# **Oxygen migration in doped BaGdInO4**

# Kuganathan, K., Davazoglou, K., Vovk, R. & Chroneos, A.

# Author post-print (accepted) deposited by Coventry University's Repository

# Original citation & hyperlink:

Kuganathan, K, Davazoglou, K, Vovk, R & Chroneos, A 2021, 'Oxygen migration in doped BaGdInO4', *Solid State Ionics*, vol. 369, 115729. https://dx.doi.org/10.1016/j.ssi.2021.115729

DOI 10.1016/j.ssi.2021.115729 ISSN 0167-2738

**Publisher: Elsevier** 

© 2021 Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International http://creativecommons.org/licenses/by-nc-nd/4.0/

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

# Oxygen migration in doped BaGdInO<sub>4</sub>

Navaratnarajah Kuganathan<sup>1,2,a)</sup>, Konstantinos Davazoglou<sup>3</sup>, Ruslan V. Vovk<sup>4</sup>, and Alexander Chroneos<sup>1,2,b)</sup>

<sup>1</sup>Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom <sup>2</sup>Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV15FB, United Kingdom

<sup>3</sup>Department of Informatics and Telecommunications, National and Kapodistrian University of Athens, GR 15784 Athens, Greece

<sup>4</sup>Physics Department, V. Karazin Kharkiv National University, Svobody Sq. 4, 61077 Kharkiv, Ukraine

# Abstract

Doped-BaGdInO<sub>4</sub> is a promising material for many applications including solid oxide fuel cells due to its high oxide-ion conductivity. Here we employ atomistic simulations to show that the activation energy for oxygen migration in Ca-doped BaGdInO<sub>4</sub> is lower as compared to undoped BaGdInO<sub>4</sub> and importantly divalent doping will form oxygen vacancies. The results are consistent with recent experimental work that determined an increase in the diffusivity of Ca-doped BaGdInO<sub>4</sub> as compared to the undoped case. Additionally, the most thermodynamically feasible defect in this material is the Gd-In anti-site. Promising isovalent dopants on the Ba, Gd and In were found to be the Sr, Al and Sc respectively. The most favourable dopant on the Gd site to produce oxygen vacancies is Ca and its solution energy is lower only by 0.02 eV than that calculated for Sr. Ba<sup>2+</sup> ion conduction in this material is slow with the migration energy barrier being higher than 2 eV.

Keywords: BaGdInO<sub>4</sub>; defects; dopants; atomistic simulation

\*Corresponding authors, e-mail: a) n.kuganathan@imperial.ac.uk ; b) alexander.chroneos@imperial.ac.uk

#### 1. Introduction

Oxide-ion conductors attract the attention of the research community because of their application in solid-oxide fuel cells (SOFC), oxygen sensors, catalysts and oxygen separation membranes [1-10]. Structure and composition are key to achieve high oxide-ion conductivity and there are a number of oxide families (such as perovskites, fluorites, melilites, apatites etc.) that are important in this respect [11-16]. An interesting oxide family is monoclinic BaRInO<sub>4</sub> (where R = Nd, Sm, Ho, Y, Er) and the recently synthesized orthorhombic BaGdInO<sub>4</sub> [17,18]. The resent study by Yaguchi *et al.* [18] indicated that oxygen migration in orthorhombic BaGdInO<sub>4</sub> is one-dimensional and not two-dimensional as in the related monoclinic BaRInO<sub>4</sub> materials. Additionally, it was determined that divalent doping at the Gd site considerably increases the oxygen ion conductivity of the orthorhombic phase as in the resultant BaGd<sub>1-x</sub>A<sub>x</sub>InO<sub>4-x/2</sub> (where A = Mg, Ca, Sr) there is an excess of oxygen vacancies that mediate the oxygen transport [18].

When unravelling the physical properties of an oxide material it is important to understand its intrinsic and extrinsic defect processes. This information can be subsequently used to tailor the material properties for specific applications. Classical atomistic simulations can efficiently be used to investigate the defect properties energy related oxide materials [19-22]. In the present study we examine the defect properties of orthorhombic BaGdInO<sub>4</sub> with a focus on oxygen migration and the impact of divalent doping (Fe, Co, Mn, Ni, Mg, Ca and Sr).

# 2. Computational Methodology

Atomistic simulations based on the classical pair potentials were employed to investigate the crystal structure, defect energetics, diffusion properties and solution of dopants. All calculations were performed using a classical simulation code GULP (generalised utility lattice program) [23]. This methodology uses ionic [long-range (Coulombic) and short-range (electron-electron repulsion and van der Waals attraction)] interactions. Buckingham potentials [24-26] (refer to Table 1) were applied to model short-range interactions. Both ionic positions and lattice constants were relaxed simultaneously using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [27]. Point defects and migrating ions were modelled using the Mott-Littleton method [28]. This method divides the lattice into two spherical regions namely the inner region (region I) and the outer region (region II). Atoms in the inner region are relaxed explicitly. In region II, forces on the atoms are relatively weak and approximate quasi-continuum methods are used to relax the atoms in this region. A

supercell containing 502 atoms in region I and 3501 atoms in region II was used for all defect calculations.

