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Citation: JOLLEY, K., ASUVATHRAHMAN, R. and SMITH, R. 2017. Inter-atomic potentials for radiation damage studies in CePO₄ monazite. Nuclear Instruments and Methods B, 395 (Feb), pp.93-96.

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Metadata Record: https://dspace.lboro.ac.uk/2134/22991

Version: Published

Publisher: © The Authors. Published by Elsevier B.V

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Inter-atomic potentials for radiation damage studies in CePO$_4$ monazite

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**Abstract**

An original empirical potential used for modelling phosphate glasses is adapted to be suitable for use with monazite (CePO$_4$) so as to have a consistent formulation for radiation damage studies of phosphates. This is done by adding a parameterisation for the Ce–O interaction to the existing potential set. The thermal and structural properties of the resulting computer model are compared to experimental results. The parameter set gives a stable monazite structure where the volume of the unit cell is almost identical to that measured experimentally, but with some shrinkage in the $a$ and $b$ lengths and a small expansion in the $c$ direction compared to experiment. The thermal expansion, specific heat capacity and estimates of the melting point are also determined. The estimate of the melting temperature of 2500 K is comparable to the experimental value of 2318 ± 20 K, but the simulated thermal expansion of $49 \times 10^{-6}$ K$^{-1}$ is larger than the usually reported value. The simulated specific heat capacity at constant pressure was found to be approximately constant at 657 J kg$^{-1}$ K$^{-1}$ in the range 300–1000 K, however, this is not observed experimentally or in more detailed ab initio calculations.

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**1. Introduction**

One of the challenges in nuclear energy technology is the immobilisation (in a durable host matrix) of high level radioactive waste (HLW), arising from the reprocessing of spent nuclear fuel. The radioactive elements in HLW have a very long half-life [1] and therefore they must be isolated from the biosphere for several thousand years. Monazite (the lighter rare-earth (La to Gd) orthophosphate, RPO$_4$) is a natural mineral known to exist for billions of years with appreciable amounts of the radioactive elements U and Th [2]. Monazites also possess excellent thermal stability and chemical durability [3]. These facts lead to the suggestion that analogues of monazite could be a potential host for the immobilisation of HLW [4,5]. Recently, it was reported that Ca doped CePO$_4$ can be a versatile matrix for the immobilisation of HLW due to the mixed valence character of Ce in this compound [6,7]. The thermophysical properties of monazite were also reported by us [8,9].

Due to the excellent stability of monazite and its ability to retain U, Th and Pb, it is used in geochronology [10]. Monazites are also used in synthesising machine ceramics [11], as support for catalysts [12] and as proton conductors [13]. Monazite is compatible with hundreds of minerals including alumina [14] and is therefore used in ceramic–ceramic composites and thermal protection coatings [15].

The crystal structure of monazite (CePO$_4$) is monoclinic [16] (P21/n, No.14) with four formula units per unit cell. It consists of a network of CeO$_5$ polyhedra and PO$_4$ tetrahedra. The CeO$_5$ polyhedra have an interpenetrating CeO$_7$ pentagon and CeO$_4$ tetrahedra. The Ce-O and P-O bond lengths are all different and therefore the CeO$_5$ polyhedra and PO$_4$ tetrahedra are highly distorted. Along the $c$-axis the CeO$_5$ polyhedra and PO$_4$ tetrahedra share edges and form chains and there are four such chains per unit cell.

There are several reports available in the literature on the computer simulation of monazite (rare-earth orthophosphates). Most computer simulation work has been performed using ab initio methods such as density functional theory (DFT). Kowalski et al. [17] investigated the heat capacities of lanthanide and actinide monazite-type ceramics using first principles calculations and more recently have computed the excess thermodynamic properties and the elastic moduli for a series of monazite-type single substitution solid solutions [18]. Experimental measurements of the heat capacity of CePO$_4$ have been reported by Thiriet et al. [19].

DFT calculations of the structural parameters have been performed by Rustad [20] and Blanca-Romero et al. [21]. Rustad [20] also performs electronic structure calculations using DFT to estimate the formation enthalpies of monazites. Feng et al. [22] study the thermal conductivity, heat capacities, and expansion...
coefficients of monazite-type REPO₄ (RE = La, Ce, Nd, Sm, Eu and Gd) from first-principles. The thermodynamic mixing properties computed using DFT of monazite-type solid solutions were reported by Li et al. [23]. Wang et al. [24] report the elastic stiffness of LaPO₄ monazite calculated using the first-principles plane-wave pseudopotential total energy method. The shear modulus of LaPO₄ is reported to be relatively small and it is explained that the weak La–O covalent bonds accommodate inhomogeneous shear strain locally leading to intrinsic low shear resistance.

