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Modeling the structure of zircon ($ZrSiO_4$): empirical potentials, ab initio electronic structure

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Abstract

In this paper the ability of two complementary simulation approaches to reproduce the structure of crystalline zircon is assessed. The first approach based on Born–Mayer–Huggins empirical potential reproduces within 5% the characteristics of each of the zircon phases, but not their relative stability. The second one, namely ab initio electronic structure calculations, reproduces with better than 1% agreement the structural properties of zircon. The relative stability of the phases is correctly simulated as well. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Zircon has raised considerable interest in the nuclear industry and in geological circles, as one of the new crystalline matrices currently investigated for the disposal of long-lived actinides – notably in US, where it is being considered for disposal of weapons-grade plutonium [1]. Zircon is an extremely durable and resistant material with the added capability of accommodating a large quantity of actinides, which are substituted for zirconium atoms. Its structure and behavior under irradiation have been investigated in many experimental studies [2,3].

A theoretical approach to the problems raised by this oxide as a disposal medium from the standpoint of material science requires several complementary methods. Either empirical potentials or ab initio electronic structure methods may be used, depending on the physical phenomenon. Irradiation effects involving a very large number of atoms can only be studied by classical methods such as molecular dynamics, for example, while only a detailed study of the electronic structure can accurately describe the dopant charge state and the structural modifications induced by doping.

In order to determine the validity ranges of these two approaches to atomistic modeling for zircon, we have examined their capability to reproduce the structure of zircon as observed experimentally.

2. Structure

Zircon comprises an arrangement of SiO_4 tetrahedrons and ZrO_8 dodecahedrons. Two different arrangements corresponding to two distinct phases are observed depending on the pressure. In neither phase are the SiO_4 tetrahedrons interlinked. The structure of zircon thus resembles that of garnet [4]. In the low-pressure phase the Bravais lattice is tetragonal body-centered with a 12-atom cell. The space group is $I_{4_1/\mathrm{amd}}$ ($D_{4\mathrm{h}}^{19}$). Zircon is the prototype of a mineral family with the same structure. The high-pressure phase exhibits a scheelite structure; the Bravais lattice is also tetragonal body-centered, with the same number of atoms as in the low-pressure lattice. The space group is $I_{4_1/a}$ ($D_{4\mathrm{h}}^{6}$) [5].

The high-pressure phase occupies some 10% less volume than the low-pressure phase. The phase transition has been observed experimentally by applying hydrostatic pressure at various temperatures between 300 and 1000 K [6,7] and under the effect of shock

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Table 1
Interatomic distances and angles calculated from empirical potentials compared to experimental values (in parentheses)

	Si–O distance	Zr–O distance	O–Si–O angle
Low pressure	1.59 Å (1.62)	2.16 Å (2.13) 2.36 Å (2.27)	101° (97°) 113° (116°)
High pressure	1.63 Å (1.65)	2.18 Å (2.13) 2.27 Å (2.26)	105°(101°) 112° (114°)

experiment [8]. The hydrostatic pressure measured at the transition point ranges from 10 to 20 GPa.

3. Empirical potentials

The empirical potentials used in this study are Born–Mayer–Huggins (BMH) potentials corresponding to the following formula:

$$\phi(r_{ij}) = A_{ij}\ \exp\left(-\frac{r_{ij}-\sigma_i-\sigma_j}{\rho_{ij}}\right)+\frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}.$$

In order to assess the applicability of these potentials to zircon, we investigated the stability of both phases using molecular dynamics and the structure obtained by rapid quenching. The study considered groups of 5184 atoms containing 432 tetragonal body-centered cells of 12 atoms each. The parameters were assigned the numeric values determined by Delaye and Ghaleb [9] in their study of glasses, except for σ_{Zr}. The parameters associated with silicon and oxygen ions are well known.