Vacancy mediated Ca ion diffusion was calculated considering seven interstitial Ca ions between local Ca hops. Activation energy of migration was defined as the local maximum energy along the diffusion path. Similar methodology has been used to calculate the O ion diffusion pathways and their corresponding activation energies of migration in many oxide materials **[29-33]**. The present calculation is based on the full ionic charge model within the dilute limit. Therefore, the defect energies will be overestimated, however, the relative energies, and the trends will be consistent **[34]**. Thermodynamically the defect parameters (formation and migration energies) considered can be defined by the comparison of the real defective crystal to an isobaric (present study) or isochoric non defective crystal and be connected through thermodynamic relations **[35-38]**.

# 3. Crystal structures of BaGdInO<sub>4</sub>

BaGdInO<sub>4</sub> crystallises in the orthorhombic *Pnma* Ba<sub>2</sub>Y<sub>2</sub>CuPtO<sub>8</sub>-type structure **[18]**. In the BaGdInO<sub>4</sub> crystal structure, there are eight Ba cations, four InO<sub>6</sub> octahedra, four InO<sub>5</sub> square pyramids and eight GdO<sub>7</sub> monocapped trigonal prisms (see Figure 1). The experimental lattice parameters reported by Yaguchi *et al.* **[18]** are a = 13.8015(7) Å, b = 5.8913(3) Å and c = 10.6432(5) Å at 20 °C. Here we calculated the lattice parameters as a = 13.8463 Å, b = 5.8790 Å and c = 10.6702 Å in excellent agreement to the determined lattice parameters indicating the efficacy of the atomistic simulations employed (refer to Table 2).

#### 4. Results and discussion

# 4.1. Intrinsic defects

Material properties such as electrochemical properties can be significantly influenced by point defects. The calculated isolated point defect energies were used to compute the Frenkel and Schottky defect energies. Cation anti-site defects in which cations exchange their positions in the forms of isolated and cluster were also calculated. While the defects are calculated separately in their isolated form, cluster formation considers the defects close to each other. Many experimental and theoretical studies are available reporting these defects in a number of systems [39-45]. For example, Armstrong *et al.* [44], found that a small amount of Li-Fe cation anti-site is present in Li<sub>2</sub>FeSiO<sub>4</sub> during the process of cycling. Relaxed structures of defects are provided in the electronic supplementary information (ESI). The following equations as written using using the Kröger-Vink notation [46] were used to describe the Frenkel, Schottky and anti-site defect processes. Both vacancy and interstitial defect energies

were considered with full ionic charges. The charges of Ba, Gd, In and O were +2, +3, +3 and -2. Although different charge states are possible, point defects in a highly ionic material might be expected to be in their fully ionic charge states.

Ba Frenkel: 
$$Ba_{Ba}^{X} \rightarrow V_{Ba}^{\prime\prime} + Ba_{i}^{\bullet\bullet}$$
 (1)

Gd Frenkel: 
$$Gd_{Gd}^{X} \rightarrow V_{Gd}^{\prime\prime\prime} + Gd_{i}^{\bullet\bullet\bullet}$$
 (2)

In Frenkel: 
$$\ln_{\text{In}}^{\text{X}} \rightarrow V_{\text{In}}^{\prime\prime\prime} + \ln_{\text{i}}^{\bullet\bullet\bullet}$$
 (3)

$$0 \text{ Frenkel: } \mathbf{0}_{\mathbf{0}}^{\mathbf{X}} \to V_{\mathbf{0}}^{\bullet\bullet} + \mathbf{0}_{\mathbf{i}}^{\prime\prime} \tag{4}$$

Schottky: 
$$Ba_{Ba}^{X} + Gd_{Gd}^{X} + In_{In}^{X} + 4 O_{O}^{X} \rightarrow V_{Ba}^{''} + V_{Gd}^{'''} + V_{In}^{'''} + 4 V_{O}^{\bullet\bullet} + BaGdInO_{4}$$
 (5)

BaO Schottky: 
$$Ba_{Ba}^{X} + O_{O}^{X} \rightarrow V_{Ba}^{\prime\prime} + V_{O}^{\bullet\bullet} + BaO$$
 (6)

$$Gd_2O_3$$
 Schottky:  $2 Gd_{Gd}^X + 3O_0^X \rightarrow 2 V_{Gd}^{\prime\prime\prime} + 3 V_0^{\bullet\bullet} + Gd_2O_3$  (7)

$$In_2O_3 \text{ Schottky: } 2 In_{In}^X + 3O_0^X \to 2 V_{In}^{\prime\prime\prime} + 3 V_0^{\bullet\bullet} + In_2O_3$$
(8)

