Computational study of rutile tin-oxide (SnO_2)

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Abstract. Rutile structured tin-oxide ceramics have been intensively studied in recent years because of their potential in sensing and fuel cells. The present work uses classical molecular dynamics simulations focused on the structure and possible transformation of rutile tin-oxide to other phases. The empirical Buckingham potential has been used to describe the interatomic interactions in tin-oxide. The total energy of the NPT hoover ensemble at various temperatures has been calculated in order to determine the transition temperature and pressure. The results obtained showed an energy increase with temperature which was constantly compared with experiments. The radial distribution functions for the two structures suggest the transformations at temperature above 900 K in agreement with the experiments.

1. Introduction

Metal-oxides like tin-oxide (SnO_2) are increasingly being used in the chemical, pharmaceutical, ceramic, and electronic industries. These materials can be synthesized using chemical and physical methods. The chemical methods include the sol-gel, whereas the physical methods involve vapor deposition. In both methods, the production of qualitative materials play a great role and is influenced by the interatomic interactions and the thermodynamics environment of the material. Molecular dynamics (MD) is often used together with these experimental methods to obtain the reliable method of synthesis.

SnO_2 is an attractive *n*-type semiconducting material with a wide band gap. It has outstanding applications due to its structural, electronic, optical, and chemical properties [1]. SnO_2 can be applied in catalytic reactions, in optoelectronic devices, in gas sensing, as an electrode for flat panel displays, and in solar cells. Under normal conditions SnO_2 crystallizes in tetragonal rutile structure, which belongs to the $P4_{2/mnm}$ space group. Experiments and calculations have shown that under high different pressures SnO_2 transforms from rutile to pyrite, to fluorite and then cotunnite structures.

This works intends to explore rutile SnO_2 and its kinetics through high pressure, high temperature environments. This can be attained by exploring the energy-temperature relations and the radial distribution functions effects in this material. It is apparent from Alvarez and Valladares [2] that the atomic topology also determines the electronic properties of the structured materials, and therefore any understanding of the RDF's and the atomic distribution is relevant in the characterization of the structural and optical properties of tin-oxide. In the process, information about the nanoparticle grain size and morphology necessary for the sensor application could be obtained. Sverjensky [3] has theorized that the bulk crystal and interfacial dielectric constant play an important role in controlling whether hydrated ions adsorb directly onto the oxide surface or form electrostatically adsorbed outer-sphere complexes, which is crucial in gas sensing.

In this work, structural and thermodynamic properties of rutile SnO_2, using the MD simulation based on the Buckingham empirical interatomic potential is being investigated. The RDF's of rutile

SnO_2 are also being investigated, specifically different temperature Sn-Sn, Sn-O, and O-O pair distributions.

2. Computational details

The DL_POLY package has been used to perform all the empirical bond-order molecular dynamics calculations of SnO_2. A supercell with a 4.41 Å cutoff, 1250 atoms, and a sufficiently large number grid points for the fast Fourier transformations (NGX = 32, NGY = 32, and NGZ = 24) has been used throughout the calculations. The controlled experimental crystal structure for bulk SnO_2 is according to Bolzan *et al*. [4]. The material as is used for the MD modeling is described by its lattice parameters as listed in Table 1, and a set of parameters required for the Buckingham potential are taken from AV Bandura *et al*. [5] and P Amstrong *et al*. [6].

Table 1 Lattice parameters and relative sites of anions and cations ina tin-oxide crystal lattice [6]

anions:						
cations:						

3. Results and discussion

A bulk SnO_2 in the rutile form was studied with the MD code as described in the previous section. In order to check the stability of rutile SnO_2 structure at various temperatures within the Buckingham potential, the pair distribution functions of are presented in Figure 1 and 2. From the peak positions positions, the most probable distances between the various atoms can be determined. In the 400 K temperature the peaks appear around 1.85, 2.15, and 3.65 Å, respectively for the Sn-O, O-O, and Sn-Sn bond-lengths, whereas at 900 K the peaks are around 1.85, 2.65, and a double peak around 3.85, 3.90 Å for the very same bond-lengths. A O-O, and Sn-Sn peak shifts at 900 K suggest a possible phase transformation which might occur in agreement with first principle calculations of Yanlu Li *et al*. [1].

