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Determination of the thermal stability and isothermal bulk modulus of the ZrO_2 polymorphs at room temperature by molecular dynamics with a semi-empirical quantum-chemical model

A.L. Ortiz [a,*], J. Sánchez-González [a], L.M. González-Méndez [b], F.L. Cumbrera [c]

[a] *Departamento de Electrónica e Ingeniería Electromecánica, Escuela de Ingenierías Industriales, Universidad de Extremadura, Badajoz 06071, Spain*
[b] *Departamento de Física, Centro Universitario de Mérida, Universidad de Extremadura, Mérida 06800, Spain*
[c] *Departamento de Física, Facultad de Ciencias, Universidad de Extremadura, Badajoz 06071, Spain*

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Abstract

We evaluated the thermal stability and isothermal bulk modulus of the cubic (c), tetragonal (t), and monoclinic (m) ZrO_2 polymorphs at room temperature by molecular dynamics with a semi-empirical quantum-chemical model. The procedure used was based on the semi-empirical calculation of the lattice energy of the different polymorphs as a function of the lattice volume, followed by fitting the Murnaghan equation of state to these lattice energy–volume curves. This yields directly the equilibrium lattice energy (E_0), the equilibrium lattice volume (V_0), and the bulk modulus (B_0). The monoclinic form ($E_0^{\mathrm{m}} = -119.41\,\mathrm{eV/ZrO_2}$) was found to be more stable than the tetragonal form ($E_0^{\mathrm{t}} = -119.29\,\mathrm{eV/ZrO_2}$), which in turn was more stable than the cubic form ($E_0^{\mathrm{c}} = -119.21\,\mathrm{eV/ZrO_2}$). We thence deduced the existence of the cubic–monoclinic and tetragonal–monoclinic phase transformations, and calculated the volume changes associated with these phase transformations (~3.9–4.5%) from V_0^{c}, V_0^{t}, and V_0^{m}. Also, we found that the bulk moduli of the ZrO_2 polymorphs are close to 200 GPa, and are in the sequence $B_0^{\mathrm{t}} > B_0^{\mathrm{c}} > B_0^{\mathrm{m}}$. All these results were in clear agreement with the literature data, obtained by complex ab initio molecular dynamics and/or sophisticated experimental techniques. This suggests that applications of molecular dynamics with semi-empirical quantum-chemical models may have an important role to play in the theoretical design of ceramic materials.

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1. Introduction

Determination of the thermal stability and bulk elastic properties (particularly of the bulk moduli) of ceramic materials is vital to understanding their thermomechanical behaviour under real-service conditions. It is not surprising, therefore, that the subject has been receiving much attention lately. Its relevance is not only to high temperatures where metals fail and have to be replaced by ceramics, but also at room temperature where ceramics have applications too. Traditionally, the thermal stability and bulk elastic properties of advanced materials have been most widely studied using fairly sophisticated experimental techniques, in particular, in situ diffractometry (X-ray, neutron, or electron beams) and thermal/differential thermal analysis for the thermal stability [1,2], and high hydrostatic pressure diffractometry (X-ray or neutron beams), sonic resonance, impulse excitation, and three- or four-point bending for the bulk moduli [3–7]. More recently, these two magnitudes have also been studied theoretically by fitting a suitable equation of state to either the pressure–volume curves or the lattice energy–volume curves, obtained previously by ab initio molecular dynamics.[1] Typical isothermal equations of state are those of Birch [8], Vinet et al. [9], Poirier and Tarantola [10], Murnaghan [11], and Holzapfel [12], inter al. The most

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* Corresponding author. Tel.: +34 924289600x6726; fax: +34 924289601.
E-mail address: alortiz@unex.es (A.L. Ortiz).

[1] The estimates obtained theoretically by ab initio molecular dynamics have been found to compare favourably with those obtained experimentally. For example, a bulk modulus of 195.3 ± 2 GPa has been found experimentally for ThO_2, and the generalized gradient approximation to the exchange correlation potential yields 198 GPa [6].

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widely used of these equations of state is that of Murnaghan [11]. It has the form:

$$E(V) = -E_0 + \frac{B_0 V}{B_0^{/}}\left[\frac{(V_0/V)^{B_0^{/}}}{B_0^{/}-1}+1\right] - \frac{V_0 B_0}{B_0^{/}-1} \qquad (1)$$

where $E(V)$ is the lattice energy per volume V, E_0 and V_0 are the coordinates of the minimum in the structural energy versus volume curve, and B_0 and $B_0^{/}$ are, respectively, the zero-pressure isothermal bulk modulus and its first derivative. The Murnaghan equation of state is derived under the assumption that the bulk modulus varies linearly with pressure, and is preferred over the others due to its simplicity. Note that Eq. (1) gives the bulk modulus of the material under study directly, and also provides the equilibrium lattice energy from which the thermal stability of the crystal structures can be deduced.