The σ_{Zr} parameter was adjusted through repeated quick quenching of the experimental low-pressure zircon structure. An additional requirement was that the molecular dynamic calculations at a 'reasonable' temperature – i.e. below the temperature (about 1750 K) at which the material decomposes to form ZrO_2 and SiO_2 – preserve the crystalline structural properties. The repulsion around the zirconium ions was therefore diminished by reducing the σ_{Zr} parameter value from 1.45 to 1.31.

The interatomic distances and angles obtained by fast quenching of the experimental structure are indicated in Table 1, where it may be noted that the Zr–O distances are overestimated and the Si–O distances underestimated. The calculated O–Si–O angles are closer to those of an ideal tetrahedron (109°) than the experimentally observed angles.

Moreover, regardless of the simulation temperature between 300 and 1750 K, structural amorphization was not observed at the simulation time scale (4×10^{-12} s). However, when the repulsion value was diminished around the Zr ions, amorphization occurred quickly irrespective of the temperature. Maintaining the crystalline structure at high temperatures thus required the use of parameter values that slightly overestimate the Zr–O distances (Table 1).

After optimizing the parameter values as above, the crystal energy was calculated for different elementary cell volumes. The zero-pressure equilibrium volume corresponding to the minimum point on the calculated energy/volume curves (Fig. 1) is indicated for both phases in Table 2. As atmospheric pressure is very near zero compared with the phase transition pressure, the calculated zero-pressure equilibrium volumes can be compared with the experimental ambient-pressure volumes; the resulting agreement was satisfactory for both phases.

The bulk modulus determined using Murnaghan's formula [10] is indicated in Table 2 for the low-pressure phase; the value is relatively consistent with the experimental finding.

The relative positions of the two calculated energy/volume curves indicate that the denser scheelite phase is more stable at ambient and higher pressures. Experimentally, however, this phase is stable only at pressures exceeding 10–20 GPa; the relative stability of the two phases is thus not reproduced.

4. Ab initio electronic structure

These calculations were performed from the standpoint of density functional theory in the local density approximation (DFT-LDA) [11]. In this formalism, the electronic Hamiltonian comprises the interaction between electrons and nuclei, the (classical) Coulomb interaction between electrons, and their (quantum) exchange and correlation interactions calculated approximately as a function of the local electronic density. We used the Ceperley–Alder exchange and correlation function [12]. Among the various DFT-LDA calculation procedures we chose to use the plane wave method, which easily yields the forces acting on the atoms after calculating the electronic wave functions. The calculations were performed using the plane wave self-consistent field (PWSCF) code in collaboration with the European Center for Atomic and Molecular Computations (CECAM [1]).

Pseudopotentials were required for silicon, oxygen and zirconium in order to deal properly with zircon. We used the pseudopotential generated by Car [13] for sili-

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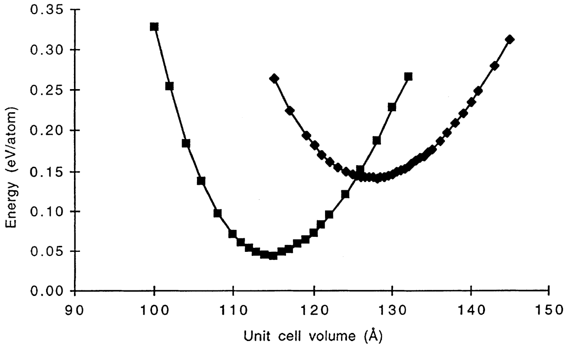

Fig. 1. Energy/volume curves calculated from empirical potentials (diamonds and squares correspond to low-pressure and high-pressure phases, respectively).

con, and the Trouillier–Martins (TM) pseudopotential [14] obtained by Vast [15] for oxygen.

