

## PAPER

[View Article Online](#)  
[View Journal](#) | [View Issue](#)Cite this: *J. Mater. Chem. A*, 2020, 8, 21265Mechanism of enhanced ionic conductivity by rotational nitrite group in antiperovskite  $\text{Na}_3\text{ONO}_2$ †Lei Gao,<sup>‡abc</sup> Hao Zhang,<sup>‡da</sup> Yuechao Wang,<sup>e</sup> Shuai Li,<sup>bc</sup> Ruo Zhao,<sup>abc</sup> Yonggang Wang,<sup>‡f</sup> Song Cao,<sup>a</sup> Jinchao He,<sup>ghi</sup> Hai-Feng Song,<sup>e</sup> Ruqiang Zou<sup>‡\*a</sup> and Yusheng Zhao<sup>‡\*bc</sup>HPSTAR  
1049-2020

Sodium-rich antiperovskite (NaRAP) ionic conductors have been considered promising inorganic electrolytes for all-solid-state sodium batteries due to their low fabrication cost, high sodium ionic conductivity and good structural tolerance. The high structural flexibility of NaRAPs allows variety of chemical substitutions to improve conductivity; in particular, the substitution of the anion cluster has effectively proved promoting  $\text{Na}^+$  migration, both experimentally and theoretically. Herein, we report an unexpected boost in  $\text{Na}^+$  ionic conductivity that climbs to  $0.37 \text{ mS cm}^{-1}$  at 485 K by introducing  $\text{NO}_2^-$  groups in the antiperovskite  $\text{Na}_3\text{ONO}_2$  system. Its mechanism was fully investigated by neutron powder diffraction and DFT calculations, proving that the  $\text{NO}_2^-$  group on the lattice center, can utilize its terminal  $\text{O}^{2-}$  anion to facilitate the  $\text{Na}^+$  migration via the Na–O interaction, when thermally excited at 485 K. The detailed migration path is also discussed by both maximum entropy method (MEM) and DFT calculations.

Received 21st July 2020  
Accepted 27th September 2020

DOI: 10.1039/d0ta07110b

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## 1. Introduction

The increasing demands for large-scale energy storage systems in many fields stimulate the development of rechargeable battery technologies.<sup>1,2</sup> Rechargeable sodium (Na)-ion batteries are promising candidates owing to the low cost and high abundance of sodium resources.<sup>3,4</sup> Furthermore, Na-ion batteries have the advantage that many high capacity Na-cathodes do not contain cobalt, a common and high-cost

component in commercial lithium (Li)-ion cathodes.<sup>5</sup> The all-solid-state Na-ion batteries employing inorganic solid electrolytes have been considered as the best choice, due to their low flammability, absence of leakage and high safety.<sup>6–8</sup> Indeed, solid-state  $\beta\text{-Al}_2\text{O}_3$  electrolytes have been commercialized in high-temperature sodium-sulfur (NAS) batteries,<sup>9</sup> and an ionic conductivity over  $1 \text{ mS cm}^{-1}$  has been reported in NASICON-type oxide crystals at room temperature (RT).<sup>10</sup> However, most of these electrolytes either require an elevated sintering temperature to optimize the grain-boundary resistance or have poor electrolyte–electrode contact.<sup>11</sup>

Lithium-rich antiperovskite (LiRAP) superionic conductors have been considered promising solid-state electrolytes since they (a) exhibit high ionic conductivity;<sup>12</sup> (b) have good electrochemical stability and structural tolerance;<sup>13–15</sup> (c) are compatible with lithium metal anodes;<sup>16</sup> (d) can be processed into the desired shape and thickness at a low melting point.<sup>12,16,17</sup> Meanwhile, the sodium-rich antiperovskite (NaRAP) analogues possess the same advantages as LiRAP and have also attracted increasing attention.<sup>18–21</sup>  $\text{Na}_3\text{OX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) are typical NaRAP electrolytes, and the ionic conductivity of  $\text{Na}_{2.9}\text{Sr}_{0.05}\text{OBr}_{0.6}\text{I}_{0.4}$  electrolytes can reach a high  $\text{Na}^+$  conductivity of  $1.89 \text{ mS cm}^{-1}$  at 473 K through chemical manipulation.<sup>18</sup> The isotropic three-dimensional  $\text{Na}^+$  migration path in the NaRAP system is considered superior over other series.

To further improve the conductivity, researchers are focusing their attention to anion groups. Substituting X with a cluster (*i.e.*,  $\text{Na}_3\text{S}(\text{BCl}_4)$  and  $\text{Na}_3\text{O}(\text{BF}_4)$ ) was predicted to be an effective way to achieve higher ionic conductivity.<sup>20</sup> However,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ta07110b

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unfortunately, their experimental synthesis route is still unclear. A well-established example for  $\text{Na}^+$  conductors in which the superhalogen cluster substitution is experimentally realized is the recently discovered  $\text{Na}_3\text{OBH}_4$  electrolyte, which shows extremely high ionic conductivity ( $\sim 4.4 \text{ mS cm}^{-1}$ ) even at RT due to the rotation of the  $\text{BH}_4^-$  anion group.<sup>21</sup> The theoretically predicted rotational effect was finally proved by experiments, inspiring us to investigate more anion groups on the X site for faster ionic transportation.

However, only a few anion clusters can be introduced into the NaRAP lattice with careful consideration of the cluster size and strict control over the synthesis conditions (atmosphere, temperature, reagent, *etc.*). The reason that the  $\text{NO}_2^-$  anion group was specifically chosen in this work is as follows. First, the reagents  $\text{Na}_2\text{O}$  and  $\text{NaNO}_2$  are chemically active species so that the product  $\text{Na}_3\text{ONO}_2$  can be fabricated at a low temperature without  $\text{NaNO}_2$  decomposition. Second, if the  $\text{NO}_2^-$  cluster can be introduced into the lattice and form the stable NaRAP structure, then it is possible to disturb the lattice in a similar way through free rotation as  $\text{BH}_4^-$  does (paddle-wheel effect). Third, the non-centrosymmetric  $\text{NO}_2^-$  group may introduce intriguing behavior to the  $\text{Na}^+$  migration compared with the centrosymmetric  $\text{BH}_4^-$  group.

