Solid State Ionics 263 (2014) 9–14

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Molecular dynamics simulations of Mg-doped beta″-alumina with potential models fitted for accurate structural response to thermal vibrations

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ARTICLE INFO

Article history:
Received 26 February 2014
Received in revised form 17 April 2014
Accepted 27 April 2014
Available online 20 May 2014

Keywords:
Beta″-alumina
Potential model
Molecular dynamics
Sodium conductivity
Autocorrelation function

ABSTRACT

A new interatomic potential model has been developed for Mg-doped beta″-alumina, using free energy optimization. By including the thermal expansion during potential fitting, the new potentials allow for an improved description of the structural behavior at different temperatures in molecular dynamics (MD) simulations. The new model was applied to study the detailed structural responses to temperature and transport properties of Mg-doped beta″-alumina. Results suggest that the sodium diffusion in beta″-alumina is highly correlated, and reliable electrical conductivity of beta″-alumina can only be extracted from molecular dynamics with substantial simulation duration and resolution, which may be best provided by long time scale classical simulations with accurate potentials.

1. Introduction

The beta-alumina family of materials, especially beta″-alumina, is a set of technologically important fast ionic conductors. Solid electrolytes made from sodium beta″-alumina materials are key components in various designs of Na-beta batteries that are valuable in applications such as grid-storage [1,2]. Beta″-alumina belongs to the family of layered spinel structures, which includes the beta-alumina and magnetoplumbite structures. In these structures, spinel-structured layers (consisting of four close-packed planes of oxygen containing Al cations) are separated by planes containing alkali or alkaline earth cations and oxygen. In the beta- and beta″-aluminas these planes provide the pathways for the fast ionic conduction which makes the materials technologically useful. Ideal sodium beta″-alumina has a formula of $NaAl_{11}O_{17}$; however, in the crystallographic unit cell there are six equivalent positions for the sodium, which means that half of the available sodium sites are vacant. The sodium concentration can be modified by dopants such as Mg^{2+}. As Mg^{2+} dopants substitute for the Al^{3+} in the spinel blocks, and is charge-compensated by additional Na^{+} in the conduction plane, the chemical formula becomes $Na_{1+x}Mg_xAl_{11-x}O_{17}$. Substantial efforts have been made in the past decades to study the material. Experiments have found interesting phenomena regarding the ionic conductivity, such as non-Arrhenius behavior and strong dependence on the material preparation conditions [3,4]. To appreciate how these phenomena influence the critical property of ionic conductivity, a better understanding of the sodium ion conduction mechanism, as well as related issues, such as defect interactions, is needed. In this respect, atomistic simulations can provide invaluable insight.

Classical molecular dynamics (MD) simulations are particularly useful because of their ability to examine the systems with tens of thousands of atoms over several hundreds of picoseconds or longer. Such large system sizes allow for the incorporation of random dopant distributions at low doping concentrations, and the long time scales allow for reliable diffusion coefficient calculations. Both of these are crucial for simulating fast ion conductors like doped beta″-alumina.

The value of MD simulations was appreciated very early in the development of β″-alumina solid electrolytes [5–8]. However, although useful information was obtained from these simulations, they suffered from the limited computational power available at the time (especially when compared to present day capabilities). Simplified potential models (in particular, the use of rigid ion models), short simulation durations and small system sizes were necessarily adopted in those studies. As will be discussed later, these compromises may have introduced artifacts that resulted in less accurate or even misleading conclusions in some important issues, such as the source of the non-Arrhenius behavior of the conductivity observed in experiments.

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http://dx.doi.org/10.1016/j.ssi.2014.04.018
0167-2738/

With the current accelerated applications of beta″-alumina based devices, deeper insights into the material provided by accurate atomistic simulations are urgently needed. The drastic improvement in the computational power during the past decades has enabled not only the simulation of larger systems for longer periods, but also the incorporation of more refined descriptions of the physics. In light of such points, Mg-doped beta″-alumina has been re-examined with a new set of potential models which was developed with a new fitting scheme aimed to improve the accuracy in MD simulations by better describing thermal effects. In addition, improved MD simulation setups such as larger systems and longer run times, or trajectories were used.

In the next section, the development of an improved potential model will be described. This will be followed by a presentation of the results obtained with the model, along with a discussion of the results.

2. Computational methodology

2.1. Interatomic potential models

The simulations discussed here are based on the Born Model of the solid, in which the ions are represented by point charges which interact both electrostatically and through short-range potentials. These latter have their physical origin in the Pauli repulsion associated with the overlap of the electron density distributions on neighboring ions. In the Born Model, then, the lattice energy of the simulated material can be constructed from long-ranged, electrostatic, potential and short-ranged interactions, as described in Eq. (1).

$$U = U^{long-ranged} + U^{short-ranged} = U^{polarization} \tag{1}$$

The Born Model does not itself include the effects of polarization (i.e. distortion of electron densities), which is known to influence strongly the properties of dielectric materials such as the oxides being discussed here. Dick and Overhauser introduced, originally for alkali halides [9], a simple mechanical model, known as the Shell Model (see below), to account for this polarizability and so a third term, $U^{polarization}$, is added to improve the description of the atomic polarization.

