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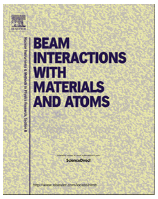

BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Derivation of enhanced potentials for cerium brannerite and the calculation of lattice and intrinsic defect properties

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ABSTRACT

A new potential has been derived for ceria and used to calculate its lattice and defect properties. The $Ce^{4+} \cdots O^{2-}$ potential is obtained *via* a combination of empirical fitting to crystal structural data and parametric fitting to additional physical properties, while the $O^{2-} \cdots O^{2-}$ potential is transferred from earlier publications on UO_2 and PuO_2. The overall potential is subsequently verified and validated by calculation of elastic and dielectric constants, whose values agree favourably with those measured experimentally. The potential is then employed to calculate intrinsic defect formation energies and predict the most favourable type of intrinsic disorder.

1. Introduction

High Level Waste (HLW), containing up to 95% of the radioactivity associated with a nuclear power station [1], comprises energetic fission products many of which have long half-lives and must therefore be isolated from the biosphere [2]. Borosilicate glass is currently the most commonly employed immobilizing matrix. However, the limited solubility of some HLW components and suggestions of inhomogeneity of the borosilicate matrix, has led to active research of ceramics, particularly those with mineral analogues, as alternative host matrices [3].

The mineral brannerite, UTi_2O_6, has a high actinide content and is extremely durable despite a wide variety of chemical substitution on both cation sites [4]. Synthetically, brannerite is a significant minor phase in pyrochlore-zirconolite ceramics designed for HLW immobilization [5]. It is therefore important to consider the applicability of brannerite as an actinide immobilizing matrix. Cerium is often used as an actinide simulant [6], particularly for plutonium, and $CeTi_2O_6$ is iso-structural with both UTi_2O_6 and $PuTi_2O_6$ [7].

Included in the detailed study of the structural properties of $CeTi_2O_6$ by Stennett et al. [7], are atomistic simulations employing potentials from the library of Woodley et al.[8] However, the reported results were not reproducible with the listed potentials. Moreover, the interatomic potential employed for the anion interactions includes an attractive r^{-6} term that causes unphysical and catastrophic attraction when the anions are separated by less than 1.85 Å. In addition, as seen when other potentials from the same library were used in the simulation of κ-alumina [9], these potentials give rise to further anomalies.

In this study, methods similar to those adopted previously for UO_2 [10] are applied to CeO_2 in order to obtain information about lattice properties and defect behaviour. This is an important preliminary step in modelling cerium brannerite which is the subject of ongoing work and a future publication.

2. Computational methodology

The computational methods used in this work are established techniques that have been used in many applications [11,12]. The pairwise interactions in the material are defined by a linear sum of an electrostatic interaction term and an interatomic potential (Eq. (1)):

$$V_{ij} = \underbrace{A_{ij}\ \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^{6}}}_{\text{Buckingham}} \underbrace{+\frac{q_i q_j}{r_{ij}}}_{\text{Electrostatic}} \tag{1}$$

For the interatomic potential term, the Buckingham form is employed in which q_i and q_j are the formal charges on the ions and the parameters A, ρ and C are specified, through empirical fitting, for each interaction type. Ion polarization by highly charged

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ions and defects is incorporated using Dick and Overhausers shell model [13] and intrinsic defects are modelled with the computationally efficient Mott Littleton [14] procedure.

2.1. Anion – anion potential

The interactions between the anions are described using a Buckingham four range potential: this was reported for UO_2 [10,15] and has subsequently been used in simulations of SiO_2 [16], PuO_2 [17] and ThO_2 [18]. Its use here is reasonable as CeO_2 adopts the same cubic crystal structure, with the anions arranged with the same symmetry within unit cells of a similar size. The potential is defined by the intervals given in Eq. (2) such that only the relevant terms of the Buckingham function are used over specific interaction distances. At the points $\mathrm{cut}_1, r_{\mathrm{minimum}}$ and cut_2, the functions are splined such that their first and second derivatives are continuous. Furthermore, the function is constrained to have a minimum stationary point at $r_{\min}$. Values for the necessary parameters, are reported by Jackson et al. and the constants for the polynomials calculated using the spline fitting procedure embodied within the GULP [19] code.

$$\phi^{\mathrm{Buck4}}(r_{ij}) = \begin{cases} A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) & \text{if } r_{\min} < r_{ij} \leqslant \mathrm{cut}_1, \\ \sum_{m=0}^{5} a_m\, r_{ij}^m & \text{if } \mathrm{cut}_1 < r_{ij} \leqslant r_{\mathrm{minimum}}, \\ \sum_{n=0}^{3} b_n\, r_{ij}^n & \text{if } r_{\mathrm{minimum}} < r_{ij} \leqslant \mathrm{cut}_2, \\ -\frac{C_{ij}}{r_{ij}^6} & \text{if } \mathrm{cut}_2 < r_{ij} \leqslant r_{\max} \end{cases} \qquad (2)$$