Grechanovskya et al. [25] investigated the radiation resistance of monazite LaPO₄ and zircon YbPO₄ using molecular dynamics methods and report that LaPO₄ monazite is more radiation resistant than YbPO₄ zircon. The theoretical prediction of bonding characteristics, thermal expansibility and compressibility of rare-earth phosphates and arsenates are reported by Li et al. [26]. Chemical bond theory using a dielectric description was used in the computer simulation. It is reported that the lattice energies, thermal expansion coefficients and bulk moduli vary linearly with the ionic radii of lanthanides for both the monazite and zircon structure.

In the present work an attempt is made to produce an empirical interatomic potential for CePO₄ monazite in order to have a model that will be also suitable for large scale radiation damage studies across a wide range of phosphate materials. In doing the fitting to the monazite crystal structure we also calculate the thermophysical properties of CePO₄ predicted by this model, and compare with the experimental values.

Section 2 briefly outlines the computational methods used and the potential fitting. Then in the following Section (3), the results are presented and discussed. Finally we present our conclusions in Section 4.

2. Methodology and potential fitting

The computer simulations are performed using classical molecular dynamics (MD) with fixed charge potentials. This work builds upon previous work on iron phosphate glass and crystals [27–29]. Only a brief overview of the methods are presented here, while full details can be found in the original papers.

The pairwise interactions are modelled using the Buckingham potential (Eq. 1).

\[
\Phi(r_{ij}) = A_{ij} \exp \left(-\frac{r_{ij}}{\rho_q}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}
\]

The parameters \( q_i \) and \( q_j \) that appear in the Coulomb term, are the partial ionic charges. These charges remain fixed throughout the simulation, and are given by: \( q_{Ce} = 1.8 \), \( q_{P} = 3.0 \) and \( q_{O} = -1.2 \). For each interaction, the constants \( A_{ij}, \rho_q \), and \( C_{ij} \) are fit to ensure the correct bonding of each atomic interaction.

To simulate the monazite crystal, parameters for the P–O, O–O and P–P interactions were set to values used previously [29]. The ionic charges were also left unchanged. To ensure that the monazite unit cell has a net zero charge, the charge on the Ce ions was required to be set to 1.8. Only Coulomb interactions were used for the Ce–Ce and Ce–P terms (i.e., \( A_{ij} = C_{ij} = 0 \)). Therefore, the only fitting required is that for the Ce–O interaction.

For the Ce–O interaction, the values of \( A_{ij}, \rho_q \) and \( C_{ij} \) were varied from (0, 0.1, 1) to (0.1, 1, 100) in steps of (0.1, 0.1, 100), at each point. GULP [30] was used to optimise a monazite unit cell at constant pressure. The parameter set was chosen such that the optimised lattice fits as close as possible to the experimental unit cell dimensions. This fitting was further optimised by performing finer steps around the best point from the initial scan. The parameter values found are given in Table 1. Table 2 shows the lattice parameters of the optimised unit cell compared to experimental results.

The bulk modulus computed by GULP was found to be 137 GPa for the optimised structure. This value is an average of the three conventions reported by GULP.

It is known, that the Buckingham potential does not correctly model the short range interactions between atomic nuclei, that can occur during radiation cascades. Therefore, as in our previous work, the Buckingham and ZBL potentials [31] are smoothly joined together with a splining function, \( F(r) = f_0 + f_1 r + f_2 r^2 + f_3 r^3 + f_4 r^4 + f_5 r^5 \) + offset. The parameters \( f_0 \) to \( f_5 \) are chosen such that the potential is continuous in value and its first and second derivatives [27–29]. The spline points: A, B and the offset, are given in Table 1.

Three-body interactions within the O–P–O and P–O–P triplets, are modelled by a three-body potential as in our previous work [28,29].

3. Results

A series of constant temperature simulations were performed using both GULP and our own MD code, LBOMD, which has been used in previous work over many years at Loughborough, see for example [32] for oxides, and [33] for borosilicate glasses.

The GULP MD simulations were a 3 × 3 × 3 super–cell consisting of 648 atoms. This simulation had periodic boundaries, and was run at a constant pressure of zero (NPT ensemble). The LBOMD simulations were an isolated 6 × 6 × 6 super–cell consisting of 5184 atoms. Here, the monazite crystal was placed in a much larger simulation box, and therefore had free surfaces exposed to a vacuum. This simulation was then run at constant volume (NVT ensemble).

