Developing pair potentials for simulating radiation damage in complex oxides

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Abstract

Atomistic simulation of radiation damage in oxides is a relatively new field compared to similar work in metals and semiconductors, and presents new challenges. We describe the development of a simplified empirical model for the $(Sr_{1-3x/2}La_x)TiO_3$ perovskite system, which contains partially-ordered cation vacancies and has interesting radiation resistance properties. Pair potential parameters are fitted to a range of experimental and new ab initio data, and the resulting model accurately reproduces important properties of the system, including local cation ordering effects.
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1. Context

The study of radiation damage in oxide materials is a rapidly growing field. Many oxide materials are being considered as host materials for high-level radioactive waste, including the synroc-type titanate minerals [1]. In this context, as in other solid-state applications, the atomic-level radiation response properties are very important for predicting long-term stability. Much experimental work has been done in this area, but the atomic-level physics underlying radiation damage and recovery is often unknown. One area of interest is the effect of charge-compensating defects on radiation resistance. This study focuses on the series of $(Sr_{1-3x/2}La_x)TiO_3$ perovskites, which contain cation vacancies. These materials have varying degrees of long- and short-range vacancy ordering [2,3], and show surprising behaviour under external ion irradiation, with a maximum radiation resistance at room temperature near $x = 0.2$ [4]. This system has many levels of complexity: multiple cation types, partial covalency, charge-compensating defects and short-range ordering, all of which may affect radiation hardness.

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Computer simulation is an important tool for explaining and predicting atomic-level effects of radiation. Simulation of oxide materials presents many new challenges, including the development of pair potentials. Most simulations have used formal point charges with Buckingham short-range potentials (Born–Mayer repulsion plus dispersion), which are often fitted to binary oxides and modified to reproduce the cell parameters of the system of interest. Such models often miscalculate important properties such as the bulk modulus, thermal expansivity, heat capacity and defect energies, and can be unnecessarily complex in form. Here we demonstrate the development of a sound, yet simple, model for the $(Sr, La)TiO_3$ perovskite system, which accurately reproduces bulk and short-range properties, including local order/disorder effects.

2. Lessons from TiO_2

We consider first rutile-structured TiO_2 as the prototype titanate system. Rutile consists of a network of TiO_6 octahedra, which are corner- and edge-linked; such octahedral networks form the backbone of many other synroc-type titanates. The similarities in structure between rutile and perovskites are seen in Fig. 1, which depicts the crystal structures of rutile, $SrTiO_3$ perovskite and the lowest energy supercell configuration of $Sr_{0.625}La_{0.25}TiO_3$ (containing one vacancy at the centre). Despite its apparent simplicity, rutile is a difficult structure to model, due to its octahedral distortion, large dielectric constants and partial covalency. This is reflected in the multitude of TiO_2 models in the literature, and their shortcomings (see Collins [5] for a review).

Three main types of models have been developed for TiO_2 in the literature: formal charge, partial charge and variable charge models. We have previously shown that variable charge models in their current form are inadequate for simulating ionic solids [6]. Collins [5] notes that partial charge models are far more successful than formal charge models in predicting elastic constants and surface formation energies in TiO_2. We have previously calculated [6] partial charges in TiO_2 using Mulliken partitioning of electron density in density functional theory (DFT) calculations with a localised atomic basis set. The value of the titanium charge was found to be 2.23, which corresponds well to the value of 2.196 used in the partial charge model of Matsui and Akaogi [7], as calculated from experimental phonon dispersion curves. This validates ab initio calculation of Mulliken charges as a method of assigning partial charges.

