


Cite this: *RSC Adv.*, 2022, 12, 20029

# Unravelling the alkali transport properties in nanocrystalline $A_3OX$ ( $A = Li, Na, X = Cl, Br$ ) solid state electrolytes. A theoretical prediction

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Transport properties of the halogeno-alkali oxides  $A_3OX$  ( $A = Li, Na, X = Cl, Br$ ) nanocrystalline samples with the presence of  $\Sigma 3(111)$  grain boundaries were computed using large-scale molecular dynamic simulations. Results on the diffusion/conduction process show that these nanocrystalline samples are characterized with higher activation energies as compared to previous theoretical studies, but closer to experiment. Such a performance can be attributed to the larger atomic density at the  $\Sigma 3(111)$  grain boundary regions within the nanocrystals. Despite a minor deterioration of transport properties of the mixed cation  $Li_2NaOX$  and  $Na_2LiOX$  samples, these halogeno-alkali oxides can also be considered as good inorganic solid electrolytes in both Li- and Na-ion batteries.

Received 30th May 2022

Accepted 1st July 2022

DOI: 10.1039/d2ra03370d

rsc.li/rsc-advances

## 1. Introduction

The search for affordable inorganic electrolytes for future all solid state alkali-ion batteries is one of the current hot topics due to the urgent need for high energy density materials and relevant safety issues.<sup>1–5</sup> Exploration and prediction of the properties of electrolytes are crucial for the improvement of performance and durability of the battery.<sup>1–7</sup> Of particular interest, the development of inorganic solid electrolyte faces critical issues, such as the lower electrical conductivity as compared to conventional liquid electrolytes, interfacial resistance with the electrodes, narrow electrochemical window that constrain its practical applications.<sup>4–7</sup>

Of the compounds with special interest for inorganic solid electrolyte, the Li-rich anti-perovskite  $Li_3OX$  ( $X = Cl^-, Br^-$ ) has attracted large scientific interest due to the high Li ionic conductivity ( $\approx 1 \text{ mS cm}^{-1}$ ) and stability with the electrode, and low Li activation energy ( $\approx 0.2 \text{ eV}$ ).<sup>8–12</sup> Nevertheless, a higher activation energy ( $\approx 0.6 \text{ eV}$ ) and a lower ionic conductivity for  $Li_3OX$  have recently been reported experimentally.<sup>12–14</sup> Further studies concerning the composition screening of Li and Na anti-perovskite structure were performed disclosing the defect chemistry and ionic transport in pristine,  $Li_3OCl_{1-y}Br_y$  and  $Li_{3-x}Na_xOCl_{1-y}Br_y$  compositions.<sup>15–18</sup> For instance, in mixed

anionic samples the Cl/Br mixing have small contribution to the conducting properties as compared to the pristine samples, but this doping strategies can be used for fine tuning the transport properties in such anti-perovskite structures.<sup>16</sup>

Dawson *et al.*<sup>15</sup> reported the ionic transport at stable grain boundaries of  $Li_3OCl$  as a model polycrystalline electrolyte. These authors predicted high concentrations of grain boundaries and disclosed that the Li-ion conductivity is lower through the grain boundaries with higher activation energies for Li-ion conduction than that of the bulk crystal, thereby confirming the high grain boundary resistance in this material.<sup>15,17</sup> The vast contribution of the grain boundary to the overall conducting properties of  $Na_3OBr$  and  $Li_3OCl$  was reported,<sup>12,15</sup> and further confirmed by theoretical studies taking the grain boundaries into account.<sup>15,17,19</sup>

In a solid polycrystal, a grain boundary is a planar defect dividing two grains with different crystallographic orientation. According to the coincidence lattice site theory, two independent grains are tilted by an angle until the individual surface plane coincides, resulting in the desired grain boundary  $\Sigma(a,b,c)$  where  $\Sigma$  denotes the coincidence index and  $(a,b,c)$  the grain boundary plane.<sup>15,17</sup> Despite earlier studies concerning the transport properties of individual grain boundaries and bulk  $A_3OX$  materials,<sup>15,17</sup> the explicit influence of the grain boundaries in polycrystalline samples has not been reported yet. Besides, the  $\Sigma 3$  grain boundary type has the lowest segregation energy in compounds such as inverted perovskite structures.<sup>15,19</sup> The  $\Sigma 3$  grain boundary type is thus expected to appear with high density in real nanocrystalline samples due to their low energy, but the role of this grain boundary remains almost unexplored.

Motivated by the above considerations, we set out to investigate in the present study the influence of the  $\Sigma 3(111)$  grain

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boundary type on the transport properties in  $A_3OX$  ( $A = Li^+, Na^+$ ,  $X = Cl^-, Br^-$ ) by using large-scale molecular dynamics computations. Alkali diffusion in nanocrystalline  $A_3OX$  samples, which is of vital importance for understanding of the role of grain boundary, is investigated. This study also includes the case of intercalated samples such as  $Li_2NaOX$  and  $Na_2LiOX$  with the aim to elucidate their capabilities as inorganic solid electrolytes for future Li and Na solid state batteries. The main difference of the present results with respect to the previous studies consists in that we are disclosing the Li and Na transport properties of pristine  $A_3OX$  and  $Li_2NaOX$  and  $Na_2LiOX$  nanocrystals, with the presence of the  $\Sigma 3(111)$  grain boundaries, to simulate the insertion/disinsertion process in the polycrystalline  $A_3OX$  solid state electrolytes.

