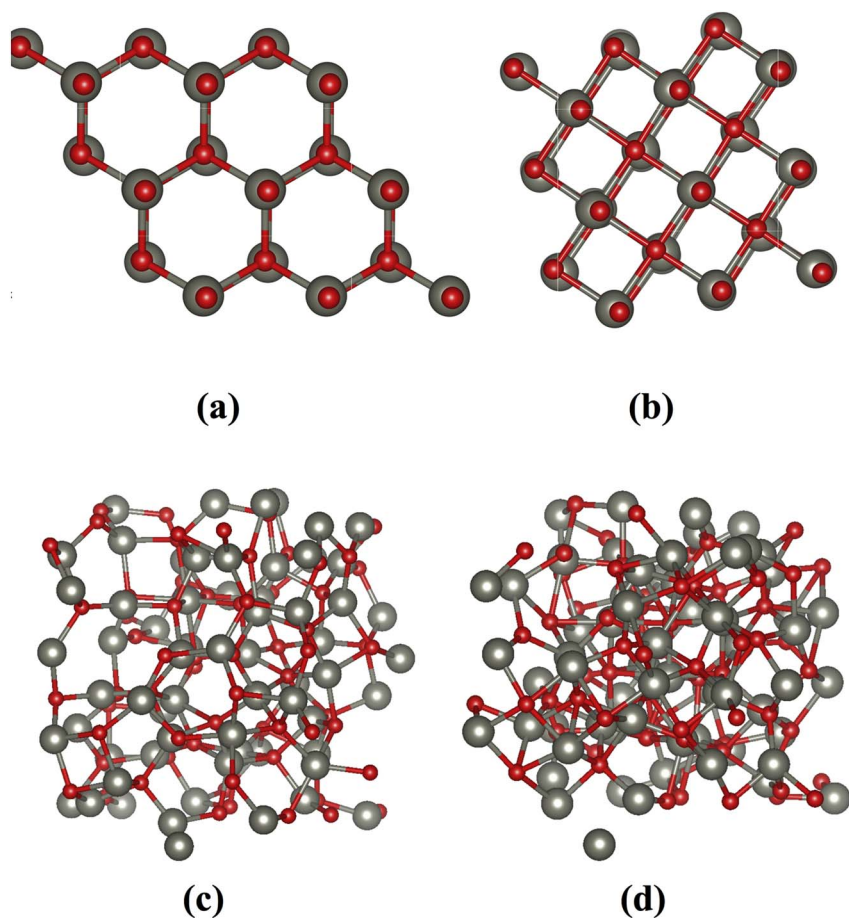


Fig. 1. Ball stick representation of (a) the WZ crystal (b) the RS structure obtained at 35 GPa, (c) the initial a-ZnO model and (d) the high coordinated amorphous phase at 54 GPa.

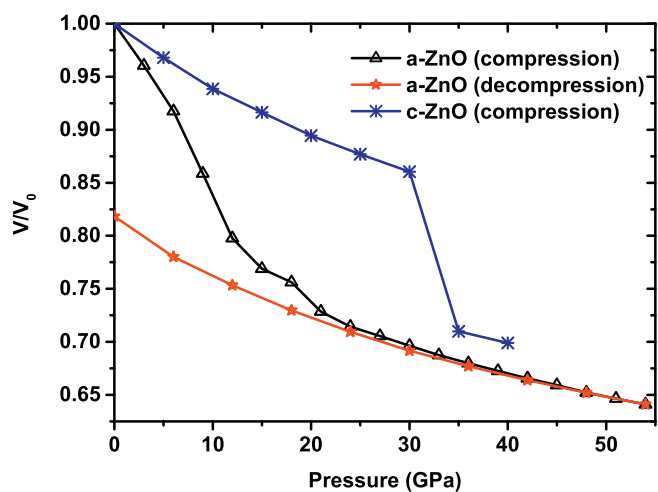


Fig. 2. Pressure volume relation of the crystalline phase under pressure and of a-ZnO on compression and decompression.

Rahman method [13]. The external pressure was gradually applied up to 54 GPa for a-ZnO using an increment of 3 GPa and up to 45 GPa using an increment of 5 GPa for the crystalline ZnO. The VESTA [14] program was used to visualize the structures.

### 3. Results

In order to verify that the parameters (pseudopotentials, basis, etc.) chosen in the simulations are trustworthy to investigate the high-pressure behavior of a-ZnO, first we test them for the WZ crystal. As

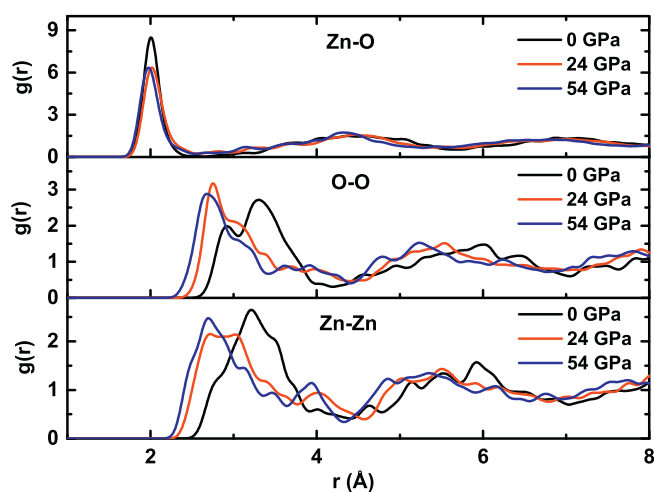


Fig. 3. Partial pair distribution functions at some pressures.

shown in Figs. 1 and 2, a phase transformation from the WZ crystal to a RS crystal at a theoretical pressure of 35 GPa with a first order nature is successfully observed throughout the simulation. This observation shows that the parameters used in the present work are good enough to capture the experimentally revealed phase transformation and hence they can be securely applied to a-ZnO. It should be noted here that the phase transformation from the WZ crystal to a RS structure in the simulation happens at an exaggerated critical pressure of 35 GPa, relative to the experimental value of 10 GPa. The overestimation in transition pressures is usually perceived in the Parrinello-Rahman dynamics [15,16] and can be linked to some limitations such as time scale, no

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