Figure 3 shows the volume of rutile SnO_2 as a function of temperature. The simulation data was fitted to the polynomial functions of temperature as

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The thermal expansion coefficient is then calculated from the temperature derivative of the volume,

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The volume thermal expansion coefficient is determined from the above equation to be3.68×10^{-5} K^{-1}. Peercy and Morosin [7], have measured the volume thermal expansion of SnO_2 from 93 to 700 K using Raman spectroscopy to be 11.7×10^{-6} K^{-1}. It has also been noted that the volume-temperature data for the rutile SnO_2 is quite disordered. A huge difference could be associated with the choice of our Buckingham potential parameters for the SnO_2.

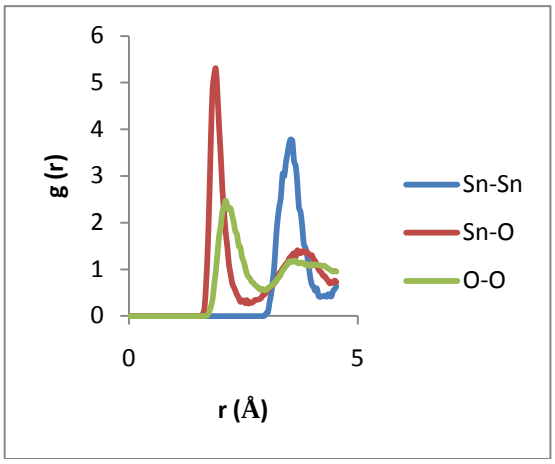

Figure 1 pair correlation function for rutile tin-oxide at 400 K.

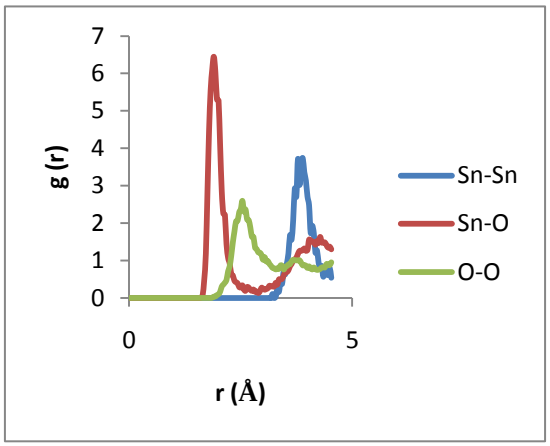

Figure 2 pair correlation function for rutile tin-oxide at 900 K.

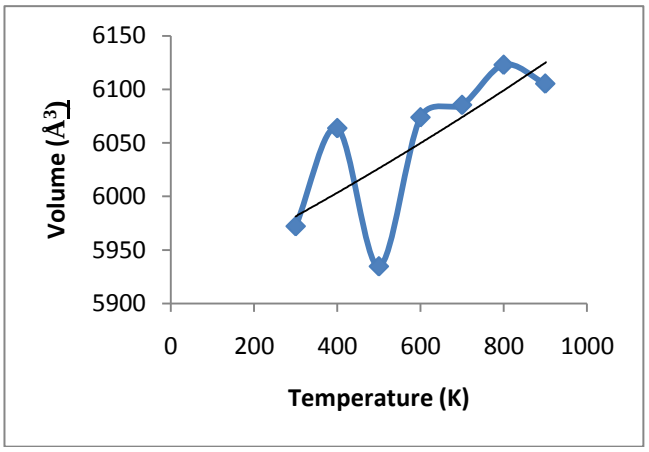

Figure 3 The rutile tin-oxide volume as a function of temperature.

4. Conclusions

The validity of the Buckingham empirical potential for rutile SnO_2 has been investigated using the structural and pair distribution analysis. The pair distribution functions suggest a possible phase transformation at high temperatures. The proposed Buckingham potential parameters for the rutile SnO_2 does not give conclusive results. The ionic nature of SnO_2 should be considered in future. The Sn-O bond appears rigid and constant at 1.85 Å in both temperature regions.

5. Acknowledgements

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