## 2. Computational protocols

Fig. 1a displays the conventional representation of the  $A_3OX$  ( $A = Li^+, Na^+$ ,  $X = Cl^-, Br^-$ ). In this particular anti-perovskite structure with space group  $Pm\bar{3}m$  No. 221, the body center is occupied by oxygen, whereas the eight vertices by the  $X^-$  anions and the six face centers are occupied by the  $A^+$  alkali ions.<sup>15,17,18</sup> The lattice parameters  $a$  for  $Li_3OBr$  and  $Na_3OBr$  are 3.981 and 4.541 Å, respectively, whereas values for  $Li_3OBr$  and  $Na_3OBr$  amount to 3.991 and 4.613 Å, respectively.<sup>15,17–20</sup> Following the coincidence site theory, the symmetric tilt  $\Sigma 3(111)$  grain boundary,<sup>15,19</sup> depicted in Fig. 1c, is construed from the  $A_3OX$  ( $A = Li^+, Na^+$ ,  $X = Cl^-, Br^-$  in an ionic form) lattice structures.

Nanocrystalline  $A_3OX$  samples are constructed employing the Voronoi tessellation method implemented in the Atoms

code.<sup>21</sup> In this method, samples with three grains with average grain volume of 17.20 nm<sup>3</sup> are built by filling in a cubic box with randomly distributing seeds. We use the  $\Sigma 3(111)$  grain boundary as the seed for generating the samples, considering the fact that the resulting nanocrystals are constituted by three grains connected with a  $\Sigma 3(111)$  grain boundary.

The simulation cubic box has a size of  $80 \times 80 \times 80 \text{ Å}^3$ , containing 42 945 atoms with ionic compositions of 25 780  $A^+$ , 8615  $O^{2-}$  and 8550  $X^-$ . In order to eliminate free surface effects, the periodic boundary conditions are imposed in all directions. Therefore, the overlapped atoms within 1.5 Å distances are separated in 0.2 Å and double atoms are deleted to eliminate the initial unwanted artificial defects which may arise from the tessellation process. The extra net charge introduced by the tessellation process is compensated by the  $A^+$  and  $X^-$  vacancies generated randomly. Inclusion of  $A^+$  and  $X^-$  vacancies is in line with the predicted alkali halide partial Schottky defects, leading to an  $A^+$  vacancy migration mechanism, which is the most favorable scheme with low formation energy.<sup>11,16</sup> These pair defects can be expressed according to Kröger-Vink notation by eqn (1):



where  $A_A^\times$  and  $X_X^\times$  denote the  $A^+$  and  $X^-$  ion in their lattice position, whereas  $V_A'$  and  $V_X'$  represent a  $A^+$  and  $X^-$  vacancy, respectively, and  $AX$  the alkali halide. In eqn (1), for each A-vacancy, one X-vacancy is generated for charge compensation resulting in a stoichiometric  $A_{3-y}OX_{1-y}$  formula. As mentioned above, eqn (1) is used during the construction of the simulation boxes, resulting in a representative defect concentration of  $y = 0.118$ . Note that the nanocrystalline  $A_3OX$  structures inherently exhibit a conduction mechanism *via* an alkali vacancy ( $V_A'$ ) as described in eqn (1).

The resulting polycrystalline samples  $A_3OX$  with  $A = Li^+, Na^+$ ,  $X = Cl^-, Br^-$  are depicted in Fig. 1b. For large-scale molecular dynamics simulations (MD) the LAMMPS code is used to determine the  $Li^+$  and  $Na^+$  diffusion data of nanocrystalline  $A_3OX$  as each can be split in terms of ions  $A = Li^+, Na^+$  and  $X = Cl^-, Br^-$  samples.<sup>22</sup> The potential parameters reported in ref. 16 are adopted to model the particle interactions. These potential parameters consider the pure electrostatic interactions for long-range together with a Buckingham-type potential for the short-range pair ion interactions. Further details concerning the potential parameters can be found in ref. 16. In addition, formal valence charge is used for all the species in each nanocrystal. The simulations are performed in a temperature ( $T$ ) range of 500–1200 K each step of 100 K. The simulation boxes are first relaxed using an isothermal-isobaric ensemble (NTP) for reaching the thermodynamic equilibrium; the production runs are carried out with an isothermal-isochoric ensemble (NVT) recording the mean square displacement (MSD) for the  $A^+$  ions. The diffusion coefficients ( $D$ ) are obtained from the MSD plots by eqn (2):