The lattice energy as a function of lattice volume for Eq. (1) is usually calculated from first principles through either the local density approximation [13] or the generalized gradient approximation [14] to density functional theory. Unfortunately, in both cases the time required for the calculations is too demanding computationally. To shorten the time-scale, semi-empirical quantum-mechanics methods have to be adopted. These methods couple a rigorous quantum-mechanics formulation with experimentally obtained empirical parameters, allowing one to simplify the most complex calculations (e.g., the integral for overlapping orbitals). Examples include the extended Hückel, complete neglect of differential overlap, intermediate neglect of differential overlap (INDO), modified neglect of differential overlap, inter al. Which method is chosen depends on the nature of the compound under study, in each case aiming to ensure sufficient accuracy in the estimates. Surprisingly in view of the evident interest in the thermo-mechanical characterization of materials, semi-empirical methods have met with limited use in the ceramics community.

In the present work, we use ZrO_2 as a model system to investigate the utility of molecular dynamics with a semi-empirical quantum-chemical model coupled with the Murnaghan equation of state in determining the thermal stability and bulk modulus of relevant ceramics. We chose ZrO_2 because: (i) it exhibits the phenomenon of polymorphism with three crystal variants (cubic, tetragonal, and monoclinic) of known thermal metastability [15]; (ii) it has crystal structures that depart from the classic ionic model for oxides with MO_2 stoichiometry and that can not be properly rationalized in terms of the ionic radius ratio[2] [16–18]; and (iii) it possesses interesting properties for structural and functional applications [15]. The distinguishing feature of our approach is the use of a semi-empirical method instead of ab initio methods to compute the lattice energy as a function of volume (the $E(V)$ curves), both parameters being per ZrO_2 molecule. Also, the calculations were done on a conventional personal computer, rather than a sophisticated work-station. The results will be compared with those given in the literature, and finally the implications resulting from the comparison will be discussed.

2. Method

The molecular dynamics calculations were done using the canonical ensemble (constant pressure and temperature), with a Verlet "leap-frog" time integration algorithm [20] and a Berendsen et al. thermostat [21]. In the latter, the instantaneous temperature is tuned to the setpoint temperature by rescaling the velocities of the atoms at each time step. The interactions between the atoms were described by the semi-empirical Z-INDO quantum-chemical model [22], which is an optimization of the INDO model for molecules with first or second transition row metals. The simulations were performed on a conventional personal computer, for 27 unit cells with three-dimensional periodic boundary conditions and at room temperature. The time for the complete simulation was 1.1 ps with a 0.1 fs the time step. In practice, the temperature and the total energy stabilized after 0.2 ps, and therefore the time-averaged lattice energy was evaluated only within the interval 0.2–1.1 ps.

To build the lattice energy–volume curves, the lattice energy was computed as a function of the lattice volume. The lattice volumes were obtained by varying the unit-cell volume isostatically around a reference volume taken from the literature [23]. The Murnaghan equation of state was then fitted by the Levenberg-Marquardt algorithm [24] to the resulting lattice energy–volume curves, yielding directly the parameters E_0, V_0, B_0, and $B_0^{/}$.

3. Results and discussion

Fig. 1 shows the lattice energy–volume curves (per ZrO_2 molecule) for the cubic, tetragonal, and monoclinic ZrO_2 polymorphs, and Table 1 lists the parameters of the corresponding fitted Murnaghan equations of state for the