Considering the large number of species in our system of interest, it is important that the functional form of the model contain as few parameters as possible, while still accurately describing structural, elastic and thermodynamic properties. We used the GULP program [8] to fit many different models for TiO_2, using point charges and Buckingham-type pair potentials (see Gale and Rohl [9] for details of the Buckingham potential and its terms). A variety of experimental data was used, and various terms were included or omitted to weigh their usefulness. We found that many terms add complexity without adding signif-
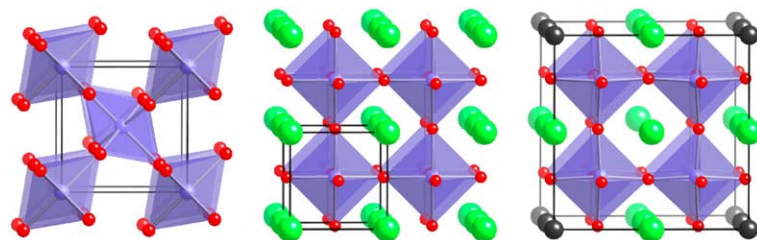

Fig. 1. Crystal structures of rutile TiO_2 (left), $SrTiO_3$ perovskite (centre) and the lowest energy $2 \times 2 \times 2$ supercell of $Sr_{0.625}La_{0.25}TiO_3$ (right). Shaded octahedra: Ti (blue) at centre, O (red) at corners. Outside octahedra: Sr (green) or La (black). Black lines indicate the unit cell. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

icantly to the performance. Firstly, *cation–cation* Buckingham terms have very little effect and can be simply omitted. Next, we fitted models with and without *dispersion* and found them to be equally successful. We also studied *atomic polarisability* in the form of the shell model, finding that even shell models fail to predict the soft phonon modes in rutile, which produce the large dielectric constants. In fact, many shell models are unphysical and lead to unrealistic behaviour at defects and surfaces. In summary, we found that the simplest practical model consists of Born–Mayer pair potentials (excluding cation–cation), and partial charges, that is,

$$U = \sum_{i<j} \left(A_{ij} e^{-r_{ij}/\rho_{ij}} + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right), \tag{1}$$

where U is the total potential energy over all atoms i and j separated by distance r_{ij}, q_i is the partial charge, and A_{ij} and ρ_{ij} are the Born–Mayer parameters, with $A_{ij} = 0$ for cation–cation interactions. Hence there are only two fitted parameters per atom type, plus charges that can be determined using Mulliken partitioning of ab initio electron density. This simplified model is expected to be a good approximation for related ionic solids in which electrostatic forces far outweigh dispersive interactions.

3. Fitting the SrTiO₃ model

Next we develop a model for the cubic perovskite $SrTiO_3$. The first step involves calculating ab initio Mulliken charges in $SrTiO_3$ using DFT with a local basis set (CRYSTAL code [10]), giving charges of 1.84 for Sr, 2.36 for Ti and −1.40 for O. These values are similar to those derived by Katsumata [11] using less rigorous electronegativity arguments, and are quite reasonable: Sr is mostly ionic and Ti less so.

There are now six parameters to fit: two for each of the Sr–O, Ti–O and O–O Born–Mayer terms. However, there are only three pieces of experimental data due to the high symmetry of $SrTiO_3$: one cell parameter and two independent elastic constants (since the Cauchy discrepancy can not be reproduced with a pair potential). To fill this gap we use experimental data on a similar structure, $Sr_3Ti_2O_7$. This is a Ruddlesden–Popper [12] structure composed of two layers of $SrTiO_3$ alternating with one layer of SrO, as shown in Fig. 2. To use these data in fitting, we first compute the Mulliken charges (since the stoichiometry is different to $SrTiO_3$), which are also shown in Fig. 2, aligned with the appropriate atomic layer. The charges are very similar to those in $SrTiO_3$ (shown in Fig. 2 in brackets), particularly for atoms within the perovskite layer. Using this structure together with the $SrTiO_3$ data, we obtain a unique fit of the Born–Mayer parameters, which are shown in Table 1. With this model, the cell parameters of $SrTiO_3$ and $Sr_3Ti_2O_7$ are reproduced exactly (and atomic coordinates within 1%), while for $SrTiO_3$ the bulk modulus is predicted within 4%,