$$MSD = 6Dt \quad (2)$$

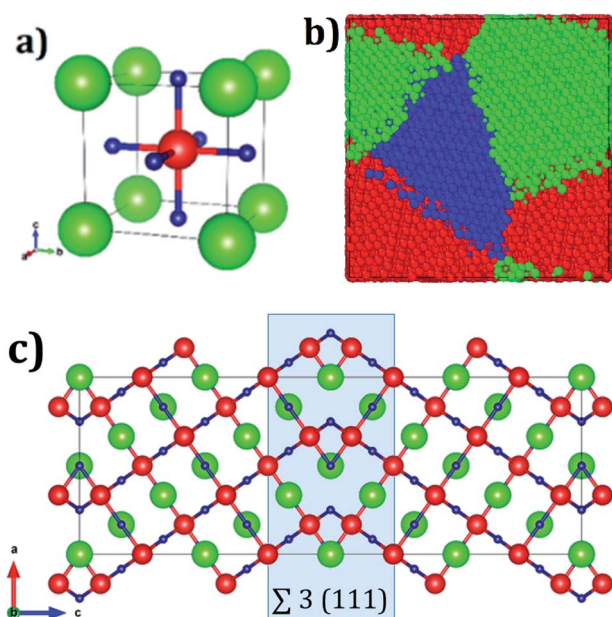


Fig. 1 (a) Unit cell of  $A_3OX$  ( $A = Li^+, Na^+$ ,  $X = Cl^-, Br^-$ ) lattice structures, green, red and blue represents  $X^-$ ,  $O^{2-}$  and  $A^+$  ions respectively, (b)  $A_3OX$  nanocrystal with three grains, and (c)  $\Sigma 3(111)$  grain boundary, where the shaded square highlights the grain boundary region. Color coding in (b) represents a unique grain.



where  $t$  is the simulation time. Each production run is limited to 2 ns with a time step of 2 fs.

The ionic conductivity or direct current conductivity ( $\sigma_{DC}$ ) can be obtained employing the Nernst–Einstein formulation (3):

$$\sigma(T) = H_V N q^2 D(T) / k_B T \quad (3)$$

where  $q$  is the charge of the mobile ion,  $N$  the charge density of the mobile ion,  $k_B$  the Boltzmann constant, and  $H_V (=1)$  represents the Haven's ratio used to consider the effect on the mobility of the charge carrier (ion) of the external electric field in real samples.<sup>23–25</sup> Following application of this procedure for various temperature values, we obtain a series of values for  $D(T)$  and  $\sigma(T)$ , that can be fitted with the aid of an Arrhenius-type function (4):

$$D(T) = D_0 \exp(-E_a/k_B T); \sigma(T) = \sigma_0 \exp(-E_a/k_B T) \quad (4)$$

to obtain the simulated activation energy ( $E_a$ ) for diffusion and electrical conduction, respectively. In eqn (4),  $D_0$  and  $\sigma_0$  are pre-exponential factors for diffusion and conduction, respectively. The simulated values of  $D(T)$  and in particular of  $\sigma(T)$  are valuable parameters as they can be directly compared to the experimental results reported in the literature.<sup>6,15,23–25</sup>

### 3. Results and discussion

#### 3.1 Alkali ion migration in $A_3OX$ ( $A = Li^+, Na^+$ , $X = Cl^-, Br^-$ ) nanocrystals

The temporal evolution of the MSD values of each  $A_3OX$  nanocrystal is illustrated in Fig. 2. In all cases, the MSD dependence is clearly linear, and the slope increases upon increasing temperature, indicating a long-range alkali atom migration within the respective nanocrystalline structure. It is noteworthy that the  $Li_3OX$  samples have higher values of MSDs as compared with  $Na_3OX$  counterparts. Therefore, the order of MSDs in  $Li_3OCl$  is similar to that for  $Li_3OBr$ . On the contrary, a difference of the first-order of MSDs is observed in  $Na_3OCl$  and  $Na_3OBr$  samples. This is attributable to the difference between the ionic radius and atomic mass of the  $Li^+/Na^+$  ions. In addition, the lattice parameters of  $Na_3OX$  lattice structure are larger than those of  $Li_3OX$ ,<sup>16,20</sup> and consequently the jump distance is larger in  $Na_3OX$  structures as compared with  $Li_3OX$  limiting the ease of Na-ion migration in  $Na_3OX$  structures *via* a  $Na^+$  vacancy mechanism.

Alkali diffusion coefficient and conductivity at each temperature for each  $A_3OX$  nanocrystal are obtained from eqn (2) and (3), respectively. The Arrhenius-type dependence of both diffusion coefficient and conductivity is depicted in Fig. 3. Table 1 compiles the results of activation energy for diffusion and conduction, including the interpolated values at 300 and 500 K of conductivity of  $A_3OX$  nanocrystals ( $\sigma(300\text{ K})$  and  $\sigma(500\text{ K})$ , respectively). The  $Li_3OCl$  samples have the largest value of conductivity, followed by  $Li_3OBr$ ,  $Na_3OCl$  and  $Na_3OBr$  in a decreasing order. This behavior was previously reported by Dawson *et al.* in monocrystalline samples (*i.e.* without grain boundaries).<sup>16</sup> The activation energy for diffusion is consistently



Fig. 2 Mean square displacement versus simulation time of each  $A_3OX$  nanocrystalline sample.

lower as compared to that for the conduction, indicating the existence of non-efficient jumps contributing to the conductivity, despite the difference between mass and charge transport phenomenon.