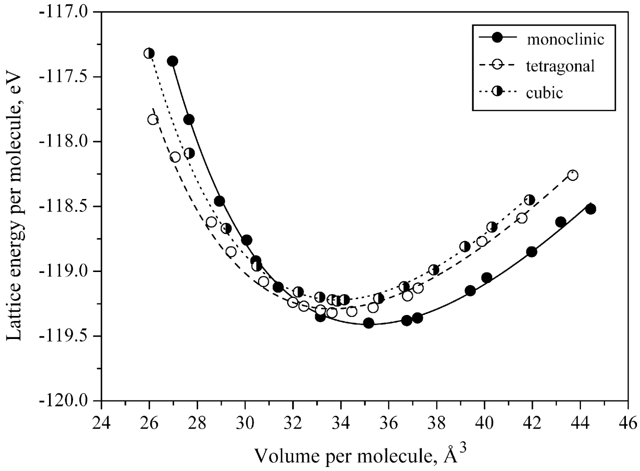

Fig. 1. Lattice energy as a function of the volume (both per ZrO_2 molecule) for the cubic, tetragonal, and monoclinic ZrO_2 polymorphs obtained at room temperature using molecular dynamics with the semi-empirical quantum-chemical model. The points are from the molecular dynamics calculations; the lines are the fits of the Murnaghan equation of state.

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[2] Note that the classical models predict the rutile structure as the ground state for ZrO_2 [19], contrary to experimental observations [15].

Table 1
Parameters of the Murnaghan equation of state for the cubic, tetragonal, and monoclinic ZrO_2 polymorphs at room temperature

ZrO_2 polymorph	Parameters of the Murnaghan equation of state			
	E_0 (eV/ZrO_2)	V_0 (Å^3)	B_0 (GPa)	$B_0^{/}$
Cubic	−119.21	33.851	199 ± 6	4.8 ± 0.2
Tetragonal	−119.29	33.632	207 ± 10	4.4 ± 0.3
Monoclinic	−119.41	35.161	192 ± 6	5.0 ± 0.1

sake of comparison. One observes that the energy of the equilibrium state is quite similar for the three polymorphs—the differences are less than 0.2 eV/ZrO_2 in ∼119 eV/ZrO_2. Nevertheless, despite the similarity, it is clear that the lowest equilibrium lattice energy corresponds to the monoclinic form ($E_0^{\rm m} = -119.41\,{\rm eV/ZrO_2}$), followed by the tetragonal form ($E_0^{\rm t} = -119.29$ eV/ZrO_2), and finally by the cubic form ($E_0^{\rm c} = -119.21\,{\rm eV/ZrO_2}$). One deduces, therefore, that the monoclinic form is stable at room temperature, whereas the cubic and tetragonal forms are not. The physical implication is that the unstable cubic and tetragonal forms will transform irremediably to the stable, monoclinic form. As deduced from Fig. 1 and Table 1, these phase transformations will necessarily be accompanied by expansion in volume, since the lattice volumes in the equilibrium states are $V_0^{\rm c} = 33.851$ Å^3, $V_0^{\rm t} = 33.631$ Å^3, and $V_0^{\rm m} = 35.161$ Å^3 for the cubic, tetragonal, and monoclinic forms, respectively. Taking these numbers, we calculated the volume expansions associated with the cubic–monoclinic and tetragonal–monoclinic phase transformations to be 3.9% and 4.5%, respectively. The physical significance of such expansions is that they will cause massive, spontaneous microcraking of the ceramic part, rendering the pure ZrO_2 components useless for many applications. Table 1 also gives the bulk moduli of the three ZrO_2 polymorphs. They are all close to 200 GPa, being highest for the tetragonal form ($B_0^{\rm t} = 207 \pm 10$ GPa), followed by the cubic form ($B_0^{\rm c} = 199 \pm 6$ GPa), and last the monoclinic form ($B_0^{\rm m} = 196 \pm 6$ GPa).

How do the present results obtained by molecular dynamics with a semi-empirical quantum-chemical model compare with the literature data? First, let us consider the thermal stability of the three ZrO_2 polymorphs. As mentioned above, we found that the relative energies were in the sequence $E_0^{\rm c} > E_0^{\rm t} > E_0^{\rm m}$, and thence predicted the existence of cubic–monoclinic and tetragonal–monoclinic phase transformations. This theoretical prediction is in clear agreement with the experimental evidence (obtained for example by X-ray diffractometry, Raman spectroscopy, and transmission electron microscopy, inter al. techniques) [15], which also lends support to our calculated estimates of the volume expansions for these phase transformations. In practice, these undesirable phase transformations are suppressed by retaining the unstable cubic and tetragonal phases down to room temperature. This is accomplished by doping the ZrO_2 crystal structures with such stabilizing oxides as Y_2O_3, CeO_2, MgO, and CaO, inter al. The doping induces defects within the crystal structures in the form of vacancies in the oxygen sublattice for charge compensation, and it is postulated that these defects help to reduce the lattice energy of the tetragonal and cubic forms below that of the monoclinic form, thereby reversing the sequence of thermal stability. To test this hypothesis, we are currently evaluating by molecular dynamics the lattice energy of the doped crystals as a function of the nature and proportion of doping. The relevance of the stabilization of the unstable tetragonal form is that the volume expansion associated with the tetragonal–monoclinic phase transformation is in practice exploited to enhance the fracture toughness of ZrO_2 components, known as the transformation toughening of the partially stabilized ZrO_2. The basis of this phenomenon is that the metastable tetragonal grains or precipitates transform in the vicinity of the cracks, and the corresponding local volume increase creates compressive stresses that act to close the cracks, thereby increasing the fracture toughness.

