Solid State Ionics 315 (2018) 111–115

Contents lists available at ScienceDirect

Solid State Ionics

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

Evaluation of magnesium ion migration in inorganic oxides by the bond valence site energy method

Yu Nishitani[a,*], Stefan Adams[b], Kazuhide Ichikawa[a], Takuji Tsujita[a]

[a] *Material Research Laboratory, Advanced Research Division, Panasonic Corporation, 1006 Kadoma, Kadoma, Osaka 571-8501, Japan*
[b] *Department of Materials Science and Engineering, National University of Singapore, Singapore 117579, Singapore*

ARTICLE INFO

Keywords:
Bond valence site energy
Density functional theory
Magnesium
Migration
Inorganic oxides

ABSTRACT

We have applied the bond valence site energy (BVSE) method elaborated in our earlier work for alkali ion conductors to investigate the migration of Mg ions through six types of inorganic (magnesium-containing) oxides and the effect of nonequivalent Mg sites within the crystal structures. The calculated migration pathways and barrier heights are compared with the results determined by density functional theory. Not only do the favorable migration pathways obtained by both methods demonstrate consistency, the migration barrier heights are clearly correlated, with the BVSE method typically overestimating the migration barrier heights relative to the density functional theory calculations. Overall, the most suitable primary application of the BVSE method is as an approximate screening tool for the structures of materials and to estimate the migration energies and pathways of magnesium ions through inorganic oxides.

1. Introduction

The migration of multivalent ions in solid-state materials is attracting much attention due to its importance in designing novel ionic devices such as multivalent-ion secondary batteries [1–4]. However, such migrations is generally slow because of stronger Coulomb interactions between the migrating multivalent ions and the host lattice than is the case for monovalent ions such as H^+, Ag^+, Cu^+, and Li^+. Experimentally, most studies have focused on finding suitable multivalent ionic conducting materials based by considering analogous structures that favor fast conduction of monovalent ions [5–8]. Theoretically, density functional theory (DFT) calculations have been used to investigate multivalent ionic conducting materials [9,10]. However, although DFT is a powerful theoretical approach to determine optimal design guidelines for conducting materials, the computational cost can be prohibitive. For this reason, the general use of DFT as a screening tool is currently impractical, especially for amorphous or glassy materials that require a hundreds to millions of atoms for realistic simulations.

Recently, the bond valence sum and bond site energy (BVSE) methods have been applied not only to investigate preferred ionic migration pathways but also to estimate migration barrier heights [1,11,12]. In the earlier bond valence sum method, deviations of the bond valence sum from the ideal oxidation state are utilized to locate ion migration pathways and to qualitatively estimate migration barriers. In contrast the BVSE method can be understood as an empirical force field that allows the potential energy of the associated anions and cations to be calculated approximately from the bond valences and Coulomb repulsions aiming at a semi-quantitative estimate of the migration barriers. Such potential energy calculations are based on classical mechanics, which significantly reduces their computational cost; therefore, they are appropriate to screen materials for determining promising structures. Most previous reports have focused on lithium ion conducting materials [13,14], with none reporting the application of classical theory-based potential calculations to multivalent cation migration.

Accordingly, in this work we have applied the BVSE method to investigate Mg^{2+} migration in magnesium-containing oxide crystals. These results were then compared with those from DFT-based calculations to assess the broader utility of the BVSE method to examine the migration of multivalent ions in solid-state materials.

2. Methods

The BVSE calculations used to investigate the migration of Mg^{2+} are based on the *softBV* software tool [15] and the underlying computational approach derived in our earlier work [1,11,12]. For an updated version of the *softBV* bond valence parameters see Chen et al. [16]. In this method, the potential energy landscape of the Mg^{2+} ions is determined for a mesh covering the real space cell. To calculate the total

---

* Corresponding author.
E-mail address: nishitani.yu@jp.panasonic.com (Y. Nishitani).

https://doi.org/10.1016/j.ssi.2017.11.031
Received 28 July 2017; Received in revised form 27 November 2017; Accepted 29 November 2017
0167-2738/ © 2017 Elsevier B.V. All rights reserved.

Table 1
Magnesium oxides examined and their corresponding Mg^{2+} migration barrier heights (E_{mig}) calculated by the BVSE and DFT methods. (a) DFT data from this work, (b) Literature DFT data.

(a)

ICSD code	Compound	GII	Lattice system	Space group	E_{mig} (eV)			
					DFT	BVSE		
						1D	2D	3D
26374	Mg_2SiO_4	0.070	Ortho.	*Pbnm*	0.85 1.5[a] 2.0[b]	1.02 1.33	1.88	2.05 2.05
15627	Mg_2SiO_4	0.083	Ortho.	*Pbnm*	0.85	0.93	1.76	1.97
31385	$Mg_3(BO_3)_2$	0.045	Ortho.	*Pnmn*	1.5	1.41	2.13	2.13
34074[c]	$MgSiO_3$	0.137[c] → 0.099	Ortho.	*Pbca*	1.8	2.47	3.16	3.68
81229	$Mg_2B_2O_5$	0.067	Mono.	$P2_1/c$	1.3	1.00	1.77	2.33
261230[c]	$Mg_2P_2O_7$	0.314[c] → 0.119	Mono.	$P2_1/c$	1.2	1.47	2.28	2.35
261231	$Mg_3(PO_4)_2$	0.079	Mono.	$P2_1/c$	1.4	0.77[d]	0.89	1.63