Hereafter, the results are discussed on the basis of activation energy for conduction; a similar discussion can be followed for the diffusion process. The lowest values of activation energy are obtained for  $Na_3OCl$  and  $Na_3OBr$ , being 0.45 and 0.38 eV, respectively, whereas the activation energy amounts to 0.54 eV for  $Li_3OCl$  and  $Li_3OBr$ . These values are larger as compared to



**Table 1** Transport properties of  $A_3OX$  antiperovskite structures.  $E_a^D$  and  $E_a^\sigma$  (in eV) represent the activation energy for diffusion and conduction, respectively

| Structure | Specie | $E_a^D$ | $E_a^\sigma$ | $\sigma(300\text{ K})$ | $\sigma(500\text{ K})$ |
|-----------|--------|---------|--------------|------------------------|------------------------|
| $Li_3OCl$ | Li     | 0.63    | 0.55         | $4.35 \times 10^{-7}$  | $2.13 \times 10^{-3}$  |
| $Na_3OCl$ | Na     | 0.53    | 0.45         | $7.12 \times 10^{-7}$  | $7.90 \times 10^{-4}$  |
| $Li_3OBr$ | Li     | 0.62    | 0.54         | $3.44 \times 10^{-7}$  | $1.47 \times 10^{-3}$  |
| $Na_3OBr$ | Na     | 0.45    | 0.38         | $7.77 \times 10^{-7}$  | $2.9 \times 10^{-4}$   |

those reported in ref. 16 for monocrystalline samples. The conductivity at 500 K reaches the value of  $1.47$  and  $2.13 \times 10^{-3} \text{ Scm}^{-1}$ , for  $Li_3OBr$  and  $Li_3OCl$ , while  $2.9$  and  $7.9 \times 10^{-4} \text{ Scm}^{-1}$  for  $Na_3OBr$  and  $Na_3OCl$ , respectively.

With respect to the activation energies and conductivity at 500 K reported in early studies, clearly our present calculated values are quite different, with larger activation energies and slightly lower conductivities. Considering the reported underestimation of calculated values for transport properties (*i.e.*

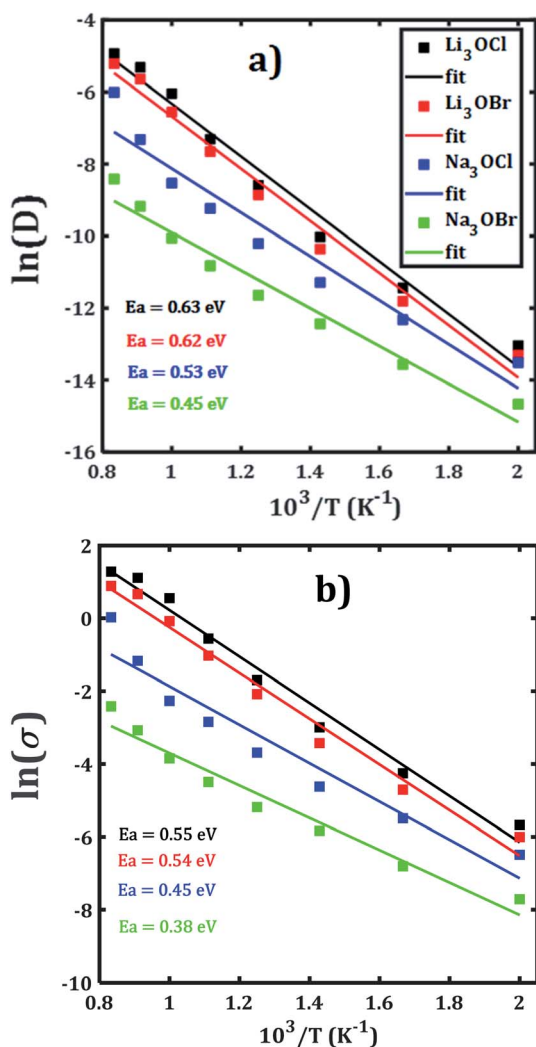
activation energy, diffusion coefficient and conductivity) for these compounds,<sup>15–17</sup> the inclusion of the polycrystalline nature with presence of  $\Sigma 3(111)$  grain boundary makes the results more credible. In general, the present trend and magnitude of the conductivity are more consistent with available experimental data. For instance, the bulk  $Li_3OCl$  is characterized with an activation energy of  $0.54$ – $0.59$  eV and a conductivity of  $5.8 \times 10^{-7} \text{ Scm}^{-1}$ .<sup>12,17,25,26</sup> A recent theoretical study of the  $Na^+$  migration in  $Na_3OBr$  which was based on a combined deep potential MD, *ab initio* MD and static simulations, revealed a diffusion activation energy of  $0.41$ – $0.43$  eV and a conductivity at ambient temperature up to  $2 \times 10^{-7} \text{ Scm}^{-1}$ ,<sup>27</sup> even a static simulation study reported an activation energy as low as  $0.34$  eV.<sup>17</sup> Earlier study of transport properties of  $Na_3OCl$  obtained a conductivity at 500 K of  $2 \times 10^{-4} \text{ Scm}^{-1}$ .<sup>16,27</sup> From the results listed in Table 1 we can conclude on a consistency between the reported findings<sup>15,16</sup> and our present results. In particular, the transport properties reported in the present paper are more realistic considering the presence of  $\Sigma 3(111)$  grain boundaries and polycrystalline nature in such  $A_3OX$  structures. Our results explicitly confirm the fact that the presence of grain boundary in the computations, particularly the  $\Sigma 3(111)$  entails the high grain boundary resistance in these compounds.<sup>15,17</sup>

Trajectory density plot is a powerful tool to visualize the ion mobility, especially in polycrystalline materials.<sup>15,24</sup> Fig. 4 depicts the Li and Na trajectory plot at 200 ps of  $A_3OX$  nanocrystals. In all cases the trajectory maps confirm the 3D characteristic of alkali migration. At 200 ps, the granulated samples are clearly visible except for  $Na_3OBr$  sample having a higher density trajectory map, which implies that the Li and Na mobility is constrained when they are close to the grain boundaries.