Second, let us consider the values of the equilibrium lattice energy of the three ZrO_2 forms. As we noted above, our calculations gave energy gaps associated with the monoclinic-tetragonal ($\Delta E_0^{\rm m-t}$) and tetragonal–cubic ($\Delta E_0^{\rm t-c}$) phase transformations of $\Delta E_0^{\rm m-t} = 0.12\,{\rm eV/ZrO_2}$ and $\Delta E_0^{\rm t-c} = 0.08\,{\rm eV/ZrO_2}$. These energy gaps have also been calculated theoretically by other workers using sophisticated ab initio molecular dynamics methods [25–27], with values in the ranges $\Delta E_0^{\rm m-t} = 0.049 - 0.061\,{\rm eV/ZrO_2}$ and $\Delta E_0^{\rm t-c} = 0.049 - 0.063\,{\rm eV/ZrO_2}$. The similarity between these literature values and our estimates is evident, the differences being only of the order of the intrinsic accuracy of the method used in the present study (see the Appendix A for details). Of course, the ab initio molecular dynamics estimates are expected to be slightly different and more accurate than the estimates obtained using molecular dynamics with semi-empirical quantum-chemical models. Nonetheless, the latter picks up the energy trends well, while reducing computation times by several orders of magnitude due to the parameterization of the force field.

Third, let us consider the values of the equilibrium lattice volume of the three ZrO_2 forms. As we indicated above, our calculations gave lattice volumes for the cubic, tetragonal, and monoclinic polymorphs of 33.851 Å^3, 33.632 Å^3, and 35.161 Å^3, respectively. These lattice volumes have also been measured experimentally by other workers, with values of 33.69 Å^3 [28], 33.58 Å^3 [29] and 35.06 Å^3 [30], respectively. Therefore, our estimates differ from the experimental values by less than 0.5%, which is evidence that the molecular dynamics with semi-empirical quantum-chemical models has high potentiality and utility.

Forth, let us consider the bulk moduli of the three ZrO_2 polymorphs. As mentioned above, we found that the magnitudes of the bulk moduli are in the sequence $B_0^{\rm t} > B_0^{\rm c} > B_0^{\rm m}$. A literature survey showed the experimentally determined bulk moduli of the cubic, tetragonal, and monoclinic forms to lie within the ranges 181 ± 9 GPa, 187 ± 8 GPa, and 169 ± 10 GPa, respectively [31–34]. The relatively large dispersion of these experimental bulk moduli reflects the variety of techniques used in their determination, including sonic resonance, four-point bending, impulse excitation, or simply from the elastic modulus (E) and Young's modulus (ν) using the expression $B_0 = E/(3–6\nu)$. The literature data thus indicate that the bulk modulus of the tetragonal form is higher than that of the cubic form (by a factor of 1.03), which in turn is higher than that of the monoclinic form (by a factor of 1.07). Clearly, our theoretical molecular dynamics analysis captured that trend in the bulk moduli well (factors of 1.04 in both cases). The differences between our theoretical results and the experimental data are only 10% to 13.6%, reduced to 1% to 3.9% if the dispersion in the experimental bulk moduli is taken into account. These discrepancies in the bulk moduli are of the same order of magnitude than the intrinsic accuracy of the lattice energies from which they were calculated. More importantly, the marked similarity between the two sets of data indicates that the calculations conducted by molecular dynamics with semi-empirical quantum-chemical models could be especially useful for estimating the elastic properties of novel compounds when there is no access to the appropriate experimental facilities. Finally, we would note that the bulk modulus of the cubic form has been estimated to be 204 GPa in an ab initio molecular dynamics calculation using density functional theory [19], where our estimate was 199 ± 6 using molecular dynamics with a semi-empirical quantum-chemical model. As was the case with the lattice energies, for the bulk moduli too there is clear agreement between the two theoretical analyses.