Ba/Gd antisite (isolated): 
$$Ba_{Ba}^{X} + Gd_{Gd}^{X} \rightarrow Ba'_{Gd} + Gd_{Ba}^{\bullet}$$
 (9)

Ba/Gd antisite (cluster): 
$$Ba_{Ba}^{X} + Gd_{Gd}^{X} \rightarrow \{Ba_{Gd}^{\prime}: Gd_{Ba}^{\bullet}\}^{X}$$
 (10)

Ba/In antisite (isolated): 
$$Ba_{Ba}^{X} + In_{In}^{X} \rightarrow Ba_{In}^{I} + In_{Ba}^{\bullet}$$
 (11)

Ba/In antisite (cluster): 
$$Ba_{Ba}^{X} + In_{In}^{X} \rightarrow \{Ba'_{In}: In_{Ba}^{\bullet}\}^{X}$$
 (12)

Gd/In antisite (isolated): 
$$Gd_{Gd}^{X} + In_{In}^{X} \rightarrow Gd_{In}^{X} + In_{Gd}^{X}$$
 (13)

$$Gd/In antisite (cluster): Gd_{Gd}^{X} + In_{In}^{X} \rightarrow \{Gd_{In}^{X}: In_{Gd}^{X}\}^{X}$$
(14)

The computed energies for the defect processes are tabulated in Table 3. The Gd-In anti-site defect cluster was found to be the most thermodynamically favourable defect with the defect energy of 0.40 eV. This indicates that a small amount of Gd<sup>3+</sup> and In<sup>3+</sup> would exchange their positions. The low formation energy for this anti-site defect is due to the +3 charge on both the Gd and In atoms. Other anti-site defect energies are highly endothermic due to the charge mismatch (e.g. +2 on the Ba and +3 on the Gd or In). The formation energy of BaO Schottky is 2.07 eV and this is the lowest Schottky defect energy process among all Schottky defects. The Ba, Gd and In Frenkel formation energies are higher than that calculated for the O-Frenkel. The formation of oxygen vacancies required for the vacancy assisted oxygen migration will be ensured by the O Frenkel.

#### 4.2. Solution of dopants

The physical properties of materials can be tailored by doping with dopants of different atomic radii and charges. In that respect, aliovalent dopants can introduce charge compensating point defects (vacancies and interstitials), which influence the diffusion properties. A significant enhancement in the oxygen diffusivity has been observed in BaGdInO<sub>4</sub> upon doping of Ca on the Gd site and this is partly due to the charge compensating oxygen vacancies that are formed [18]. This is because oxygen vacancies effectively mediated the oxygen self-diffusion and their higher number will therefore result in higher oxygen diffusivity. Here, we considered a variety of divalent dopants on the Ba site and trivalent dopants on the Ba, Gd and In sites. Appropriate charge compensating defects and lattice energies were incorporated into the reaction equations to calculate solution energies.

# 4.2.1. Divalent dopants

Divalent cations (Fe, Co, Mn, Ni, Mg, Ca and Sr) were first substituted on the Ba site. The following reaction equation was used to calculate the solution energies.

$$MO + Ba_{Ba}^{X} \to M_{Ba}^{X} + BaO \tag{15}$$

The calculated solution energies are reported in Table 4. The lowest solution energy (1.45 eV) is predicted for  $Sr^{2+}$ . The solution energy calculated for  $Ca^{2+}$  is higher only by 0.15 eV meaning that this dopant should be also investigated experimentally. Experimental studies considered the doping of Mg <sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> only on the Gd site **[18]**. The ionic radii of Ca<sup>2+</sup> and Sr<sup>2+</sup> are 1.00 Å and 1.18 Å respectively. The preference of Sr<sup>2+</sup> can be partly due to its ionic radius closer to the ionic radius of Ba<sup>2+</sup> (1.35 Å) than that of other dopants. The solution energy calculated for the Mg<sup>2+</sup> is 3.21 eV therefore this dopant requires high temperatures for the doping process. Other dopants also exhibit high solution energies meaning that they are unfavorable at room temperature.