The Li and Na mobility through the grain boundaries is not restricted because these conducting regions contain more migration paths, where the alkali-ion diffuses without the need of alkali vacancy as a conduction mechanism which is required for bulk  $A_3OX$  and monocrystalline samples. With the temporal evolution, alkali ions can migrate to the grain *via* interstitial or Li/Na vacancy conduction mechanism. At 2 ns, the trajectory plots are getting denser, in particular for  $Li_3OCl$ ,  $Li_3OBr$  and  $Na_3OCl$  the granulated structure is still visible showing a higher density near of the grain boundary regions. The  $Na_3OBr$  shows the highest density map covering the entire simulation box, implying that this compound has better Na transport properties as compared to the other cases considered. In addition, the trajectory plot becomes similar to that of a monocrystalline  $Na_3OBr$  sample.

### 3.2 Li and Na transport properties in mixed cation systems

An earlier study reported the transport properties of monocrystalline samples of mixed cation  $Li_{3-y}Na_yOX$  and  $Na_{3-y}Li_yOX$ , predicting no significant improvements on transport properties as compared to those of the  $A_3OX$  structures.<sup>16</sup> Exploration of transport properties of these systems is of interest to further elucidate the capability of pristine  $Li_3OX$ /



**Fig. 3** Arrhenius dependence of (a) diffusion coefficient and (b) DC conductivity of each  $A_3OX$  nanocrystalline samples.



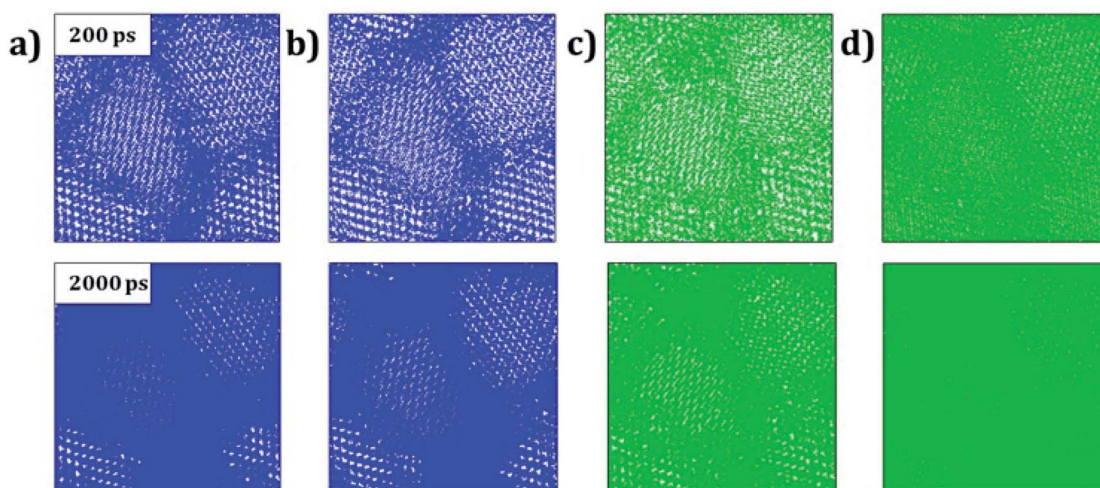


Fig. 4 Trajectory density map of (a)  $\text{Li}_3\text{OCl}$ , (b)  $\text{Li}_3\text{OBr}$ , (c)  $\text{Na}_3\text{OCl}$  and (d)  $\text{Na}_3\text{OBr}$  compounds after 200 ps (top images) and 2000 ps (bottom images). Blue and green lines represents the Li and Na trajectory lines, respectively.