The problem was more difficult for zirconium. In order to determine the appropriate pseudopotential we tested various metallic zirconium and zircon structures. Pure zirconium crystallizes into three different structures: hexagonal compact (hcp), ω and body-centered cubic (bcc). The stable phase at atmospheric pressure is the hcp phase, with a volume of 22.3 Å^3 per atom. As the pressure increases, the ω phase forms at about 2 GPa, and the bcc phase at about 30 GPa. According to a detailed ab initio study of these three phases [16], the energy differences between them are extremely slight; at ambient pressure the authors indicate 0.2 mRyd (2.7 meV) per atom between the hcp and ω phases, and about 10 mRyd (0.1 eV) per atom between the hcp and bcc phases.

The electronic configuration of an isolated zirconium atom is [Kr]$4d^2 5s^2$. The pseudopotentials taken from the Bachelet–Hamman–Schlüter (BHS) tables [17] yielded equilibrium volumes 20% greater than the experimental values for both metallic zirconium and zircon. This was also the case for all pseudopotentials based on the 4d, 5s and 5p orbitals that we tested, including those allowing for the effects of partial core correction [18].

Considering the 4s and 4p orbitals in the zirconium valence states provided much better results. We used a TM pseudopotential calculated from the Zr^{2+} ion in the ([Ar]$3d^{10}$)$4s^2 4p^6 4d^2$ configuration with cutoff radii of 1.35 (4s orbital), 1.45 (4p) and 1.55 (4d) provided by Giannozzi [19].

Generally satisfactory results were obtained with metallic zirconium. The calculated equilibrium volumes (21.5 Å^3 for the hcp and ω phases and 20 Å^3 for the bcc phase) were consistent with other experimental and calculated values [16], although the relative phase stability was not accurately reproduced: at zero pressure the order of increasing stability was $\omega \rightarrow$ hcp $\rightarrow$ bcc (the order of the first two phases was reversed). However, considering the slight energy difference (some 2.7 meV per atom between the ω and hcp phases) these results were sufficient to warrant testing this pseudopotential on zircon.

For zircon, the calculations were performed on 12-atom elementary cells, using six k points determined by the Monkhorst–Pack method [20] to sample the irreducible Brillouin zone. The cutoff energy was 95 Ryd (the 4s and 4p orbitals are very sharp, and require a high cutoff value). The calculated energy/volume curves are shown in Fig. 2; the equilibrium volumes and the bulk modulus of the low-pressure phase (Table 3) were in excellent agreement with the experimental findings, and the relative stability of the phases was correctly reproduced in this case. The calculated phase transition pressure of 5 GPa was in satisfactory agreement with the measured values of about 10 GPa.

As the plane wave method is capable of calculating the forces exerted on the atoms, we were able to optimize the elementary cell arrangement by minimizing the total system energy according to the atom positions in the cell. The results (Table 4) once again demonstrate very good agreement between the theoretical and experimental findings.

5. Discussion

The empirical potential model yields satisfactory results for each of the isolated phases. The interatomic distances and angles are satisfactorily accounted for, as are the equilibrium volumes at atmospheric pressure. The resulting structures are stable from a molecular dynamic standpoint. The energy/volume curves for each phase provide very satisfactory equilibrium volume and low-pressure bulk modulus values for calculations using empirical parameters. However, the BMH potentials introduce a very significant error on the relative stability of the two phases. This predictive error may be analyzed by considering the Si–O–Si angles of the SiO_4 tetrahe-

Table 2
Equilibrium volumes and bulk modulus: empirical potentials versus experimental values

Low-pressure equilibrium volume	High-pressure equilibrium volume	Low-pressure bulk modulus
127 Å^3 (130)	115 Å^3 (116)	167 GPa (225)

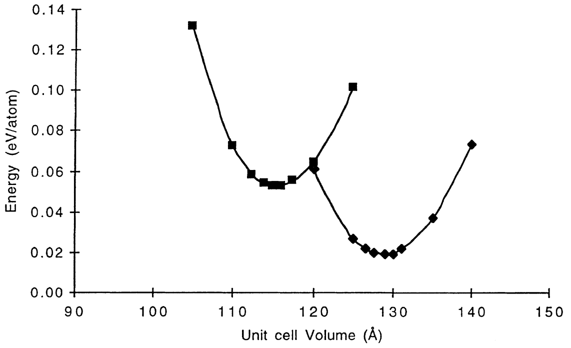

Fig. 2. Energy/volume curves calculated ab initio (diamonds and squares correspond to low-pressure and high-pressure phases, respectively).