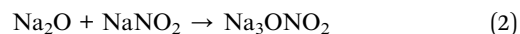
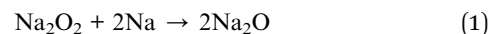
Herein, we successfully synthesized antiperovskite  $\text{Na}_3\text{ONO}_2$  using a nitrite group ( $\text{NO}_2^-$ ) as the anion cluster. From electrochemical impedance spectroscopy (EIS), its  $\text{Na}^+$  ionic conductivity at 485 K is greatly enhanced to  $0.37 \text{ mS cm}^{-1}$ , which surpasses that of non-clustered  $\text{Na}_3\text{OBr}$ . Neutron powder diffraction refinements reveal that the thermal vibration of  $\text{NO}_2^-$  considerably increases at 485 K, coincident with the conductivity enhancement. DFT calculations demonstrate that  $\text{NO}_2^-$  rotation facilitates the  $\text{Na}^+$  migration *via* the Na–O interaction, with a migration energy barrier as low as 0.37 eV. Therefore, we propose that the  $\text{NO}_2^-$  rotation is largely increased at 485 K in that more  $\text{Na}^+$  cations can be pointed by and assisted by the  $\text{O}^{2-}$  (of  $\text{NO}_2^-$ ) anions during migration, and hence the total ionic conductivity was improved at 485 K. This work brings to light how the acentric anion cluster affects the  $\text{Na}^+$  migration from the perspective of ionic interaction, which provides deeper insights into improving the antiperovskite ionic conductivity using anion clusters.

## 2. Experimental

### 2.1 Synthesis

All preparations and sample treatments were performed under Ar atmosphere. Firstly, the ground  $\text{Na}_2\text{O}$  (Sigma-Aldrich, 80% (20%  $\text{Na}_2\text{O}_2$  impurity)) and Na metal (Aladdin, 99.7%) blocks were mixed and placed in a capped alumina crucible, then heated at 523 K in a vacuum quartz tube furnace for 1 h to obtain pure  $\text{Na}_2\text{O}$  (Fig. S1†) following the reaction pathway shown in eqn (1). Experimentally, the amount of Na metal needs to be about 10% more than the  $\text{Na}_2\text{O}_2$  impurity due to evaporation. Secondly, stoichiometric amounts of purified  $\text{Na}_2\text{O}$  and  $\text{NaNO}_2$  (Aladdin, 99.99%) were mixed and ground with an agate mortar and pestle for 30 min, then the compound powder was pressed into 12 mm-diameter pellets under 300 MPa using

a stainless-steel die. Subsequently, the pellets were sealed in a quartz tube and heated to 583 K under vacuum at the rate of  $3^\circ\text{C min}^{-1}$ . The reaction was driven at the highest reacting temperature for 12 h following the pathway shown in eqn (2), and the products were allowed to cool naturally to room temperature in the quartz tube.



### 2.2 Powder X-ray diffraction and neutron powder diffraction

Powder X-ray diffraction (PXRD) measurements were conducted on a Rigaku SmartLab 9 kW diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) to identify the phases of the samples. Before measurement, each sample was sealed by Kapton film under Ar atmosphere to protect the sample from air and humidity.

Time-of-flight (TOF) neutron powder diffraction (NPD) was performed at GPPD (General Purpose Powder Diffractometer), CSNS (China Spallation Neutron Source), Dongguan Neutron Science Center. During the measurement, approximately 3 g of sample was sealed in cylindrical vanadium can, which was heated in the temperature range of 300–485 K. The data were collected using three detector banks (high-angle,  $90^\circ$ , and low-angle), covering a wide  $d$ -spacing from 0.05 to  $28.11 \text{ \AA}$ . The neutron flux at the sample position was at the order of  $10^7 \text{ n s}^{-1} \text{ cm}^{-2}$ , and the best resolution was better than 0.2% at high angle detector bank.<sup>22</sup>

### 2.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was conducted on a Setaram DSC 131 instrument, and samples were sealed in an aluminum crucible under  $\text{N}_2$  atmosphere with a heating and cooling rate of  $5^\circ\text{C min}^{-1}$  from 323 to 623 K.

### 2.4 Electrochemical impedance spectroscopy

Ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) in the temperature range of 380–513 K, using an electrochemical work station analyzer (Zennium, Zahner) at frequencies ranging from 1 Hz to 1 MHz with an amplitude of 50 mV.  $\text{Na}_3\text{ONO}_2$  powders were hot-pressed into pellets (diameter = 10 mm, thickness  $\sim 1.2 \text{ mm}$ ) under 300 MPa in an insulative die with an annealing temperature of 373 K for 5 h, and two stainless-steel rods (diameter = 10 mm) were clamped on both sides of the sample as current collectors. During the EIS measurement, the die with gaskets was hermetic enough to protect the sample from air and humidity.

### 2.5 Rietveld Refinements and maximum entropy method analysis

Rietveld Refinements on TOF NPD under different temperatures were performed by the Fullprof suite software.<sup>23</sup> The crystal lattice parameters, ion locations, and anisotropic thermal displacements were carefully refined, clearly

demonstrating the lattice expansion and higher ion vibrations as the temperature increased. Maximum Entropy Methods (MEM) were performed based on the refined structure factors.

The MEM analysis was used to reveal possible sodium ion migration pathways. The structure factors and standard uncertainties obtained by refinements were analysed by MEM with Dysnomia.<sup>24</sup> The unit cells of antiperovskites were divided into  $300 \times 300 \times 300$  voxels. The detailed method for MEM analysis can be found in ref. 25.