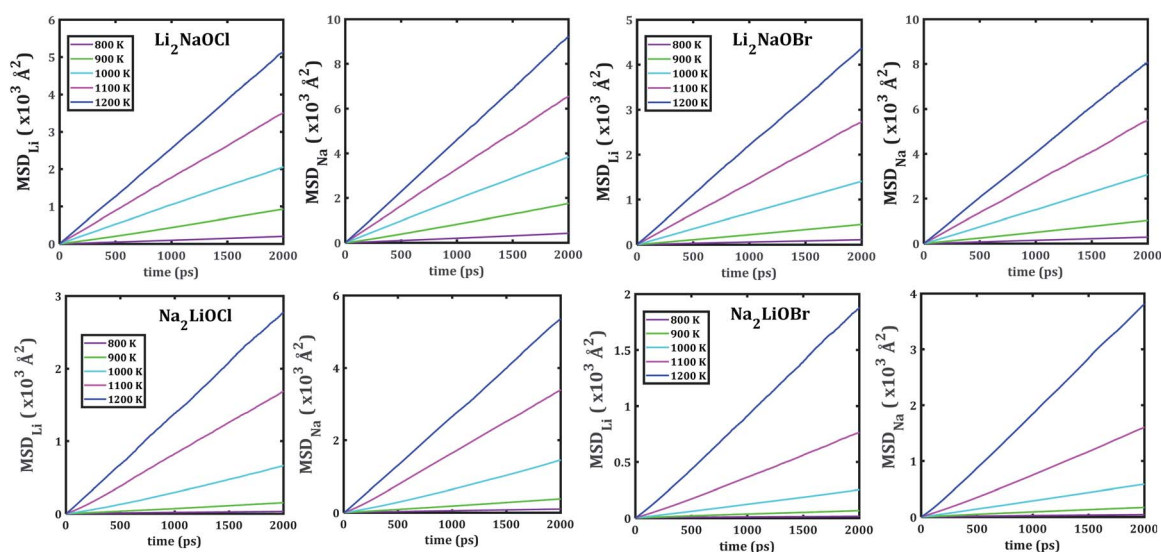


Fig. 5 Li- and Na-mean square displacement (MSD) versus simulation time of  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures.

$\text{Na}_3\text{OX}$  as inorganic solid electrolyte for lithium/sodium ion batteries. In this context, this section is aimed to a study on transport properties of the mixed nanocrystals of  $\text{Li}_{3-x}\text{Na}_x\text{OX}$  and  $\text{Na}_{3-x}\text{Li}_x\text{OX}$ . Nanocrystals are constructed by random substitution of Li/Na in  $\text{Li}_3\text{OX}$  and  $\text{Na}_3\text{OX}$  structures discussed in Section 3.1, leading a composition of 17 187  $\text{Li}^+$ , 8593  $\text{Na}^+$ , 8615  $\text{O}^{2-}$  and 8550  $\text{X}^-$ , resulting in a stoichiometric formula  $\text{Li}_2\text{NaOX}$  maintaining the defect concentration of  $\text{A}^+$  and  $\text{X}^-$  ( $y = 0.118$ ). For the sodium counterpart  $\text{Na}_2\text{LiOX}$ , the alkali composition is 17 187  $\text{Na}^+$  and 8593  $\text{Li}^+$ , maintaining the same number of  $\text{O}^{2-}$  and  $\text{X}^-$  species. Both  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  preserve the  $\Sigma 3(111)$  grain boundary as well as the amount and size of grain and the simulation box. Eqn (1) is also considered for the construction of the simulation boxes, leading  $V_A$ . The same setup described in Section 3.1 for large scale MD is

adopted, recording the MSD for  $\text{Li}^+$  and  $\text{Na}^+$  in  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures.

Fig. 5 depicts the temporal evolution of the mean square displacement of  $\text{Li}^+$  and  $\text{Na}^+$  ions in  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  nanocrystals. As shown in Fig. 5, all MSDs tend to increase linearly with the evolution of the simulation time, and the slope increases upon the temperature change. This is an indicator for the existence of long-range diffusion.

Note that in all mixed cation samples, the order of magnitude of Na-MSD is greater than that of the Li-MSD in the entire temperature range studied, which implies better migration properties for  $\text{Na}^+$  ion in all samples considered.

In order to disclose the migration properties, the diffusion coefficients are obtained by fitting the MSDs data using eqn (2). Fig. 6 shows the Arrhenius-type dependence of diffusion with the temperature of each mixed cation system. The straight lines



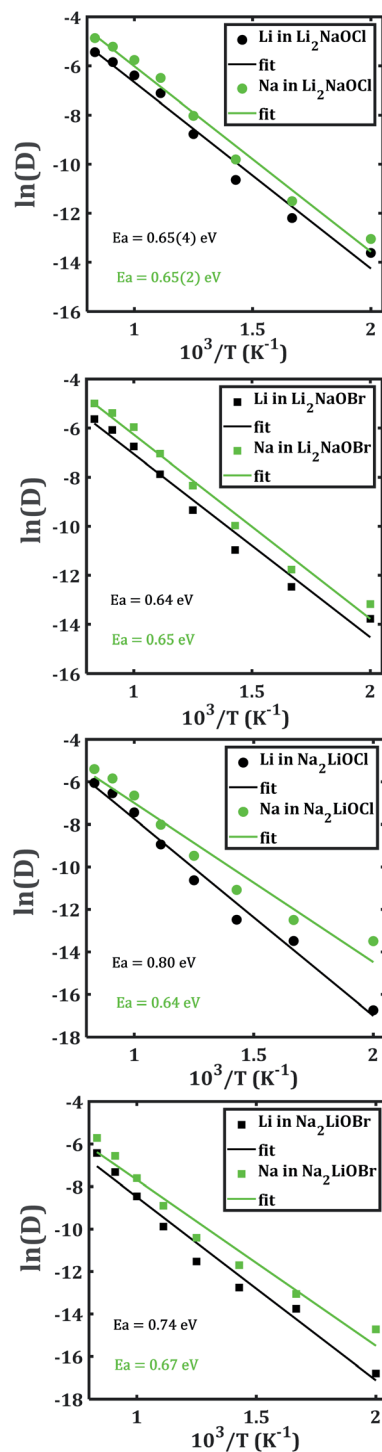


Fig. 6 Arrhenius dependence of Li- and Na-diffusion coefficient ( $D$ ) of  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures.