In sum, the trends in the lattice energies and bulk moduli inferred from the present molecular dynamics analysis with the semi-empirical quantum-chemical model agreed with those obtained by ab initio molecular dynamics and/or experimental techniques. The implication is, therefore, that using molecular dynamics with semi-empirical quantum-chemical models such as in the present study should provide an unprecedented opportunity: (i) to determine the elastic properties of ceramics which are otherwise difficult to measure, and (ii) to estimate the thermal stability of the crystal structures of ceramic compounds that have different crystallographic variants. Since these are important parameters to take into account under real-service conditions, molecular dynamics with semi-empirical quantum-chemical models may well provide important guidance for the future theoretical design of ceramic components.

4. Concluding remarks

We investigated the lattice energy, thermal stability, and bulk modulus of ZrO_2 polymorphs at room temperature via calculations conducted by molecular dynamics with a semi-empirical quantum-chemical model. The sequence of equilibrium lattice energies was found to be $E_0^c > E_0^t > E_0^m$, whence it was deduced that the monoclinic form is stable whereas the cubic and tetragonal forms are not. We also found that the cubic–monoclinic and tetragonal–monoclinic phase transformations are accompanied by volume expansions of about 3.9% and 4.5%, respectively. The calculated values of the bulk moduli of the ZrO_2 polymorphs were all close to 200 GPa, in the sequence $B_0^t > B_0^c > B_0^m$. The results of the present study were in agreement with the literature values obtained by ab initio molecular dynamics or experimental techniques. The clear advantage of the molecular dynamics with semi-empirical quantum-chemical models over other alternatives is that it uses only modest computational resources and involves no experimental facilities. Molecular dynamics with semi-empirical quantum-chemical models could, therefore, be especially useful for the preliminary thermomechanical characterization of novel, advanced ceramics.

Appendix A

To evaluate the intrinsic accuracy of the molecular dynamics with the semi-empirical quantum-chemical model used in the present work, we estimated the lattice energy of NaCl according to the procedure described in the experimental section, and then compared the resulting estimate against other theoretical and experimental estimates. The reason for the choice of NaCl was that its lattice energy can be calculated directly via the Kapustinskii formula [35], which does not require knowledge of the Madelung constant. The Kaputinskii formula is:

$$E \approx 12.582\frac{\kappa z_c z_a}{r_c + r_a}\left(1 - \frac{0.345}{r_c + r_a}\right) \qquad (2)$$

where E is the lattice energy (in eV/molecule), κ the number of ions in the chemical formula, r_c and r_a are the ionic radii of the cation and anion (in Å), and z_c and z_a are their expected atomic charges (oxidation states). Fig. 2 shows the temporal evolution (0.2–1.1 ps) of the lattice energy for NaCl, from which one determines the time-averaged lattice energy of −7.93 ± 0.01 eV/NaCl. The Kaputinskii formula yields −7.81 eV/NaCl [36], whereas the estimates obtained by other workers theoretically using ab initio molecular dynamics or experimentally using the Born–Haber cycle are 8.32 eV/NaCl [36] and −7.93 eV/NaCl [37], respectively. Thus, the intrinsic accuracy of this molecular dynamics with the semi-empirical quantum-chemical model seems to be about 0.1–0.4 eV/molecule.

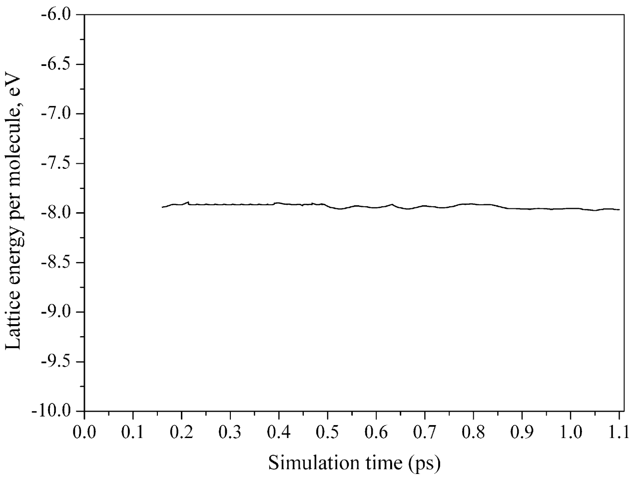

Fig. 2. Temporal evolution (0.2–1.1 ps) of the lattice energy for NaCl obtained at room temperature from molecular dynamics with the semi-empirical quantum-chemical model.

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