3.1. Thermal expansion

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{ij} )</td>
<td>124000 eV</td>
</tr>
<tr>
<td>( \rho_q )</td>
<td>0.1999 Å</td>
</tr>
<tr>
<td>( C_{ij} )</td>
<td>99.7 eV Å⁻⁶</td>
</tr>
<tr>
<td>Spline A</td>
<td>0.8 Å</td>
</tr>
<tr>
<td>Spline B</td>
<td>2.0 Å</td>
</tr>
<tr>
<td>Offset</td>
<td>20.0 eV</td>
</tr>
</tbody>
</table>

Table 2

The unit cell parameters of the optimised monazite structure compared to experimental results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental values [16]</th>
<th>Optimised value</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.7880 Å</td>
<td>6.7072 Å</td>
<td>-1.19</td>
</tr>
<tr>
<td>b</td>
<td>7.0163 Å</td>
<td>6.9572 Å</td>
<td>-0.84</td>
</tr>
<tr>
<td>c</td>
<td>6.4690 Å</td>
<td>6.2622 Å</td>
<td>2.494</td>
</tr>
<tr>
<td>( 90.0 )</td>
<td>( 90.0 )</td>
<td>( 0.0 )</td>
<td></td>
</tr>
<tr>
<td>( 103.430 )</td>
<td>( 103.277211 )</td>
<td>( -0.148 )</td>
<td></td>
</tr>
<tr>
<td>( 90.011 )</td>
<td>( 90.0 )</td>
<td>( -0.01 )</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>299.486 Å³</td>
<td>300.936 Å³</td>
<td>+0.484</td>
</tr>
</tbody>
</table>

Here, the volume of the system is measured as a function of simulation temperature. GULP reports the average cell parameters and cell volume periodically during the MD simulation. The average volume over a period of at least 100 ps is recorded for each
simulation. The percentage change in volume is plotted against system temperature in Fig. 1. For the isolated crystal in the LBOMD simulations, the volume of the convex hull of all the atoms was computed periodically. The percentage change in volume, averaged over at least 20 ps, is also plotted in Fig. 1. It can be seen that both simulation methods yield similar results.

The volume thermal expansion coefficient is then calculated using the change in volume, divided by the change in temperature, divided by the volume at 300 K (ΔV/ΔT)/V_{300K}. This gradient (indicated by the dashed line in Fig. 1) is calculated from the least squares fit of the data in the range 300–1000 K. Therefore, simulations show that the computer model predicts a volume thermal expansion coefficient of 49 × 10⁻⁶ K⁻¹. This is somewhat larger than the usually experimentally reported value of 27.4 × 10⁻⁶ K⁻¹ [8].

3.2. Estimation of the melting point

From the same set of simulations, the total energy of the system is recorded as a function of time. This value is then averaged over at least 100 ps for the GULP simulations, and 20 ps for the LBOMD simulations. Fig. 2, shows the percentage change in the total energy plotted as a function of simulation temperature. Data for both GULP and LBOMD simulations are shown. The dashed line in the Fig. 2 is a least squares fit to the data in the range 300–1000 K.

An estimate of the lower bound of the melting temperature is obtained by observing the point where the graph of the total energy against temperature departs from linear behaviour in Fig. 2. This occurs at approximately 2500 K. This compares favourably with the experimentally determined melting point of 2318 ± 20 K [34]. In future work, greater accuracy of the melting temperature measurement could be obtained by simulating a two state solid-melt system up to the the melting temperature.

The specific heat capacity at zero constant pressure, (C_p = (∆E/∆T)/M, where, M, is the system mass), is also obtained from this data. This was found to be a constant 657 J kg⁻¹ K⁻¹.

From observation of snapshots from the simulations, the crystal structure is completely stable up to its melting point.

4. Discussion and conclusion

A set of Buckingham parameters (A_{ij}, ρ_{ij} and C_{ij}) for the Ce–O interaction were added to our existing phosphate potential. This enabled MD computer simulations of monazite crystal to be performed. The optimised crystalline structure, compares well with the experimental measurements. The greatest difference was observed for the lattice c parameter, which was ≈2.5% too large.

The simulated thermo-physical properties: volume thermal expansion, melting point and specific heat capacity were measured from the simulations. While the melting point appears to compare well with experimental results, the thermal expansion was found to be too large. The specific heat capacity was found to be a constant 657 J kg⁻¹ K⁻¹ in the range 300–1000 K. However, experimental results indicate that C_p varies from 444 J kg⁻¹ K⁻¹ at 291 K to 662 J kg⁻¹ K⁻¹ at 873 K [9,19]. The bulk modulus of 137 GPa determined by GULP, is also larger than the experimental value of 100 GPa. The constructed potential is therefore not a perfect match to all experimental data but previous experience [35] has shown with other fixed charge empirical potentials, that because of the mainly ionic nature of the material, defect types and diffusion barriers for defect diffusion usually agree well with ab initio calculations. This comparison will be the next step in future work to test the suitability of the model for radiation damage studies.

Acknowledgements

Computing resources were provided by Loughborough University HPC service. The work was funded as part of a joint UK-India Nuclear Collaboration through EPSRC Grant No. EP/K007882/1.

References