## 2.6 First-principles calculation

In the present computational work, Kohn–Sham density-functional theory with the projector-augmented wave (PAW) method<sup>26,27</sup> implemented in the Vienna Ab-initio Simulation Package (VASP)<sup>28,29</sup> was used. The Climbing Image Nudged Elastic Band (CI-NEB) as implemented in the Transition State Tools for VASP (VTST) package<sup>30,31</sup> was used for the calculation of transition states and barriers. The PBEsol GGA<sup>32,33</sup> was used in all calculations. For all structural optimization and CI-NEB calculations, the plane-wave cutoff energy was set to be 400 eV, and  $\Gamma$ -centered  $6 \times 6 \times 6$   $k$ -meshes were used for the primitive unit cell of  $\text{Na}_3\text{OBr}$  and  $\text{Na}_3\text{ONO}_2$ . For the  $2 \times 2 \times 1$  supercell for calculating the migration of Na, a  $3 \times 3 \times 6$   $k$ -mesh was used. Noteworthy, the lattice parameters used in the CI-NEB calculation were based on the values obtained by Rietveld refinements according to the NPD data at the corresponding experimental temperature, and the supercell volume was fixed during calculations.

## 3. Results

### 3.1 Phase analysis

Fig. 1(a) is the PXRD pattern of  $\text{Na}_3\text{ONO}_2$  at room temperature. All peaks are assigned to the cubic NaRAP-type  $\text{Na}_3\text{ONO}_2$  phase ( $Pm\bar{3}m$ ) without any other distinct impurities. Inspired by the synthesis route of  $\text{Na}_3\text{ONO}_2$ , we also investigated the possible synthesis of NaRAP-type  $\text{Na}_3\text{ONO}_3$  with the triangular  $\text{NO}_3^-$  group *via* solid-state reactions between  $\text{Na}_2\text{O}$  and  $\text{NaNO}_3$ . To our surprise, the product is an orthorhombic  $\text{Na}_3\text{NO}_4$  phase with a tetrahedral  $\text{NO}_4^{3-}$  group rather than antiperovskite phase (Fig. S2†).<sup>34</sup> The reason can be referred to the fact that the Goldschmidt tolerance factor  $t \sim 1.08$  of  $\text{Na}_3\text{ONO}_3$  is out of the stable range from 0.8 to 1.0 (eqn (3)) for a stable perovskite structure,<sup>35,36</sup> where  $R_{\text{Na}}$  is the radius of  $\text{Na}^+$  (0.95 Å),  $R_{\text{O}}$  is the radius of  $\text{O}^{2-}$  (1.40 Å) and  $R_{\text{X}}$  is the radius of  $\text{NO}_3^-$  (2.64 Å).<sup>20,37</sup> Noteworthy, during the synthesis of  $\text{Na}_3\text{ONO}_2$ , poor vacuum conditions will cause the reagent  $\text{NaNO}_2$  to partially oxidize to  $\text{NaNO}_3$  that leads to a small amount of  $\text{Na}_3\text{NO}_4$  impurity in the final product (Fig. S2†). Therefore, the vacuum conditions need to be carefully prepared to avoid impurities.

One of the merits of antiperovskites is their low melting point feature that enables easy fabrication. The thermal stability and melting point of  $\text{Na}_3\text{ONO}_2$  were analyzed by DSC.<sup>18,21</sup> The endothermic and exothermic peaks represent the melting and crystallization temperature of the sample, respectively. As shown in Fig. 1(b), the melting point of  $\text{Na}_3\text{ONO}_2$  is about 536 K,

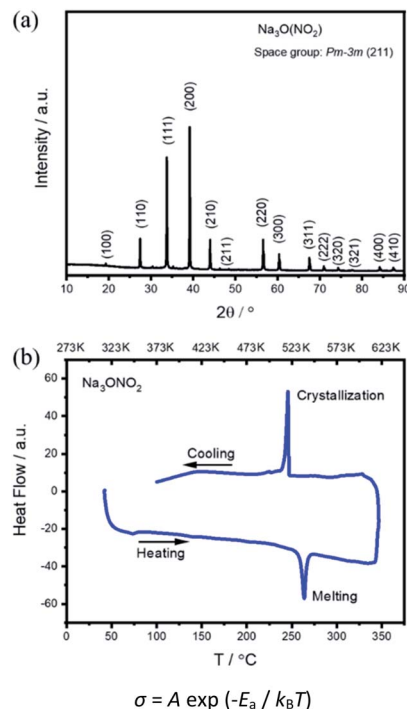


Fig. 1 (a) Powder XRD pattern of synthesized  $\text{Na}_3\text{ONO}_2$  is indexed in space group  $Pm\bar{3}m$  with assigned Miller indices. (b) Differential scanning calorimetry (DSC) curve of synthesized  $\text{Na}_3\text{ONO}_2$ .

which is higher than that of  $\text{Na}_3\text{OBr}$  and  $\text{Na}_3\text{OBH}_4$ .<sup>18,21</sup> The discontinuous  $\text{NO}_2^-$  order–disorder transition temperature is 178 K, which is out of our temperature scanning range.<sup>38</sup> Except for the melting/crystallization peaks, no other abnormal endothermic and exothermic peaks appeared in our DSC results. The melting peak is higher than that reported in early work,<sup>39</sup> and the peak related to increased  $\text{NO}_2^-$  mobility is not observed. In contrast, isomorphous  $\text{Na}_3\text{OBr}_{0.5}\text{I}_{0.5}$  needs a higher temperature of 499 K to reach  $\text{Br}^-/\text{I}^-$  disorder,<sup>18</sup> demonstrating that  $\text{NO}_2^-$  thermal vibrations are more sensitive to temperature.

$$t = (R_{\text{Na}} + R_{\text{X}}) / \sqrt{2(R_{\text{Na}} + R_{\text{O}})} \quad (3)$$