Next we considered the doping of divalent dopants on the Gd site. Experimental work by Yagucji *et al.* **[18]** indicates that Ca doping on the Gd site significantly improves the oxygen ion diffusion. This is due to the formation of oxygen vacancies in the lattice as explained by the following reaction equation.

$$2 \text{ MO} + 2 \text{ Gd}_{\text{Gd}}^{\text{X}} + \text{O}_{\text{O}}^{\text{X}} \rightarrow 2 \text{ M}_{\text{Gd}}' + \text{ V}_{\text{O}}^{\bullet \bullet} + \text{ Gd}_2\text{O}_3$$
(16)

Solution energies are reported in Table 5. The most favourable dopant for this process is the Ca<sup>2+</sup> with the solution energy of 1.40 eV. The solution energy calculated for the Sr<sup>2+</sup> is higher only by 0.02 eV meaning that this dopant is also promising. The favourability of Ca<sup>2+</sup> can be partly due to its ionic radius (1.00 Å) closely matches with that of Gd <sup>3+</sup> (0.94 Å). Solution energies calculated for Ni<sup>2+</sup> and Mn <sup>2+</sup> are 1.74 eV and 1.84 eV respectively. Solution energies calculated for both Mg<sup>2+</sup> and Co<sup>2+</sup> are almost identical. However, their solution energies are ~0.85 eV higher than that calculate for the Ca<sup>2+</sup>. The highest solution energy is calculated for the doping of Fe <sup>2+</sup> owing to its ionic radius deviates much from that of Gd<sup>3+</sup>.

Finally, a range of trivalent dopants (M = Al, Ga, Sc, Y and La) were considered on the Gd and In sites. Doping produced no charge compensating defects as charge on the Gd or In is +3 (refer to equation 17 below). The corresponding solution energies are reported in Table 6.

$$M_2O_3 + 2 Gd_{Gd}^X \to 2 M_{Gd}^X + Gd_2O_3$$
(17)

In all cases, solution energies calculated for the doping on the Gd site are remarkably higher than that calculated on the In site. This is partly due to the higher coordination number of Gd (CN =7) than that of In (CN = 5 or 6).

The most favourable dopant is  $Sc^{3+}$  on both Gd and In sites. Interestingly, the solution energy calculated on the In site exoergic (-0.02 eV) and more favourable by 4.65 eV than that calculated on the Gd site. In all cases, solution energies calculated on the Gd site are higher than 4.50 eV. The trend in the solution energies ( $Sc^{3+} > Al^{3+} > Y^{3+} > Ga^{3+} > La^{3+}$ ) are the same in both cases. The present calculations reveal that experimental verification is more promising on the In site than the Gd site. Solution energies calculated for the  $Al^{3+}$ ,  $Y^{3+}$  and  $Ga^{3+}$  are 0.27 eV, 0.28 eV and 0.31 eV respectively meaning that they are also worth testing experimentally. The highest solution energy is calculated for the  $La^{3+}$  (0.98 eV).

## 4.3. Self-diffusion of Ba2+ and O2- ions

Here, we calculate the vacancy assisted  $Ba^{2+}$  and  $O^{2-}$  ion diffusion pathways together with activation energies. Diffusion is one of the key properties that can influence the performance of a material particularly for solid oxide fuel cell applications. It has been previously determined that doping of  $Ca^{2+}$  on the Gd site can significantly increase the oxygen ion conductivity [18]. The current methodology providing information about the diffusion pathways and activation energies using methodologies that have been established previously for a range of oxide materials [47,48].

#### 4.3.1. Diffusion of Ba2+ ions

Three different Ba local hops (A, B and C) were identified (refer to Figure 2). Calculated activation energies of migration for each individual local hops with Ba-Ba distances are reported in Table 7. Figure 3 shows the energy profile diagrams for each Ba local hops. All three local hops exhibited high activation energies of migration (>2.30 eV) partly due to the longer Ba-Ba separation and larger ionic radius of Ba<sup>2+</sup>. Possible long-range diffusion pathways were constructed using local hops. Three possible pathways were identified. In the

first long range path ( $A \leftrightarrow B \leftrightarrow C \leftrightarrow B$ ),  $Ba^{2+}$  ion migrates via three dimensional network with an activation energy of 2.94 eV. The second pathway ( $B \leftrightarrow B \leftrightarrow B \leftrightarrow B$ ) consists of local hops B only and  $Ba^{2+}$  ion migrates in a zig-zag pattern in the (111) plane. Activation energy for this path is 2.46 eV. In the third pathway ( $C \leftrightarrow C \leftrightarrow C \leftrightarrow C$ ),  $Ba^{2+}$  ions migrate again in a zig-zag pattern in the (111) plane but with higher activation energy of 2.94 eV. This is due to the longer Ba-Ba separation of 4.49 Å than the other two separations. Nevertheless, in all three pathways, activation energies are high meaning that  $Ba^{2+}$  ion diffusion is slow. Nevertheless, this is useful information considering that cationic diffusion can play a role in the degradation of fuel cell materials over prolonged and high temperature use.