2.2. Cation – anion potential

Owing to the absence of a stationary point in the function of the cation–anion interactions, the Buckingham four range potential form is thus not applicable. To the best of the authors knowledge, there exists no standard Buckingham form potentials for $Ce^{4+} \cdots O^{2-}$ interactions that are consistent with the Buckingham four range potential detailed above. Thus, this is derived, with the C parameter set to zero in order to overcome the unphysical phenomenon of catastrophic attractions when ions are in close proximity: the potentials are thus formally of the Born Mayer form. The nature of the excluded $(-C/r^6)$ term is incorporated by surveying the potential landscape and sequentially selecting A and ρ parameters using an empirical fitting procedure which requires no *a priori* assumption of starting values and has been used to derive potentials for use in simulations of UO_2 [10], PuO_2 [17] and ThO_2 [18].

Initially, a range of A (650–2000 eV) and ρ (0.30–0.45Å) values is screened and the difference between the experimentally observed and predicted lattice constant plotted in Fig. 1.

Interpolation of the surface for where this difference is zero provides a solution set (Fig. 2) of several pairs of A and ρ that accurately reproduce the crystal structure.

For a robust model, however, the physical characteristics of the lattice should be described. Therefore, the predicted elastic constants are plotted as a function of the A parameter of corresponding pairs in the solution set (Fig. 3 and a value of A selected where the mean percentage difference between the predicted and observed values (overlaid in Fig. 3) of the elastic constants is a minimum. The corresponding ρ value is obtained through interpolation of the solution set.

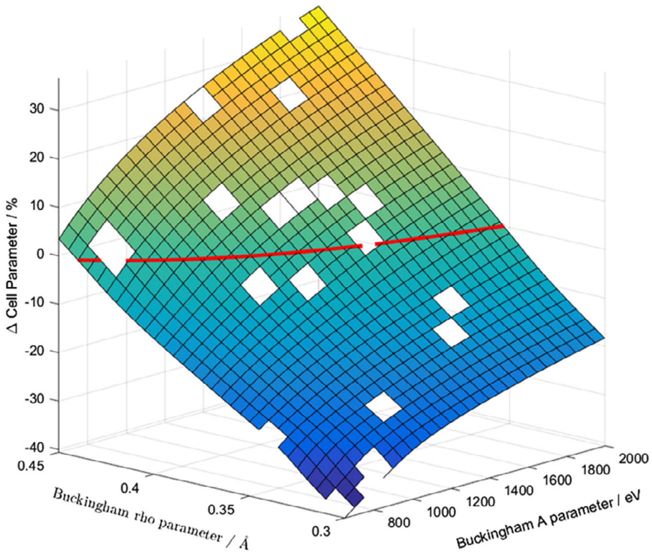

Fig. 1. Plot of the difference between predicted and observed CeO_2 lattice constant for A and ρ values of the $Ce^{4+} \cdots O^{2-}$ Born–Mayer potential.

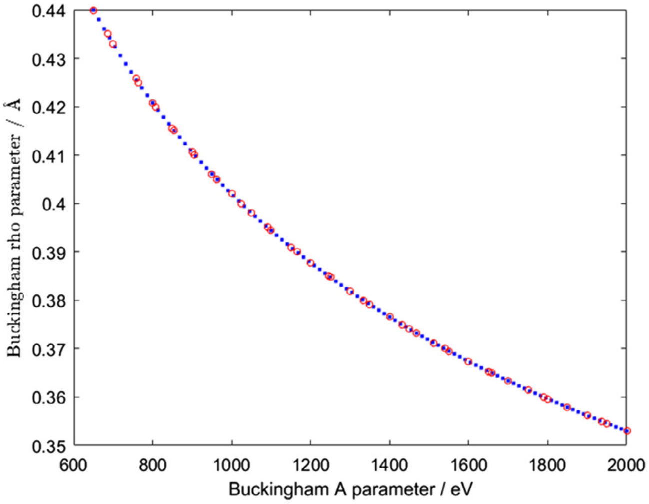

Fig. 2. Zero contour points and interpolated values of A and ρ comprising the solution set.

3. Results and discussion

3.1. Experimental data

CeO_2 adopts the fluorite structure ($Fm\bar{3}m$) and is isomorphous with UO_2, PuO_2 and ThO_2. The face centred cubic lattice has a lattice constant, a_0, of 5.4112Å [20] and a basis of a cerium ion at the origin and oxygen ions at $\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$: the anions form a simple cubic sub-lattice. There are 4 cations and 8 anions per unit cell. The fitting procedure also employs the elastic constants (C_{11}, C_{12} and C_{44}), static and high frequency dielectric constants and these are summarised, along with other bulk properties to be used for validating the simulation, in Table 2.

3.2. Perfect lattice

Values for the parameters of the $Ce^{4+} \cdots O^{2-}$ potential derived in the previous section and the Buckingham four range $O^{2-} \cdots O^{2-}$ potential are given in Table 1.

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