q(Ti) = 2.34 (2.36)

q(Sr) = 1.82 (1.84)

q(Sr) = 1.83 (1.84)

q(O) = −1.55 (−1.40)

q(O) = −1.41 (−1.40)
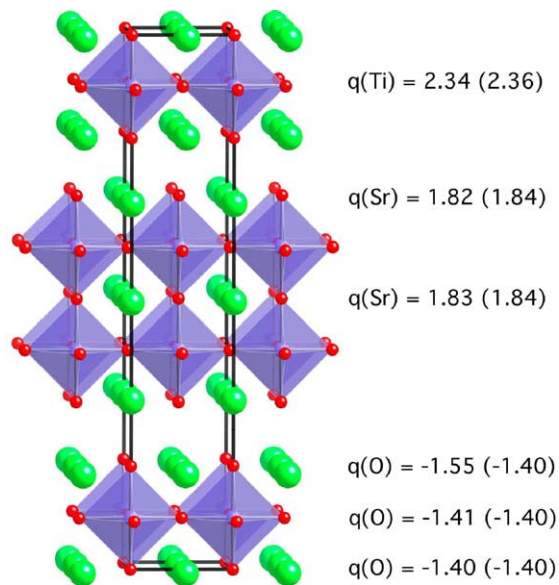
q(O) = −1.40 (−1.40)

Fig. 2. Ruddlesden–Popper $Sr_3Ti_2O_7$, with annotated partial charges in line with respective atomic layers. Numbers in brackets are atomic charges in $SrTiO_3$. Note that top and bottom atomic layers are equivalent, with black lines indicating the unit cell. Shaded octahedra: Ti (blue) at centre, O (red) at corners. Outside octahedra: Sr (green). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Born–Mayer potential parameters and partial charges for the $Sr_{1-3x/2}La_xTiO_3$ system – see Eq. (1)

	A_{ij} (eV)	ρ_{ij} (Å)	q_i (e)
Sr–O	1769.51	0.319894	1.84
La–O	1159.23	0.351884	2.76
Ti–O	14567.4	0.197584	2.36
O–O	6249.17	0.231472	−1.40

Charges are given for the first atom in the pair.

and the thermal expansion and heat capacity within 6%.

4. Fitting the (Sr,La)TiO₃ model

We now add La to the model, which introduces another two parameters for the La–O Born–Mayer term. The charge on La is not a free parameter and must be 1.5 times the Sr charge to preserve charge neutrality across the series, giving a value of 2.76. This is within 10% of the Mulliken charge of 3.0 calculated for an ordered (Sr,La)TiO₃ configuration. Crystallographic data are available for a number of (Sr,La)TiO₃ perovskites [3], with cell volume varying linearly across the series. However, the local cation configurations of these materials are not well-defined, with a mixture of local and long-range ordering. Further, the predicted cell volume and energy are found to be very sensitive to the particular "random" cation arrangement chosen, making it difficult to use these data in fitting.

The solution to this problem is found by generating ab initio data on the complete set of $Sr_5La_2Ti_8O_{24}$ and $Sr_2La_4Ti_8O_{24}$ configurations in $2 \times 2 \times 2$ supercells, using the VASP code [13], which is well-suited to defective solids. The predicted cell parameters are scaled by a constant factor determined by the ratio (0.9948) between the experimental cell parameter for SrTiO₃ at 300 K and the ab initio value. This makes the model applicable to describing (Sr,La)TiO₃ structures at around room temperature, in accordance with the other data used in fitting. The La–O pair potential is fitted to the six ab initio structures of $Sr_5La_2Ti_8O_{24}$ ($x = 0.25$), which has stoichiometry
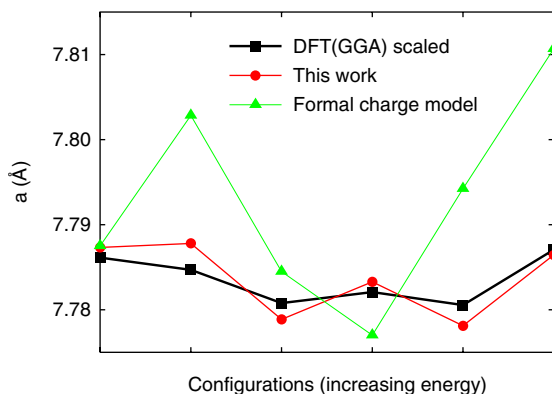