#### 4.3.2. Diffusion of O<sup>2-</sup> ions in undoped and doped BaGdInO<sub>4</sub>

Next, six possible local oxygen diffusion hops (P, Q, R, S, T and U) (see Table 8) were identified and their activation energies of migration were calculated (see Figure 4a). In general, activation energies are much lower than that calculated for the  $Ba^{2+}$  ions (see Table 8). In particular, local hops P, Q and S have very low activation energies of 0.28 eV, 0.22 eV and 0.23 eV respectively. Energy profile diagrams for these local hops are shown in Figure 5. Three possible long range pathways were identified. In all three pathways, diffusion is one dimensional and in the *b* direction as observed in the experiment. The first migration pathway  $(Q \leftrightarrow T \leftrightarrow Q \leftrightarrow T)$  consists of local hops Q and T and its overall activation energy is calculated to be 0.49 eV. The second pathway ( $R \leftrightarrow S \leftrightarrow R \leftrightarrow S$ ) has a larger activation energy (0.83 eV) than that calculated for the first pathway. The lowest activation energy calculated for the third pathway ( $P \leftrightarrow U \leftrightarrow P \leftrightarrow U$ ) is 0.56 eV. Experimentally determined activation energy of oxide- ion is 0.804 eV which is higher by ~0.25 eV than the calculated value from this study [18]. Bondvalence-based energy (BVE) analysis shows that the oxide-ions migrate along the b axis with an activation energy of 0.47 eV [18]. Both direction of the oxide- ion movement and activation energy are in good agreement with this study. We considered other directions as well. However, local hop distances and their activation energies were larger than 3.20 Å and 1.40 eV respectively.

Finally, oxygen diffusion pathways were recalculated in the presence of two  $Ca^{2+}$  ions occupying the Gd sites and a single oxygen vacancy. Migration pathways are shown in Figure 4b. Energy profile diagrams plotted for individual O hops are shown in Figure 6. Experimental study shows that the doping of Ca reduces the migration barrier by 0.165 eV. The relaxed structure of Ca-doped BaGdInO<sub>4</sub> is shown in Figure 7. However, the BVE barrier for the oxide-ion migration in Ca-doped BaGdInO<sub>4</sub> is lower by 0.06 eV than that calculated

in BaGdInO<sub>4</sub> contradicting with the experimental observation [18]. In this study, all migration barriers for individual hops except T are lowered upon Ca doping. The overall activation energy for the third pathway ( $P\leftrightarrow U\leftrightarrow P\leftrightarrow U$ ) is lowered from 0.56 eV to 0.39 eV agreeing with the experimental observation.

The reduction in the activation energy of oxygen migration can be due to several reasons. The Ca doping on the Gd site introduces an oxygen vacancy in the lattice. Both Ca dopant and oxygen vacancy perturbate the lattice by changing the oxygen local hop distances. Furthermore, the electrostatic attraction between the  $Gd^{3+}$  and  $O^{2-}$  ions in the lattice is reduced by the doping of  $Ca^{2+}$  on the Gd site. It is anticipated that the formation of oxygen vacancy and perturbation in the chemical environment around the Ca dopant influence the reduction of activation energy.

# 5. Conclusion

We have employed atomistic simulation to gain insights into the defect, diffusion and dopant processes of BaGdInO<sub>4</sub>. The most favourable intrinsic defect process is calculated to be the Gd-In anti-site. The oxygen ion diffusion in this material is found to be higher than the Ba ion diffusion. Consistently with experiment the doping of Ca on the Gd introduces oxygen vacancies in the lattice and enhances the oxygen ion diffusivity by increasing the number of vehicles that mediate diffusion. The second most favourable dopant for this process is the Sr and its solution energy is higher only by 0.02 eV. The Sr, Al and Sc are found to be the most favourable isovalent dopants on the Ba, Gd and In sites respectively.

## Author statement:

Navaratnarajah Kuganathan: Conceptualization, Methodology, Investigation, Writing -Original Draft. Alexander Chroneos: Writing- Reviewing and Editing. Konstantinos Davazoglou: Analysis. Ruslan V. Vovk: Analysis.

#### Acknowledgements

The research leading to these results has received funding from the European Union's H2020 Programme under Grant Agreement no 824072– HARVESTORE. Computational facilities and support were provided by High Performance Computing Centre at Imperial College London.

Competing interests: The authors declare no competing interests.