drons. Experimentally, the tetrahedrons are distorted: the O–Si–O angles tend to deviate from the ideal value of 109°. As noted in Table 3, the BMH potentials tend to minimize the distortion; this is logical, as the BMH potentials favor the most symmetric possible configuration for an isolated tetrahedron. For the two zircon phases, the low-pressure tetrahedrons show greater distortion than those of the high-pressure phase; not unexpectedly, therefore, the scheelite phase (with the most symmetrical tetrahedrons) is artificially stabilized by the BMH potentials compared with the zircon phase. This error cannot be corrected by assigning an empirical three-body term to the silicon atoms, as this term is added to favor a symmetrical arrangement of the SiO_4 tetrahedron. The result would be the opposite of the desired effect, as the symmetrical tetrahedrons are already favored by the potentials used.

Very satisfactory results – much better than with empirical potentials – were obtained with ab initio electronic structure simulations. The relative phase stability was correctly reproduced, and the predicted phase transition pressure was in satisfactory agreement with the measured value. The interatomic angles and distances are reproduced with better than 1% precision, compared with 5% for empirical potentials. Note that the 4s and 4p electrons must be taken into account in the zirconium valence states, increasing the number of electrons in the calculations from 4 to 12 per zirconium atom. In addition, the cutoff energy must be increased since the 4s and 4p orbitals are much sharper than the outer zirconium orbitals. These two factors severely penalize the run time, making it illusory to consider more than twenty or thirty atoms with currently generation of computers. Allowance for a larger number of atoms would require the use of pseudopotentials involving fewer plane waves, such as ultrasoft pseudopotentials [21].

6. Conclusions

The validity domain of BMH empirical potentials was delimited for crystalline zircon, and the interatomic distances and angles were reproduced within 5%. The properties of each of the individual phases were correctly reproduced, but not their relative stability. Nevertheless, in view of the satisfactory reproduction of the interatomic and angular distances as well as equilibrium volumes, we consider that these potentials can be used for molecular dynamics simulations of this material to investigate its behavior under the effect of α decay [22]. The wrong relative stability of the two crystalline phases should not be a problem in this case as it is known from experiment that the scheelite is not involved in the α decay induced amorphisation process. Moreover we have checked that the amorphized material has an higher energy than the crystalline one, the energy difference being in agrement with experimental results (see Ref. [22] for details).

Ab initio calculations accurately reproduce the structural properties of zircon, with better than 1% agreement on the interatomic distances and angles. The relative stability of the phases is correctly simulated as well. The 4s and 4p semi-core states were found to be important in the electronic structure of zirconium compounds.

Table 3
Equilibrium volumes and bulk modulus: calculated ab initio versus experimental values

Low-pressure equilibrium volume	High-pressure equilibrium volume	Transition pressure	Low-pressure bulk modulus
129 $Å^3$ (130)	116 $Å^3$ (116)	5G Pa (10)	245 GPa (225)

Table 4
Interatomic distances and angles calculated from ab initio electronic structure compared to experimental values (in parentheses)

	Si–O distance	Zr–O distance	O–Si–O angle
Low pressure	1.63 Å (1.62)	2.11 Å (2.13) 2.26 Å (2.27)	96° (97°) 117° (116°)
High pressure	1.63 Å (1.65)	2.18 Å (2.13) 2.27 Å (2.26)	102° (101°) 113°(114°)

With this background, we can now begin an investigation of point defects in the zircon lattice, such as the substitution of a plutonium ion for a zirconium ion, or the existence of an oxygen vacancy.

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