### 3.2 Ionic conductivity

The ionic transport properties of  $\text{Na}_3\text{ONO}_2$  were analyzed by temperature-dependent EIS. The Nyquist curves reflect the current response of  $\text{Na}_3\text{ONO}_2$  electrolyte at different frequencies and temperatures under a voltage disturbance (Fig. 2(a)). Taking the Nyquist curve at 395 K as a representative, as shown in Fig. 2(b), it exhibits a typical semicircle (in fact two superimposed semicircles) at high frequency representing the bulk and grain boundary resistance in series, and one Warburg-type region at low frequency representing ion blocking electrode. These are characteristics of a pure ionic conductor. Fitting this plot at 395 K by the equivalent circuit leads to a total resistance of 389.1 kΩ, including the bulk resistance  $R_1$  of 29.1 kΩ and the grain boundary resistance  $R_2$  of 360 kΩ. The grain boundary resistance  $R_2$  is one order of magnitude higher than the bulk

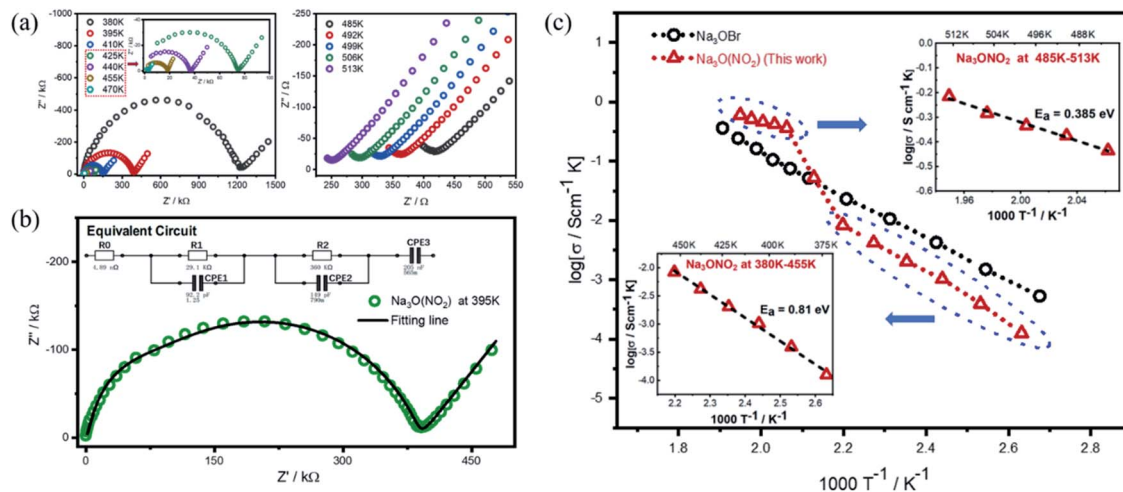


Fig. 2 (a) Nyquist curves of  $\text{Na}_3\text{ONO}_2$  in the temperature range from 380 to 513 K. (b) Fitting curve with the equivalent circuit for Nyquist plot of  $\text{Na}_3\text{ONO}_2$  at 395 K. (c) Arrhenius conductivity plot of  $\text{Na}_3\text{ONO}_2$  in the temperature range from 380 to 513 K, the conductivity data of  $\text{Na}_3\text{OBr}$  are reproduced from the work of Wang *et al.*<sup>18</sup>

resistance  $R_1$ , demonstrating the fact that oxide electrolytes usually have high grain boundary resistance.

Fig. 2(c) is the Arrhenius plot illustrating the relationship between  $\text{Na}^+$  conductivity and temperature in the range from 380 K to 513 K. The  $\text{Na}^+$  conductivity in reported  $\text{Na}_3\text{OBr}$  is used for comparison.<sup>18</sup> In contrast to the  $\text{Na}_3\text{OBr}$ , of which the ionic conductivity steadily increases in the whole range, the ionic conductivity of  $\text{Na}_3\text{ONO}_2$  at first stays lower below 455 K, then suddenly jumps to  $0.37 \text{ mS cm}^{-1}$  at 485 K that even surpasses the reported  $\text{Na}_3\text{OBr}$ .<sup>18</sup> This unexpected sharp increase renders the  $\text{Na}_3\text{ONO}_2$  superior to  $\text{Na}_3\text{OBr}$  in the range from 485 to 513 K. Noteworthy, this measurement is reversible (Fig. S3 and S4†), and the sharp increase occurs before the melting peak ( $\sim 536 \text{ K}$ ), so it should be related somehow to an intrinsic behaviour and does not result from melting behaviour. The insets in Fig. 2(c) present two distinct activation energies,  $E_a \sim 0.81 \text{ eV}$  from 380 to 455 K and  $E_a \sim 0.385 \text{ eV}$  from 485 to 513 K, obtained from the slope in the Arrhenius plots based on eqn (4), where  $\sigma$  is the conductivity,  $A$  is the pre-exponential parameter,  $E_a$  is the activation energy,  $T$  is absolute temperature and  $k_B$  is the Boltzmann constant.

$$\sigma = A \exp(-E_a/k_B T) \quad (4)$$

### 3.3 Structural determination

The unexpected enhancement of the  $\text{Na}^+$  ionic conductivity from 410 to 485 K should be ascribed to the  $\text{NO}_2^-$  group. Firstly, we explain from the perspective of the crystal structure. The neutron powder diffraction measurements were performed at selected temperatures before and after the enhancement to identify structural changes, as shown in Fig. 3(a). All peaks can be simulated by the Rietveld refinement and the schematic crystal structure with anisotropic thermal displacements is provided in Fig. 3(b). In the cubic lattice (Fig. 3(b) and S5†), the O anions at the vertex (0, 0, 0) serve as the center of the  $\text{Na}_6\text{O}$