in Fig. 6a and b are almost parallel, which implies similar activation energies (being  $\approx 0.65$  eV) for both  $\text{Li}^+$  and  $\text{Na}^+$  migrations in  $\text{Li}_2\text{NaOX}$  systems. These activation energies for diffusion in  $\text{Li}_2\text{NaOX}$  are similar as compared to their pristine  $\text{Li}_3\text{OX}$  counterpart ( $\approx 0.63$  eV). Surprisingly, the diffusion coefficient of  $\text{Na}^+$  is higher by one order of magnitude with respect to the  $\text{Li}^+$  diffusivity in all cases, suggesting that these systems

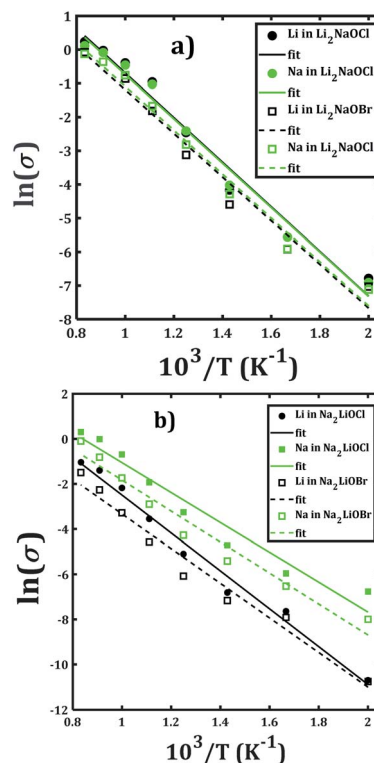


Fig. 7 Arrhenius-type dependence of Li and Na dc-conductivity of (a)  $\text{Li}_2\text{NaOX}$  and (b)  $\text{Na}_2\text{LiOX}$  nanocrystalline sample.

have some potential in application as inorganic solid-state electrolyte for future Na-ion batteries. Analogously, the diffusion data are converted to the dc conductivity with the aid of eqn (4).

Fig. 7 depicts the Arrhenius-type dependence of the  $\text{Li}^+$  and  $\text{Na}^+$  dc-conductivity for  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures. While Fig. 7a shows the case of conductivity dependence in  $\text{Li}_2\text{NaOX}$ , Fig. 7b is related to  $\text{Na}_2\text{LiOX}$  structures. The alkali conductivities for  $\text{Li}_2\text{NaOCl}$  and  $\text{Li}_2\text{NaOBr}$  structures are similar to each other (Fig. 7a). At lower temperature ( $<900$  K) the conductivity values are higher by two, even three orders of magnitude in  $\text{Li}_2\text{NaOX}$  with respect to the  $\text{Na}_2\text{LiOX}$  compound, except for the Na conduction in  $\text{Na}_2\text{LiOCl}$  structure with similar values upon temperature change.

Table 2 Transport properties of  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  antiperovskite structures.  $E_a^D$  and  $E_a^\sigma$  (in eV) represent the activation energy for diffusion and conduction, respectively

| Structure                 | Specie | $E_a^D$ | $E_a^\sigma$ | $\sigma(300\text{ K})$ | $\sigma(500\text{ K})$ |
|---------------------------|--------|---------|--------------|------------------------|------------------------|
| $\text{Li}_2\text{NaOCl}$ | Li     | 0.65(4) | 0.57(0)      | $9.86 \times 10^{-8}$  | $6.68 \times 10^{-4}$  |
|                           | Na     | 0.65(2) | 0.56(7)      | $1.02 \times 10^{-7}$  | $6.62 \times 10^{-4}$  |
| $\text{Li}_2\text{NaOBr}$ | Li     | 0.64    | 0.55(8)      | $8.34 \times 10^{-8}$  | $4.68 \times 10^{-4}$  |
|                           | Na     | 0.65    | 0.56(1)      | $8.38 \times 10^{-8}$  | $4.97 \times 10^{-4}$  |
| $\text{Na}_2\text{LiOCl}$ | Li     | 0.80    | 0.72         | $2.57 \times 10^{-10}$ | $1.87 \times 10^{-5}$  |
|                           | Na     | 0.64    | 0.57         | $6.84 \times 10^{-8}$  | $4.64 \times 10^{-4}$  |
| $\text{Na}_2\text{LiOBr}$ | Li     | 0.74    | 0.66         | $5.90 \times 10^{-10}$ | $1.66 \times 10^{-5}$  |
|                           | Na     | 0.67    | 0.59         | $1.77 \times 10^{-8}$  | $1.67 \times 10^{-4}$  |