Fig. 3. Model fitting: one cell parameter (a) for six configurations of $Sr_5La_2Ti_8O_{24}$, as calculated using DFT, the model developed in this work, and a published formal charge model [14].

close to the region of interest for radiation damage studies. The resulting parameter values are given in Table 1, and the model performance in predicting one of the cell parameters is shown in Fig. 3. Also included in this figure is the performance of a published formal charge model for SrTiO₃ with incorporated La [14]. Our model was then tested against the ab initio structures and relative energies of the 16 $Sr_2La_4Ti_8O_{24}$ configurations, with results shown in Figs. 4 and 5, along with the formal charge model. This latter composition contains a

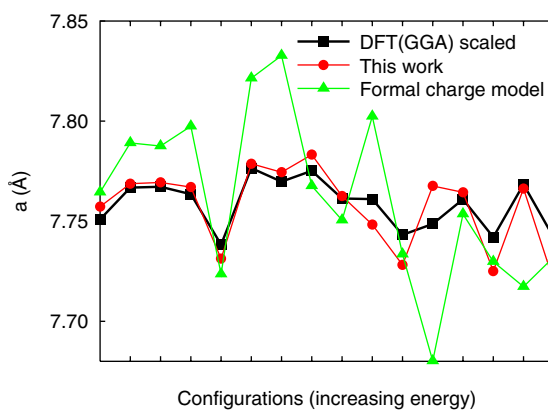Fig. 4. Model testing: one cell parameter (a) for sixteen configurations of $Sr_2La_4Ti_8O_{24}$, as calculated using DFT, the model developed in this work, and a published formal charge model [14].
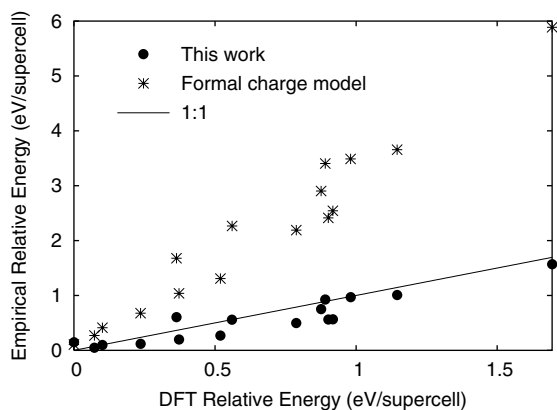
Fig. 5. Model testing: empirical versus ab initio (DFT) relative total energy per supercell for sixteen configurations of $Sr_2La_4Ti_8O_{24}$, using the model developed in this work and a published formal charge model [14].

higher concentration of vacancies than that used in fitting, indicating that the model is able to describe defective states. This gives us confidence that the model is applicable to configurations far from equilibrium, as encountered in radiation damage simulations. As a final check, a sensitivity analysis was performed on the $(Sr,La)TiO_3$ model, allowing variation in charges and various Born–Mayer potential parameters. The model was found to be stable with regard to all these variations.

5. Conclusions and further work

Simple, yet sound, empirical pair potentials for the $(Sr,La)TiO_3$ perovskite system have been determined using a combination of strategies, which may be applicable to other complex oxide systems. The model presented here successfully describes defect structures and energies as well as macroscopic properties, making it suitable for simulating the atomic-level effects of radiation damage. Further work on this system will include a study on short-range cation ordering, followed by simulations of radiation damage as a function of La concentration, looking at both primary damage formation and annealing of defects.

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