octahedra, and these octahedra are corner-linked *via* Na cations in the middle of the lattice edges (0.5, 0, 0). Each cubic lattice only has one  $\text{NO}_2^-$  group around the lattice center, but has 6 and 24 crystallographically equivalent positions for each N and O anion, respectively. The occupation is therefore 1/6 for each N position and 2/24 for each O position. The structural model adopted here is a disordered one, which could be further discerned as six different orientations of the  $\text{NO}_2^-$  group by NMR.<sup>38</sup> The anisotropic thermal displacements are also shown here as ellipsoids (Fig. 3(b)), and we notice that Na mainly vibrates along the vertical plane of the lattice edge. Detailed information on the refinement results and parameters are provided in Tables 1 and S1.† The most significant change is the thermal displacements of  $\text{Na}^+$  and the  $\text{NO}_2^-$  group. In Fig. 3(c), their anisotropic displacement parameters *versus* temperature are plotted. From room temperature to 410 K, their displacements rise gradually. But from 410 to 485 K, all the  $\text{Na}^+$ ,  $\text{N}^{3+}$ , and  $\text{O}^{2-}$  undergo a sudden increase in their anisotropic displacements. In the  $\text{NO}_2^-$  group, the  $\text{N}^{3+}$  axial parameter ( $U_{11}$ ) jumps from 0.0217 at 410 K to 0.0540 at 485 K, indicating that the thermal vibration becomes stronger along the axial direction. In the meantime, its bonding  $\text{O}^{2-}$  also exhibits much higher thermal displacements, with all three parameters ( $U_{11}$ ,  $U_{22}$ ,  $U_{33}$ ) increasing. Apparently, the thermal vibration of the  $\text{NO}_2^-$  group grows much stronger from 410 to 485 K. For  $\text{Na}^+$ , its axial ( $U_{11}$ , towards the octahedral center) and equatorial displacements ( $U_{22} = U_{33}$ ) all exhibit considerable increases after 410 K. The most intriguing thing is that this sudden increase in  $\text{Na}_3\text{ONO}_2$  does not appear in  $\text{Na}_3\text{OBr}$ , of which the  $\text{Na}^+$  thermal displacements ( $U_{11}$ ,  $U_{22}$ ,  $U_{33}$ ) seem to reach saturation from 410 K to 485 K. Considering the fact that the conductivity is also enhanced in this range, the sudden increase of  $\text{Na}^+$  and  $\text{NO}_2^-$  displacements should correlate with the  $\text{Na}^+$  conductivity enhancement. In Fig. 3(d), the lattice parameter of  $\text{Na}_3\text{ONO}_2$  keeps expanding all the way. One may argue that this lattice thermal expansion can also be the explanation for the



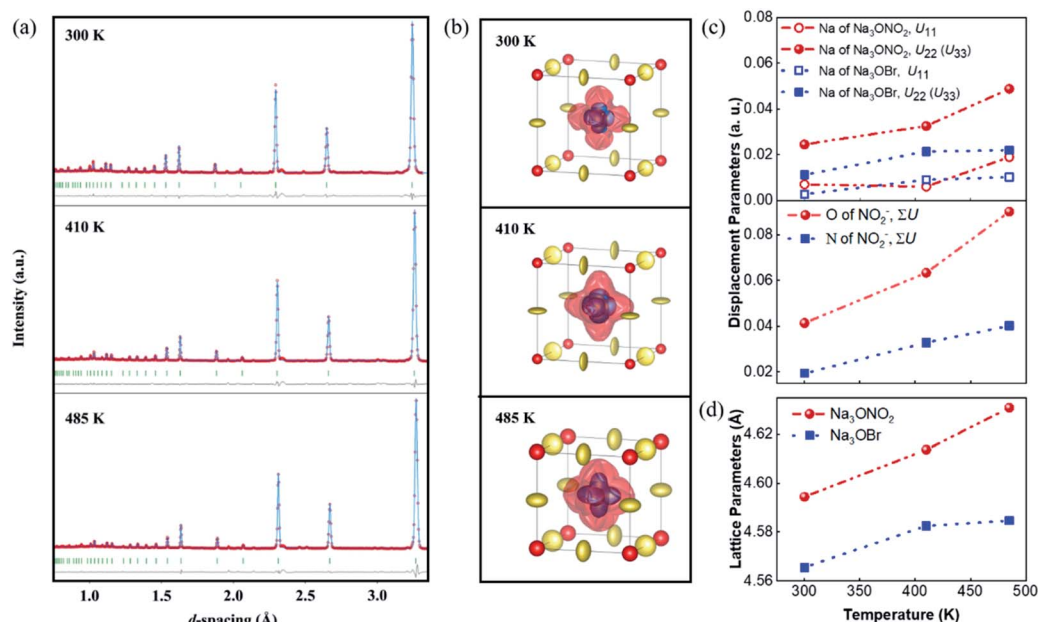


Fig. 3 (a) Rietveld refinement of  $\text{Na}_3\text{ONO}_2$  based on NPD at 300 K, 410 K and 485 K. (b) Schematic crystal structure of  $\text{Na}_3\text{ONO}_2$  at 300 K, 410 K and 485 K with anisotropic thermal displacements. Yellow sphere represents Na, red represents O, and blue represents N. (c) Displacement parameters of Na atoms in  $\text{Na}_3\text{ONO}_2$  and displacement parameters of N and O atoms in the  $\text{NO}_2^-$  group as a function of temperature in the range 300–485 K. (d) Lattice parameters of  $\text{Na}_3\text{ONO}_2$  and  $\text{Na}_3\text{OBr}$  as a function of temperature in the range 300–485 K.

enhancement, since larger space is usually beneficial for  $\text{Na}^+$  migration. However, we notice that the parameter of  $\text{Na}_3\text{ONO}_2$  grows more steadily, in sharp contrast to the  $U$  of O ( $\text{NO}_2^-$ ). If lattice expansion is the reason, then the ionic conductivity should exhibit a steady increase rather than a boost. Hence, it is highly possible that the significantly intensified thermal vibration of  $\text{NO}_2^-$  at high temperature promotes the  $\text{Na}^+$  migration, while isotropic  $\text{Br}^-$  in  $\text{Na}_3\text{OBr}$  has no such effect.