Table 2 summarizes the activation energies for Li and Na diffusion and conduction, including the conductivity at 300 and 500 K in  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures. As in the case of the pristine  $\text{A}_3\text{OX}$  compounds, the activation energy for both alkali ions diffusion is larger than that for conduction, due to non-effective jumps contributing to the long-range conductivity.  $\text{Li}_2\text{NaOX}$  have smaller activation energies, being between 0.65/0.56 eV for diffusion/conduction, respectively. Our calculated results of conductivity at 300 K reach to the values of  $1.02 \times 10^{-7}$  and  $6.62 \times 10^{-4} \text{ Scm}^{-1}$  at 500 K for  $\text{Na}^+$  conduction in  $\text{Li}_2\text{NaOCl}$  nanocrystalline sample; both quantities lie well in a range for those obtained for the pristine  $\text{Na}_3\text{OCl}$ .<sup>16</sup> Our results are also consistent with the reported Li conductivity of  $\approx 10^{-4} \text{ Scm}^{-1}$  which was reported for  $\text{Li}_2\text{NaOX}$  at 500 K.<sup>16</sup> In the case of  $\text{Li}_2\text{NaOBr}$ , the  $\text{Li}^+$  and  $\text{Na}^+$  conductivities at 300 K and 500 K are in the order of  $8 \times 10^{-8}$  and  $5 \times 10^{-4} \text{ Scm}^{-1}$ , respectively. For  $\text{Na}_2\text{LiOX}$  structures, again the  $\text{Na}^+$  conduction suggests its better transport properties in view of their lower activation energy and higher diffusion coefficient and conductivity at 300 and 500 K. Among the  $\text{Na}_2\text{LiOX}$  structures,  $\text{Na}_2\text{LiOCl}$  presents us with some better Na transport properties.

The origin of the higher diffusion coefficient and conductivity in mixed  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures can be rationalized by the defect formation energy of Li/Na halide partial Schottky defects. For instance, the formation energy of Na-halide Schottky defect in  $\text{Na}_2\text{LiOCl}$  and  $\text{Na}_2\text{LiOBr}$  is lower as compared to their Li-halide counterparts.<sup>16</sup> For  $\text{Li}_2\text{NaOX}$  compounds, the Li/Na-X formation energy is similar, in accordance with the results on diffusion/conduction data depicted in Fig. 6 and 7. On the other hand, reports concerning the contradiction of conventional typecast are based on the ionic radius difference between Li (0.59 Å) and Na (0.99 Å).<sup>28–30</sup> Considering the  $\text{A}^+$  ionic size as indicated by the mean ionic radius of Li and Na (*i.e.*  $r(\text{A}) = 0.79 \text{ Å}$ ), one can conclude that a substitution of Na occupying the A-site results as

a consequence in a strong local strain/stress in the  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures, reducing the Na - $\text{V}_\text{A}$  distance and the diffusion length. Besides, a Li occupancy of an A-site enlarges the Li-  $\text{V}_\text{A}$  distance. An A-halide Schottky defect leads to A-vacancies together with the competition between Li and Na atoms to reach the vacancies of A, and thereby constitutes the origin of the conductive behaviour in  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures.

Fig. 8 displays the trajectory density plots of  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures at 2 ns. The density map profiles are similar to those discussed in the case of  $\text{A}_3\text{OX}$  materials. The main difference consists in the fact that both Li and Na ion transports are favoured with marginally higher activation energies and lower conductivity at operative temperatures. Similar findings of individual alkali ion migration were discussed,<sup>16</sup> where it was concluded that these mixed cation systems (*i.e.*  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$  structures) are unfavourable to be used as inorganic electrolytes on the basis of the activation energy and diffusion/conduction at operative temperatures.

## 4. Conclusions

The influence of the presence of  $\Sigma 3(111)$  grain boundaries on the transport properties of  $\text{A}_3\text{OX}$  nanocrystalline samples was disclosed. Large scale molecular dynamic simulations showed that these nanocrystalline samples have higher activation energies as compared to values reported in previous theoretical studies, but much closer to the experimental data. This is attributed to the higher atomic density at the  $\Sigma 3(111)$  grain boundaries. The pristine  $\text{Na}_3\text{OBr}$  sample is characterized by the lower activation energies for Na-ion diffusion and conduction, making this compound promising for future solid state electrolyte in Na-ion batteries technologies. Despite some lowering of transport properties of the mixed samples  $\text{Li}_2\text{NaOX}$  and  $\text{Na}_2\text{LiOX}$ , they can also be considered as inorganic solid electrolytes in both Li- and Na-Ion batteries.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

LVD is thankful to the Van Lang University.

## Notes and references

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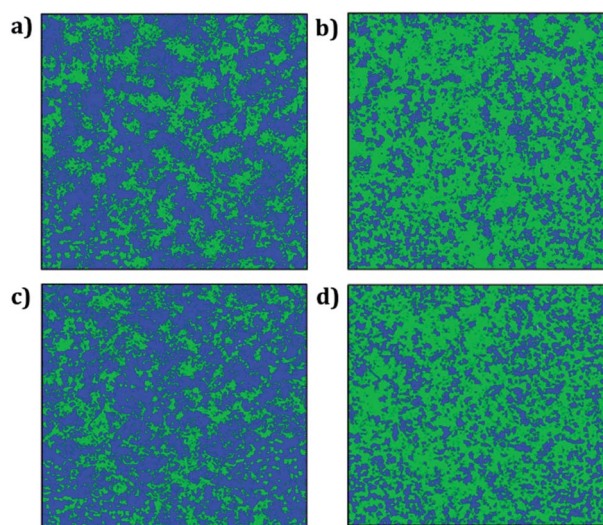


Fig. 8 Trajectory plots of Li and Na in (a)  $\text{Li}_2\text{NaOCl}$ , (b)  $\text{Na}_2\text{LiOCl}$ , (c)  $\text{Li}_2\text{NaOBr}$  and (d)  $\text{Na}_2\text{LiOBr}$  compounds after 2 ns. Blue and green lines represent the Li and Na trajectory lines, respectively.



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