The potential set developed in this work used the Buckingham potential form shown in Eq. (2).

$$U_{ij}^{(short-ranged)} = U_{ij}^{(Buckingham)} = A\exp\left(-r_{ij}/\rho\right) - C/r_{ij}^{6} \tag{2}$$

2.2. Derivation of potential model parameters: inclusion of temperature

The parameters for the short-ranged potentials are typically fitted from experimental material properties, and this is the case for the previous MD simulations on beta″-alumina [5–8]. Traditionally, the fitting process has been conducted using static lattice optimizations, which implies a zero kelvin temperature, even though experimental measurements were made, and the MD simulations are usually conducted, at higher temperatures, e.g., room temperature and above in the case of fast ion conductors. Thus such fitting schemes inevitably introduce some inaccuracy in the derived potentials when subsequently used for explicitly simulating temperature effects, such as in MD. Furthermore, the absence of temperature effects in the fitting method can also lead to underrepresentation of the thermal behavior by the resulting potentials. The simulated structural response to the temperature, e.g. thermal expansion, and the concomitant dynamic behavior of the material will then not be modeled accurately.

In the improved fitting scheme, used in the present work, the temperature effect is explicitly included in the energy minimization by the means of free energy optimization, an approach which is, conveniently, coded into the GULP package [10]. The free energy optimization in GULP optimizes the crystal structure by minimizing the Helmholtz free energy: the thermal contribution is calculated by lattice dynamics through the vibrational partition function from the phonon density of states. The method assumes that the thermal vibration is harmonic, an approximation that has been found to be reasonable at temperatures below around half of the melting point [11].

With the free energy minimization, the fitting can be done at the temperatures at which the physical properties are experimentally measured. Such an approach has been proven to produce reliable classical potentials [12]. Moreover, free energy minimization allows the temperature dependent properties to be calculated during the fitting process, to evaluate the ability of the potential to reproduce the thermal effect in simulations with explicit temperatures, such as MD. In this study, the coefficient of thermal expansion (CTE) was chosen to evaluate the potential because it is a direct indicator of the structural response to thermal vibration and it is available in the literature for the materials of interest. With this new scheme, the performance of the potentials in MD simulations can now be directly controlled during fitting.

However, since fitting to the CTE was not supported by GULP, it was conducted manually. For each material, an initial fitting without the CTE was conducted first with GULP. Structure optimization was performed simultaneously with the fitting in this stage by utilizing the relaxed fitting scheme in GULP. After the initial fitting, a series of potential parameters in the vicinity of the initial fitting results were then tested in GULP to calculate the structure, elastic and dielectric properties and the CTE. While elastic and dielectric properties can be directly obtained in GULP, the CTE was calculated by optimizing the structure at a series of temperatures and fitting the lattice parameter and temperature relationship linearly. All the calculated properties were then compared with experimental data so that the weighted sum of the squares of the residues could be calculated. The weights were chosen to normalize the magnitudes of different properties. The best potential was identified by the smallest sum of squares for a given set of weights. It should be noted that, although free energy minimization is a reasonable approximation for fast calculations of thermal properties, it tends to underestimate the thermal effects because anharmonic vibrations are not included. This may pose difficulties for the fitting since, in that case, a smaller CTE should be used for free-energy fitting so that the resulting potentials can reproduce the exact CTE in MD. However, it was found that a balance between reproducing various properties such as lattice parameters, elastic constants and thermal expansion usually yielded a reasonably good potential set for MD. Nonetheless, some fine-tuning and a final validation of the potentials in MD should always be performed.

The O – O potential was based on the work of Gale et al. and Grimes [13,14]. To obtain the Mg – O and Al – O potentials, MgO and α-Al_2O_3 were fitted simultaneously, employing the procedures just described, using the structures, elastic and dielectric properties, and CTE of the two materials reported in the literature. A modification made to the C parameter in the O – O potential achieved a good fit to both of the materials. The final potential parameters thus obtained are listed in Table 1. A cutoff of 12 Å was used for short-range potentials.

2.3. Polarizability: the Shell Model

The Dick and Overhauser Shell Model used to describe atomic polarizations was also developed at this step [9]. In this model, an ion is

Table 1
Buckingham potential parameters.

Interaction	A (eV)	ρ (Å)	C (eVÅ^6)
Al^{3+}–O^{2-}	766.41	0.3399	0.0
Mg^{3+}–O^{2-}	858.83	0.3201	0.0
Na^{+}–O^{2-}	595.90	0.3746	0.0
O^{2-}–O^{2-}	9547.96	0.2192	29.0