Maximum Entropy Method (MEM) calculations were performed based on the neutron diffraction data at 485 K. The (100), (020), (001) planes were specifically provided to show the nuclear density around the  $\text{Na}^+$  ions at the plane intersection (Fig. 4(a)). From the (100) plane distribution (Fig. 4(b)), it is readily observed that  $\text{Na}^+$  ions transport among the nearest-neighbouring  $\text{Na}^+$  sites along the edges within the  $\text{Na}_6\text{O}$  octahedron, as indicated by the arrow. The  $\text{Na}^+$  ions move close to the central  $\text{O}^{2-}$  before migrating to the neighboring  $\text{Na}^+$  position. Compared with  $\text{Na}_3\text{OBr}$  (Fig. S6†), the nuclear density distributions along the lattice edges are more obvious, which is consistent with the  $\text{Na}^+$  conductivity enhancement facilitated by stronger  $\text{NO}_2^-$  group vibration.

DFT calculations were performed to reveal how the  $\text{NO}_2^-$  group affects  $\text{Na}^+$  migration. As shown in Fig. 5, at the start (I), a  $\text{Na}^+$  vacancy (yellow circle) was introduced on the corner between two adjacent  $\text{Na}_6\text{O}$  octahedra. This decreases the electron density around  $\text{O}^{2-}$  of  $\text{NO}_2^-$ , so its  $\text{O}^{2-}$  has to get closer to the migrating  $\text{Na}^+$  to compensate for its electron density. After structural optimization, the  $\text{O}^{2-}$  would always point toward the migrating  $\text{Na}^+$ . The whole process (I–VI) involves  $\text{Na}^+$ /vacancy migration (yellow arrow),  $\text{NO}_2^-$  group rotation (red arrow), and corresponding structure adjustments. Here, the  $\text{Na}^+$  migration energy barrier is considered the key factor in determining the ionic conductivity. The distance (grey dashes) variation between migrating  $\text{Na}^+$  and  $\text{O}^{2-}$  is also scrutinized to help understand the whole process. Finally, the energy barrier at 485 K in this model is calculated to be 0.37 eV, which is about 0.05 eV lower than the 0.42 eV of  $\text{Na}_3\text{OBr}$ , indicating that the migration activity is higher, which is consistent with the above conductivity measurements.

The  $\text{NO}_2^-$  group directly participates in the migration process in a rotational way, with its  $\text{O}^{2-}$  anion (red arrow) pointing towards the migrating  $\text{Na}^+$  cation. In the beginning,

Table 1 Refined Crystal Parameters Based on NPD for  $\text{Na}_3\text{ONO}_2$  at 300, 410, and 485 K

Formula	Lattice params ( $\text{\AA}$ )	Thermal params (Na)			Thermal params (N)	Thermal params (O of $\text{NO}_2^-$ )
		$U_{11}$	$U_{22}$	$U_{33}$	$\Sigma U$	$\Sigma U$
$\text{Na}_3\text{ONO}_2$	$a = 4.594(4)$ at 300 K	0.007	0.025	0.025	0.01933	0.04133
	$a = 4.616(6)$ at 410 K	0.006	0.033	0.033	0.03283	0.06333
	$a = 4.630(9)$ at 485 K	0.019	0.049	0.049	0.0402	0.09017

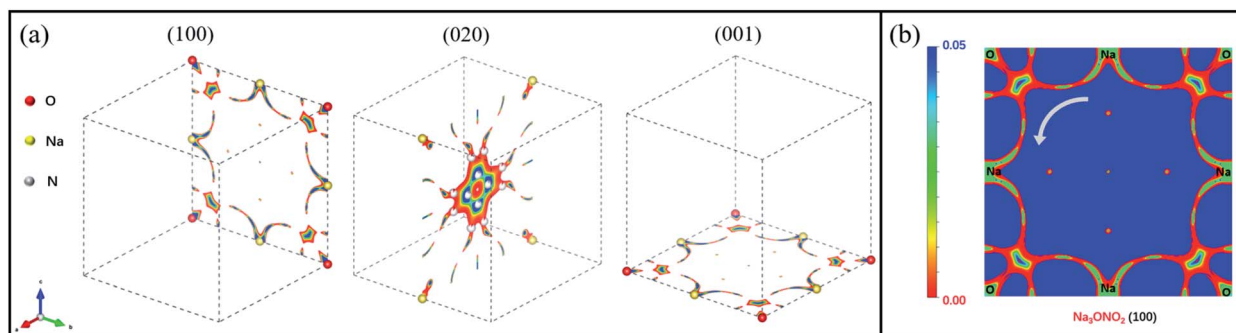


Fig. 4 The nuclei density distributions of  $\text{Na}_3\text{ONO}_2$  deduced from MEM analysis based on NPD at 485 K: (a) (100) (020) (001) planes. The  $\text{NO}_2^-$  density distribution around the lattice center is also shown in the (020) plane. (b) The detailed two-dimensional contour maps sliced on the (100) plane. The arrow represents the  $\text{Na}^+$  migration path.

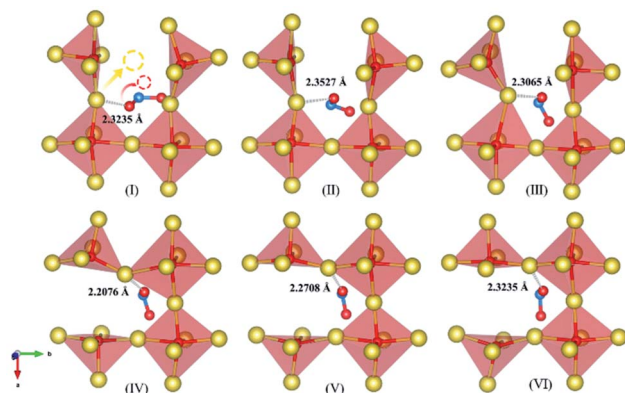


Fig. 5 Detailed information on the migration process at 485 K. We extracted several calculation steps from the whole process, including the beginning (I) stage, four intermediate stages (II–V), and the final stage (VI). Yellow spheres represent Na and red spheres represent O. The yellow arrow and red arrow represent the  $\text{Na}^+$  migration and  $\text{NO}_2^-$  rotation. The yellow circle is the Na vacancy, and also the final position for the migrating  $\text{Na}^+$ . The red circle is the final position for the  $\text{O}^{2-}$  of  $\text{NO}_2^-$ .