#### References

1. J. B. Goodenough, J. E. Ruiz-Diaz, and Y. S. Zhen, *Solid State Ion.* **40-41**, 934-937 (1990).

- 2. P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux, and Y. Laligant, *Nature* 404, 856-858 (2000).
- 3. S. J. Skinner and J. A. Kilner, *Solid State Ion.* **135**, 709-712 (2000).
- 4. J. A. Kilner, *Solid State Ion.* **129**, 13-23 (2000).
- 5. D. Rupasov, A. Chroneos, D. Parfitt, J. A. Kilner, R. W. Grimes, S. Y. Istomin, and E. V. Antipov, *Phys. Rev. B* 79, 172102 (2009).
- A. Chroneos, B. Yildiz, A. Tarancón, D. Parfitt, and J. A. Kilner, *Energy & Environmental Science* 4, 2774 (2011).
- I. D. Seymour, A. Chroneos, J. A. Kilner, and R. W. Grimes, *Phys. Chem. Chem. Phys.* 13, 15305 (2011).
- F. Chiabrera, I. Garbayo, L. Lopez-Conesa, G. Martin, A. Ruiz-Caridad, M. Walls, L. Ruiz-Gonzalez, A. Kordatos, M. Nunez, A. Morata, S. Estrade, A. Chroneos, F. Peiro, and A. Tarancon, *Adv. Mater.* 31, 1805360 (2019).
- 9. M. Yashima, T. Tsujiguchi, Y. Sakuda, Y. Yasui, Y. Zhou, K. Fujii, S. Torii, T. Kamiyama, and S. J. Skinner, *Nat. Commun.* **12**, 556 (2021).
- F. Baiutti, F. Chiabrera, M. Acosta, D. Diercks, D. Parfitt, J. Santiso, X. Wang, A. Cavallaro,
   A. Morata, H. Wang, A. Chroneos, J. MacManus-Driscoll, and A. Tarancon, *Nat. Commun.* 12, 556 (2021).
- M. Mogensen, D. Lybye, N. Bonanos, P. V. Hendriksen, and F. W. Poulsen, *Solid State Ion*. 174, 279-286 (2004).
- 12. T. Ishihara, K. Nakashima, S. Okada, M. Enoki and H. Matsumoto, *Solid State Ion.* **179**, 1367-1371 (2008).
- 13. H. Yoshioka, Y. Nojiri, and S. Tanase, Solid State Ion. 179, 2165-2169 (2004).
- X. Kuang, M. A. Green, H. Niu, P. Zajdel, C. Dickinson, J. B. Claridge, L. Jantsky, and M. J. Rosseinsky, *Nat. Mater.* 7, 498-504 (2008).
- M. Li, M. J. Pietrowski, R. A. De Souza, H. Zhang, I. M. Reaney, S. N. Cook, J. A. Kilner and D. C. Sinclair, *Nat. Mater.* 13, 31-35 (2014).
- W. Zhang, K. Fujii, E. Niwa, M. Hagihala, T. Kamiyama and M. Yashima, *Nat. Commun.* 11, 1224 (2020).
- K. Fujii, Y. Esaki, K. Omoto, M. Yashima, A. Hoshikawa, T. Ishigaki and J. R. Hester, *Chem. Mater.* 26, 2488-2491 (2014).
- 18. H. Yaguchi, K. Fujii, and M. Yashima, J. Mater. Chem. A 8, 8638-8647 (2020).
- 19. M. Cherry, M. S. Islam, and C. R. A. Catlow, J. Solid State Chem. 118, 125 (1995).
- 20. C.A. J. Fisher, N. Kuganathan, and M. S. Islam, J. Mater. Chem. A 1, 4207 (2013).
- 21. N. Kuganathan, P. Iyngaran, R. Vovk, and A. Chroneos, Sci. Rep. 9, 4394 (2019).
- 22. N. Kuganathan, F. Baiutti, A. Tarancón, J. Fleig, and A. Chroneos, *Solid State Ionics* **361**, 115570 (2021).
- 23. J. D. Gale and A. L. Rohl, *Molecular Simulation* **29**, 291 (2003).

