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Dr Blake Baker  
Publishing Editor  
Royal Society of Chemistry

12 October 2021

Dear Dr Baker,

**Manuscript ID: TA-ART-09-2021-007588**  
Title: "Atomic-scale investigation of cation doping and defect clustering in the anti-perovskite Na3OCl sodium-ion conductor"

Thank you for your email of 1 October 2021. We are pleased that both reviewers recommend publication (after minor revisions) with Reviewer 1 stating “this work can give significant inspirations to world-wide researchers” and Reviewer 2 stating “this work helps to provide a framework to guide future doping studies”. We have attended to all the points raised by the referees (italics below) and trust the paper is now suitable for publication.

# Reviewer 1

## By using some references, the two doping concentrations of 0.3% and 1.2% were specified for their simulation. However, it is a very important issue to investigate the effects of doping concentration on the device performance. Most of all, in the anti-perovskite structure, small changes in the doping level (around 0.2~0.3%) can result in dramatic differences in the performance. Thus, it is suggested to conduct other doping levels between 0.3~1.2% and over 1.2%, respectively.

In this study, we have considered two divalent (Mg, Ca) and two trivalent (Al, Ga) dopant ions for our large-scale MD simulations at four different temperatures. This is a wider range of aliovalent dopants than in a single experimental study. We stress that the dopant concentrations were chosen in the range of previous experimental studies on the aliovalent doping on sodium-based anti-perovskites [refs. 26 and 44 in the manuscript]. These points are included on pages 2 and 3 of the manuscript.

Our results show that increasing the vacancy concentration from 0.3% to 1.2% via aliovalent doping leads to an increase in the ionic conductivity of Na3OCl. At the concentrations investigated (max. 1.2%), the dopant ions are over 13 Å away from each other and the formation of large cluster complexes is highly unlikely. Therefore, it is predicted that the optimal vacancy concentration is not between the values investigated. In line with the reviewer’s comments, we have also considered a higher dopant concentration (4.2%) for the most favourable Mg2+ dopant. The results are presented in the supplementary information and show that the ionic conductivity is lower than the 1.2% level.

## If the authors provide the optimal dopant and Na vacancy levels via copious DFT calculations with the electronic structure and carrier effective mass, this work can act as a navigator of simulating the anti-perovskite structure for the energy storage.

We stress that our MD analysis uses very large supercells (>17,000 ions) and very long timescales (10,000 ps). These values are orders of magnitude greater than those currently attainable by DFT-based MD. Nevertheless, future DFT calculations on the electronic structure warrants further investigation and are not within the scope of this study, which focuses on ionic transport.

# Reviewer 2

## In the manuscript, the dopant concentration was chosen according to previous experimental studies on the aliovalent doping on sodium-based anti-perovskites. But how does the dopant concentration affect the Na-ion conductivity?

In this study, we have considered two divalent (Mg, Ca) and two trivalent (Al, Ga) dopant ions for our large-scale MD simulations at four different temperatures and two different concentrations, as shown in Fig. 3. This is a wider range of aliovalent dopants than in a single experimental study.

An increased vacancy concentration allows for a higher rate of ionic migration via a vacancy migration mechanism, which results in an increased Na-ion conductivity. Our calculations show that higher dopant concentrations can indeed lead to a higher Na-ion conductivity once the clustering effect is overcome. The highest Na-ion conductivity is found for the Mg-doped system of the order of 10-5 S/cm at 500K. These points are found in Fig. 3 and pages 3 and 4.

## Why would a high level of Na-vacancy/dopant clustering hinder Na-ion conduction?

The experimental characterization of defect clusters at the atomic scale can be difficult. Our atomistic simulations determine the binding energies of dopant-vacancy pairs in Na3OCl. The results shown in Fig. 4 clearly indicate Mg with the smallest binding energy, but higher binding energies for Al in particular. Such Na vacancy/dopant clustering would hinder Na-ion conduction by “trapping” the migrating Na vacancies, which is well-known in the field of fluorite-structured oxide ion conductors.

## Please move the Figure label (a) (b) (c) to the top-left corner.

In line with reviewer’s comments, we moved the labels (a), (b) and (c) to the top-left corner.

We hope the paper is now suitable for publication and look forward to hearing from you soon.

Yours sincerely,

*Prof. M. Saiful Islam*