the rotary  $\text{NO}_2^-$  tries to drive its  $\text{O}^{2-}$  a little bit away from the migrating  $\text{Na}^+$ , with the distance increasing from the original 2.3235 to 2.3527 Å. After that, the  $\text{Na}^+$  gradually moves to the vacancy position with the help of the  $\text{NO}_2^-$  group, as seen in stages (III and IV) of Fig. 5. The distance between  $\text{Na}^+$  and  $\text{O}^{2-}$  can be as low as 2.2076 Å in the intermediate step (IV), but soon climbs to 2.2708 Å as the  $\text{Na}^+$  approaches the final position. In the final stage (VI), the  $\text{NO}_2^-$  group further rotates clockwise, and the  $\text{Na}_6\text{O}$  coordination framework makes further adjustments, with the Na–O distance recovering to 2.3235 Å. Throughout the process, the  $\text{O}^{2-}$  of  $\text{NO}_2^-$  assists the  $\text{Na}^+$  migration by pulling it into the intermediate position, then pushing it away to the final position. From these results, we propose that the rotary  $\text{NO}_2^-$  group can facilitate  $\text{Na}^+$  migration via the interaction between its  $\text{O}^{2-}$  anion and  $\text{Na}^+$  cation.

We notice that only this type of migration can lead to an energy barrier as low as 0.37 eV, which results in the superior conductivity of  $\text{Na}_3\text{ONO}_2$ . In another set of models where the  $\text{NO}_2^-$  group is fixed (not allowed to move or rotate in the whole process, Fig. S7†), the  $\text{Na}^+$  migration energy barrier climbs up to

1.37 eV. Also, if we place some restraints on the  $\text{NO}_2^-$  group (Fig. S7†), that is, keeping its N–O bond nearly vertical to the  $x$ – $y$  plane around the migrating  $\text{Na}^+$  so that the group rotation would be limited, the energy barrier increased to 0.79 eV. These comparative results further confirm the positive effects of  $\text{NO}_2^-$  free rotation. If the group is fixed or restrained, their pointed  $\text{Na}^+$  ions will suffer from a much higher energy barrier and the migration is slowed down.

The last comparative study we examined is the migration behaviour of specific  $\text{Na}^+$  ions away from  $\text{NO}_2^-$  (not pointed by its terminal  $\text{O}^{2-}$ ), since this is also possible in a real situation. This part is carefully discussed in the ESI (Fig. S8 and S9†). In this case, the lattice exhibits a higher energy in both the initial and transitional states, which means a metastable pathway is possible. Moreover, although sent away at the beginning, the  $\text{Na}^+$  will be repointed by another  $\text{NO}_2^-$  from the neighbouring lattice in the final stage, since the energy can be lower in this instance. Generally, this type of migration may not be energy favored, but still reflects the fact that when  $\text{O}^{2-}$  points to  $\text{Na}^+$ , it can stabilize the lattice.

Based on the above analysis, it is not difficult to explain the experimental results. Below 410 K, the  $\text{NO}_2^-$  thermal vibration or rotation is not high enough to promote more  $\text{Na}^+$  migration. The  $\text{NO}_2^-$  group in one lattice has a certain orientation and hence the number of  $\text{Na}^+$  that can be assisted (or pointed) by the  $\text{O}^{2-}$  of  $\text{NO}_2^-$  is actually limited. Those  $\text{Na}^+$  without the help of  $\text{NO}_2^-$  can also migrate but their paths are not that efficient. However, the situation changes as the temperature increases. Above 485 K, as revealed by neutron diffraction data, the  $\text{NO}_2^-$  thermal vibration significantly increased, indicating that the  $\text{NO}_2^-$  rotation is much stronger. Therefore, more  $\text{Na}^+$  cations have opportunities to be pointed by  $\text{O}^{2-}$  of  $\text{NO}_2^-$  and are assisted by Na–O interaction so that the  $\text{Na}^+$  conductivity of  $\text{Na}_3\text{ONO}_2$  surpasses that of  $\text{Na}_3\text{OBr}$ .

## 4. Discussion

### 4.1 Channel size

The migrating ion size and available free space in the lattice are two intuitive factors. Usually, the ionic conductivity of inorganic solid-state electrolytes can be optimized by enlarging the

**Table 2** Calculated Channel Size (CS) of  $\text{Na}_3\text{OBr}^{20}$  and  $\text{Na}_3\text{ONO}_2$ . Where LP,  $V_{\text{Na}}$ ,  $V_{\text{A}}$ ,  $V_{\text{O}}$  are lattice parameter, volume of  $\text{Na}^+$ , volume of  $\text{Br}^-$  ( $\text{NO}_2^-$ ), and volume of  $\text{O}^-$ , respectively

Crystal	LP (Å)	$V_{\text{Na}}$ (Å <sup>3</sup> )	$V_{\text{A}}$ (Å <sup>3</sup> )	$V_{\text{O}}$ (Å <sup>3</sup> )	CS (Å <sup>3</sup> )	$V_{\text{Na}}/\text{CS}$
$\text{Na}_3\text{OBr}$	4.565	6.53	25.24	8.37	61.52	0.106
$\text{Na}_3\text{ONO}_2$	4.594	6.53	32.7	8.37	55.88	0.117