- 24. C.A.J. Fisher, M.S. Islam, R.J. Brook, A Computer Simulation Investigation of Brownmillerite-Structured Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>, *Journal of Solid State Chemistry*, **128** (1997) 137-141.
- 25. A. Dwivedi, A.N. Cormack, A computer simulation study of the defect structure of calciastabilized zirconia, *Philosophical Magazine A*, **61** (1990) 1-22.
- 26. G.V. Lewis, C.R.A. Catlow, Potential models for ionic oxides, *Journal of Physics C: Solid State Physics*, **18** (1985) 1149-1161.
- 27. D. Gale, Journal of the Chemical Society, *Faraday Transactions* **93**, 629 (1997).
- 28. N. F. Mott and M. J. Littleton, *Transactions of the Faraday Society* **34**, 485 (1938).
- 29. N. Kuganathan, L.H. Tsoukalas, A. Chroneos, Solid State Ionics 335 (2019) 61.
- J.C. Treacher, S.M. Wood, M.S. Islam, E. Kendrick, *Physical Chemistry Chemical Physics* 18 (2016) 32744.
- 31. N. Kuganathan, M.S. Islam, Chemistry of Materials 21 (2009) 5196.
- 32. M.S. Islam, D.J. Driscoll, C.A.J. Fisher, P.R. Slater, *Chemistry of Materials* 17 (2005) 5085.
- 33. C.A.J. Fisher, V.M. Hart Prieto, M.S. Islam, *Chemistry of Materials* **20** (2008) 5907.
- R.W. Grimes, G. Busker, M.A. McCoy, A. Chroneos, J.A. Kilner, S.-P. Chen, Berichte der Bunsengesellschaft für physikalische Chemie, 101 (1997) 1204–1210.
- 35. P. Varotsos, Solid State Ionics, 179 (2008) 438-441.
- 36. A. Chroneos, R.V. Vovk, Solid State Ionics, 274 (2015) 1-3.
- M.W.D. Cooper, R.W. Grimes, M.E. Fitzpatrick, A. Chroneos, Solid State Ionics, 282 (2015)
   26-30.
- 38. E.S. Skordas, N.V. Sarlis, P.A. Varotsos, Solid State Ionics, 354 (2020) 115404.
- E.E. Jay, M.J.D. Rushton, A. Chroneos, R.W. Grimes, J.A. Kilner, *Phys. Chem. Chem. Phys.* 17 (2015) 178-183.
- V.V. Politaev, A.A. Petrenko, V.B. Nalbandyan, B.S. Medvedev, E.S. Shvetsova, *Journal of Solid State Chemistry* 180 (2007) 1045.
- 41. A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson, J.O. Thomas, *Electrochemistry Communications* **7** (2005) 156.
- 42. D. Ensling, M. Stjerndahl, A. Nytén, T. Gustafsson, J.O. Thomas, *Journal of Materials Chemistry* **19** (2009) 82.
- 43. M. Kempaiah Devaraju, Q. Duc Truong, H. Hyodo, Y. Sasaki, I. Honma, *Scientific Reports* 5 (2015) 11041.
- 44. A.R. Armstrong, N. Kuganathan, M.S. Islam, P.G. Bruce, *Journal of the American Chemical Society*, **133** (2011) 13031-13035.
- 45. G.R. Gardiner, M.S. Islam, *Chemistry of Materials*, **22** (2010) 1242-1248.
- F.A. Kröger, H.J. Vink, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, Academic Press, 1956, p. 307.

- 47. M.S. Islam, C.A.J. Fisher, *Chemical Society Reviews*, **43** (2014) 185-204.
- 48. E. Kendrick, J. Kendrick, K.S. Knight, M.S. Islam, P.R. Slater, *Nature Materials*, 6 (2007) 871-875.

 Table 1. Buckingham potential parameters used [24-26].

Two-body  $[\Phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$ , where A,  $\rho$  and C are parameters. The values of Y and K represent the shell charges and spring constants.

Interaction	A / eV	ρ / Å	$C \neq \mathrm{eV} \cdot \mathrm{\AA}^6$	Y / e	K ∕ eV•Å-₂
Ba <sup>2+</sup> –O <sup>2<sup>-</sup></sup>	931.70	0.3949	0.00	1.46	14.78
$Gd^{3+} - O^{2^-}$	1336.80	0.3551	0.00	3.00	99999
$In^{3+} - O^{2^-}$	1495.6	0.3310	4.325	-6.10	1680.0
$O^{2^{-}}-O^{2^{-}}$	22764.30	0.1490	27.89	-2.077	27.29

Parameter	Calculated	Experiment [18]	$ \Delta $ (%)
a (Å)	13.8463	13.8015	0.33
b (Å)	5.8790	5.8913	0.21
c (Å)	10.6702	10.6432	0.25
$\alpha = \beta = \gamma$ (°)	90.0	90.0	0.00

 $\textbf{Table 2}. Calculated and experimental lattice parameters of orthorhombic BaGdInO_{4}.$ 

Process	Equation	Reaction energy (eV)/defect
Ba Frenkel	1	4.99
Gd Frenkel	2	6.88
In Frenkel	3	6.32
O Frenkel	4	2.94
Schottky	5	2.64
BaO-Schottky	6	2.07
Gd <sub>2</sub> O <sub>3</sub> -Schottky	7	2.84
In <sub>2</sub> O <sub>3</sub> -Schottky	8	2.67
Ba-Gd anti-site (isolated)	9	2.07
Ba-Gd anti-site (cluster)	10	1.99
Ba-In anti-site (isolated)	11	2.52
Ba-In anti-site (cluster)	12	2.31
Gd-In anti-site (isolated)	13	0.45
Gd-In anti-site (cluster)	14	0.40