(b)

ICSD code	Compound	GII	Lattice system	Space group	E_{mig} (eV)			
					DFT	BVSE		
						1D	2D	3D
1504	VO_2	0.124	Tetra.	$P4_2/mnm$	0.30 [24]	0.45	–	–
75623	$MgCr_2O_4$	0.114	Cubic	*Fd-3 m*	0.63 [25]	0.55	0.55	0.55
79000	$MgAl_2O_4$	0.049	Cubic	*Fd-3 m*	0.65 [26]	0.75	0.75	0.75
16858	$MgMn_2O_4$	0.310	Tetra.	$I4_1/amd$	0.8 [25]	0.99	0.99	0.99
290600	$MgMn_2O_4$	0.115	Tetra.	$I4_1/amd$	0.8 [25]	0.43	0.43	0.43
86102	MgV_2O_5	0.140	Ortho.	*Cmcm*	1.12 [27] 1.26 [28]	1.24	1.25	1.57
250452	$MgZr_4(PO_4)_6$	0.21	Mono.	$P2_1/n$	0.1[e]	0.39	0.51	0.53
290277	$MgTi_4(PO_4)_6$	0.139	Rhomb.	*R-3c*	0.56[e]	0.41	0.41	0.41

[a] Mg(1) → Mg(2).

[b] Mg(2) → Mg(2).

[c] BVSE analyses of $MgSiO_3$ and for $Mg_2P_2O_7$ were based on DFT optimized structure models, as the relatively high GII for the experimental structure model indicates a limited accuracy. The DFT optimized models are characterized by clearly lower GII values as indicated.

[d] For the path Mg(1)-i2-i3-i1-Mg(1).

[e] Experimental data for $MgZr_4(PO_4)_6$ [29] and Co-doped $MgTi_4(PO_4)_6$ [30].

BVSE potential (E_{BVSE}), both the bond valence potential involving the Mg^{2+}–O^{2-} attractive interaction and the Coulombic potential involving the Mg^{2+}–immobile cation repulsive interaction were considered (Eq. 1).

$$E_{BVSE} = E_{Mg-O} + E_{Mg-cation} \tag{1}$$

The Mg^{2+}–O^{2-} interaction is expressed with the following Morse-type potential:

$$E_{Mg-O} = D_0 \sum_i \left[\left\{ \exp\left(\frac{R_{min} - R_i}{b} \right) - 1 \right\}^2 - 1 \right] \tag{2}$$

where R_i is the interionic distance between the Mg^{2+} ion and its adjacent anion *i*. D_0, R_{min}, and *b* are a set of empirical BVSE parameters taken from Chen et al. [16]. The cation-cation repulsive interaction is expressed using the real part of the Ewald sum as:

$$E_{Mg-cation} = \sum_j \frac{q_{Mg} q_{IMCj}}{R} \mathrm{erfc}\left\{ \frac{R}{(r_{Mg} + r_{IMCj})f} \right\} \tag{3}$$

where r_{Mg} and r_{IMCj} are the covalent radii of Mg^{2+} and the immobile cation *j*, respectively. The screening factor *f* is adapted for each structure identifying the value of *f* for which the forcefield yields an internal stress close to zero. The values of *f* in the studied Mg compounds are around 0.61 ± 0.02. q_{Mg} and q_{IMCj} are the effective charges for Mg^{2+} and the immobile cation *j*, respectively. In the *softBV* screening tool the effective fractional charge is estimated from oxidation states and principal quantum numbers of the ions, based on the assumption that ions with a higher principal quantum number carry less charge due to the screening effect of valence electrons:

$$q_{X,i} = \frac{V_{X,i}}{\sqrt{n_{X,i}}} \sqrt{\frac{\sum_j \frac{V_{M,j} N_{M,j}}{\sqrt{n_{M,j}}}}{\sum_i \frac{V_{X,i} N_{X,i}}{\sqrt{n_{X,i}}}}}, \qquad q_{M,j} = \frac{V_{M,j}}{\sqrt{n_{M,j}}} \sqrt{\frac{\sum_i \frac{V_{X,i} N_{X,i}}{\sqrt{n_{X,i}}}}{\sum_j \frac{V_{M,j} N_{M,j}}{\sqrt{n_{M,j}}}}} \tag{4}$$

where M_j is a cation, X_i is an anion, *N* represents the total number of ions of that kind, subscript *i* is an index enumerating anions and *j* with cations. The square root scaling factor ensures that the crystal structure is electroneutral.

The summations in Eqs. (2) and (3) are performed on all real space mesh points in a unit cell, with a real space resolution of 0.1 Å. In this way, the obtained BVSE potential at each mesh point maps the potential energy of the system. As a reference, the minimum potential energy for Mg in the cell is assigned as zero.

The DFT calculations were performed using the spin-polarized Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation [17] using a plane-wave basis set and the projector-augmented wave method [18,19], as implemented in the Vienna Ab initio Simulation Package [20,21]. For all calculations, the energy cutoff of the plane-wave expansion was 520 eV. The Brillouin zone was sampled using a k-point mesh of less than 0.4 $Å^{-1}$ for all axes within the Monkhorst-Pack scheme. The structures were considered optimized

Download English Version:

https://daneshyari.com/en/article/7744652

Download Persian Version:

https://daneshyari.com/article/7744652

Daneshyari.com