volume of the unit cell, which facilitates the ion diffusion in the transport channel.<sup>17,40</sup> However, both the migrating ion size and the free space for transport need to be taken into account.<sup>20,41</sup> Therefore, the ratio of the migrating ion size (volume  $V_{\text{Na}}$ ) to the channel size (CS) as a descriptor is more convincing than simply the cell volume itself. Here the CS is obtained by subtracting the N and O ion volume (except for  $\text{Na}^+$ ) from the cell volume.<sup>20</sup> As shown in Table 2, according to the structural information obtained from Rietveld refinement at RT, the lattice parameter (4.594 Å) of  $\text{Na}_3\text{ONO}_2$  is larger than that of  $\text{Na}_3\text{OBr}$  (4.565 Å), but the CS (55.88 Å<sup>3</sup>) of  $\text{Na}_3\text{ONO}_2$  is smaller than that of  $\text{Na}_3\text{OBr}$  (61.52 Å<sup>3</sup>). Since the migrating ion size is the same ( $V_{\text{Na}} \sim 6.53$  Å<sup>3</sup>), there is a smaller free space for  $\text{Na}^+$  transport in the crystal lattice of  $\text{Na}_3\text{ONO}_2$ . Hence, the lower ionic conductivity of  $\text{Na}_3\text{ONO}_2$  than that of  $\text{Na}_3\text{OBr}$  may be attributed to the smaller channel size in the low temperature range of 380 to 455 K.

#### 4.2 Rotation of $\text{NO}_2^-$

However, the conductivity enhancement from 455 to 485 K needs to be carefully discussed. First, for most inorganic crystalline solid-state electrolytes, the ionic conductivity can be enhanced by the phase transition.<sup>16,42–48</sup> The  $\text{Li}_2\text{OHCl}$  conductivity was remarkably improved after the phase transition from orthorhombic to cubic around 303–323 K.<sup>16</sup> Similarly, there are significant differences in the ionic conductivity and activation energy between tetragonal and metastable cubic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ .<sup>17,40,42</sup> However, according to the refinement of  $\text{Na}_3\text{ONO}_2$  (Table 1), there is no strong evidence corresponding to an observable structural phase transition (whether continuous or discontinuous) above 300 K. The space group remains cubic  $Pm\bar{3}m$  throughout the whole temperature range from 300 to 485 K. Second, introducing  $\text{Li}^+/\text{Na}^+$  defects is a common strategy in promoting ion migration.<sup>49–51</sup> This strategy was not adopted here in our experiment. From refinements, the Na ions are almost fully occupied (0.95–1) in both  $\text{Na}_3\text{ONO}_2$  and  $\text{Na}_3\text{OBr}$ . So, lattice defects should not be responsible for the conductivity improvement around 485 K.

The mechanism of the conductivity enhancement is the intensified rotational effect of the  $\text{NO}_2^-$  group around 455–485 K. Below 455 K, the  $\text{NO}_2^-$  is disordered with rapid rotation, but its thermal vibration/rotation is not yet strong enough to fully promote the  $\text{Na}^+$  migration and only a few  $\text{Na}^+$  ions can be facilitated by Na–O (of  $\text{NO}_2^-$ ) interaction. At this time, the channel size effect is predominant. Compared to  $\text{Na}_3\text{OBr}$ , the lower channel size in  $\text{Na}_3\text{ONO}_2$  accounts for its lower conductivity. When the temperature rises to 485 K,  $\text{NO}_2^-$  is thermally stimulated to a more intensive rotational state so that more  $\text{Na}^+$  can be facilitated *via* Na–O (of  $\text{NO}_2^-$ ) interactions and the conductivity is therefore

boosted. Meanwhile, the activation energy reduced from 0.81 eV to 0.385 eV according to the Arrhenius plot and the energy barrier is reduced to 0.37 eV (lower than  $\text{Na}_3\text{OBr}$  at 0.42 eV) according to the DFT calculation, respectively. The comparative calculation studies also support the above statement. If the rotation is restrained or totally fixed, the energy barrier would rise to 0.79 eV or 1.37 eV, respectively, indicating that the stronger free rotation is needed to boost the conductivity. More studies on the  $\text{NO}_2^-$  rotation barrier are provided in the ESI (Fig. S11†).

## 5. Conclusion

In conclusion,  $\text{Na}_3\text{ONO}_2$  was successfully synthesized by a low temperature solid-state reaction. ESI measurements show a superior ionic conductivity in  $\text{Na}_3\text{ONO}_2$  (0.37 mS cm<sup>−1</sup>,  $E_a \sim 0.385$  eV) around 485 K. Neutron powder diffraction refinements and DFT calculations reveal the mechanism of the conductivity enhancement. Above 485 K, the  $\text{NO}_2^-$  rotation is more intensified than that at lower temperature, which can significantly facilitate  $\text{Na}^+$  ion migration *via* Na–O interactions. The  $\text{Na}_3\text{ONO}_2$  migration energy barrier is calculated to be 0.37 eV lower than that of  $\text{Na}_3\text{OBr}$  (0.42 eV) with the  $\text{NO}_2^-$  rotation, which is consistent with the experimental results. This work gives a detailed explanation of how the anion cluster affects the  $\text{Na}^+$  migration behavior, which provides more insight into designing superionic antiperovskite electrolytes.

## Author contributions

Zou, R. and Zhao, Y. conceived the idea; Gao, L. and Zhang, H. designed the experiments with the guidance of Zou, R. and Zhao, Y.; Gao, L. performed the XRD, DSC and electrochemical measurements with assistance from Li, S., Zhao, R. and Gao, S.; Gao, L. performed the NPD measurements with the assistance from He, L. and Li, S.; Zhang, H. performed the Rietveld refinement and MEM analysis with the assistance from Gao, L. and Wang, Y.; Wang, Y. performed the DFT calculation with the guidance of Song, H.; Gao, L. and Zhang, H. prepared this manuscript with assistance from all other co-authors.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (51825201), Key Program of the National Natural Science Foundation of China (51732005), Natural Science Foundation of China (51902150), Guangdong Provincial Key Laboratory of Energy Materials for Electric Power (2018B030322001), Shenzhen Key Laboratory of Solid State Batteries (ZDSYS20180208184346531), the Science Challenge Project (No. TZ2016004 and No. TZ2018002), the National Key Research and Development Program of China (2017YFA0206701), National Program for Support of Top-Notch Young Professionals, and Changjiang Scholar Program.

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