 $\textbf{Table 3.} Reaction \ energies \ for \ different \ intrinsic \ defect \ processes.$ 

M <sup>2+</sup> ion	Ionic radius (Å)	Solution energy (eV/M <sup>2+</sup> ion)
Fe <sup>2+</sup>	0.61	3.28
Co <sup>2+</sup>	0.65	3.15
$Mn^{2+}$	0.67	2.43
Ni <sup>2+</sup>	0.69	2.87
$Mg^{2+}$	0.72	3.21
Ca <sup>2+</sup>	1.00	1.60
Sr <sup>2+</sup>	1.18	1.45

**Table 4.** Solution energies calculated for the isovalent dopants (M = Fe, Co, Mn, Ni, Mg, Ca and Sr) on the Ba site with respect to the  $M^{2+}$  ionic radius (see equation 15).

M <sup>2+</sup> ion	Ionic radius (Å)	Solution energy (eV/ $M^{2+}$ ion)
$\mathrm{Fe}^{2+}$	0.61	2.39
$\mathrm{Co}^{2+}$	0.65	2.23
$Mn^{2+}$	0.67	1.84
$\mathrm{Ni}^{2+}$	0.69	1.74
$\mathrm{Mg}^{_{2+}}$	0.72	2.22
$Ca^{2+}$	1.00	1.40
Sr <sup>2+</sup>	1.18	1.42

**Table 5.** Solution energies calculated for the divalent dopants (M = Fe, Co, Mn, Ni, Mg, Ca and Sr) on the Gd site with respect to the  $M^{2+}$  ionic radius (see equation 16).

M <sup>3+</sup> ion	I	Solution energy (eV/M <sup>3+</sup> ion)	
	Tonic radius (A)	Gd site	In site 0.27
Al <sup>3+</sup>	0.54	4.94	0.27
Ga <sup>3+</sup>	0.62	4.98	0.31
$\mathrm{Sc}^{3+}$	0.75	4.67	-0.02
Y <sup>3+</sup>	0.90	4.95	0.28
La <sup>3+</sup>	1.03	5.67	0.98

**Table 6.** Solution energies calculated for the trivalent dopants (M = Al, Ga, Sc, Y and La) on the Gdand In sites with respect to the  $M^{3+}$  ionic radius (see equation 17).

Migration path	Ba–Ba separation (Å)	Activation energy (eV)	
А	4.07	2.35	
В	4.14	2.46	
С	4.49	2.94	
Long rage pathway	Activation energy (eV)		
$A \leftrightarrow B \leftrightarrow C \leftrightarrow B$	2.94		
$B \leftrightarrow B \leftrightarrow B \leftrightarrow B$	2.46		
$C \leftrightarrow C \leftrightarrow C \leftrightarrow C$	2.94		

**Table 7**. Calculated Ba-Ba separations, possible long range diffusion pathways and activation energiesfor the individual local Ba hopping and long range migration (refer to Figures 2 &3).

**Table 8**. Calculated O-O separations, possible long range diffusion pathways and activation energies for the individual local O hopping and long range migration (refer to Figures 4, 5 &6). The activation energies calculated in the presence of  $Ca^{2+}$  ion on the Gd site are provided in parentheses.

Migration path	O–O separation (Å)	Activation energy (eV)	
Р	2.78	0.33 (0.28)	
Q	2.85	0.32(0.22)	
R	2.89	0.83(0.72)	
S	2.98	0.37(0.23)	
Т	3.02	0.49(0.49)	
U	3.09	0.56(0.39)	
Long rage pathway	Activation energy (eV)		
$Q \leftrightarrow T \leftrightarrow Q \leftrightarrow T$	0.49 (0.49)		
$R \leftrightarrow S \leftrightarrow R \leftrightarrow S$	0.83(0.72)		
$P \leftrightarrow U \leftrightarrow P \leftrightarrow U$	0.56 (0.39)		



Figure 1. Crystal structure of  $BaGdInO_4$ .



Figure 2. Ba-ion migration pathways in  $BaGdInO_4$ .



Figure 3. Three different energy profile diagrams for the Ba vacancy hopping between adjacent Ba sites in BaGdInO<sub>4</sub>.



Figure 4. Six possible oxygen vacancy local hops connecting long range diffusion in (a) BaGdInO4 and (b) Ca-doped BaGdInO4.



Figure 5. Six different energy profile diagrams for the O vacancy hopping between adjacent O sites in BaGdInO<sub>4</sub>.



Figure 6. Energy profile diagrams calculated for the O vacancy hopping in Ca-doped BaGdInO<sub>4</sub>.



Figure 7. Relaxed structure of Ca-doped  $BaGdInO_{4}$ .