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The Mechanism on the Ionic Conductivity Enhancement by Rotational Nitrite Group in Antiperovskite Na_3ONO_2

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1. Supplementary Experimental Results

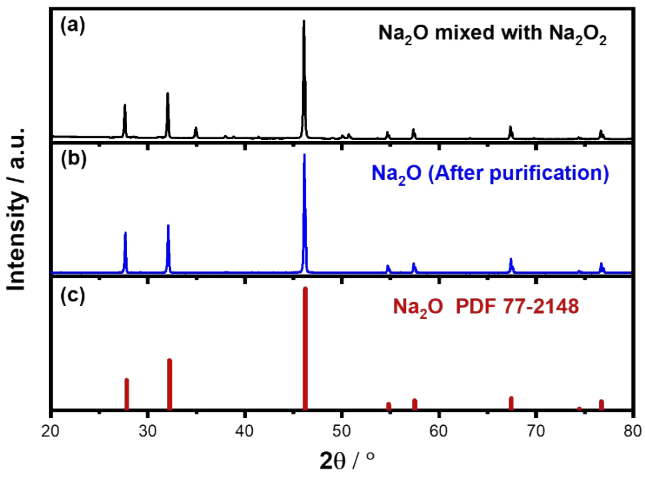

Fig. S1 (a) Powder XRD pattern of Na_2O before purification. (b) Powder XRD pattern of Na_2O after purification. (c) Powder diffraction file (PDF) of Na_2O.

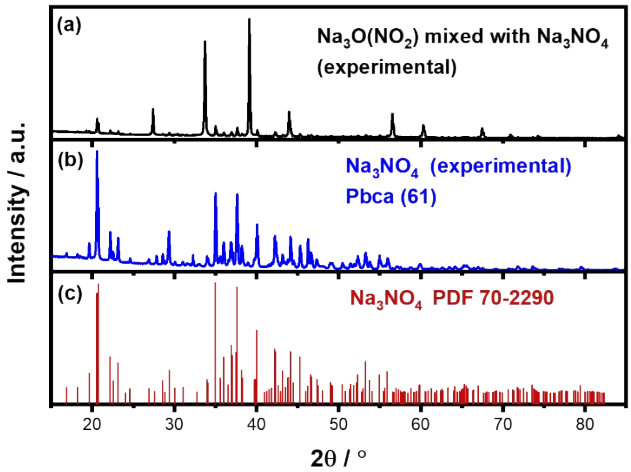

Fig. S2 (a) Powder XRD pattern of Na_3ONO_2 mixed with Na_3NO_4. (b) Powder XRD pattern of Na_3NO_4. (c) Powder diffraction file (PDF) of Na_3NO_4.

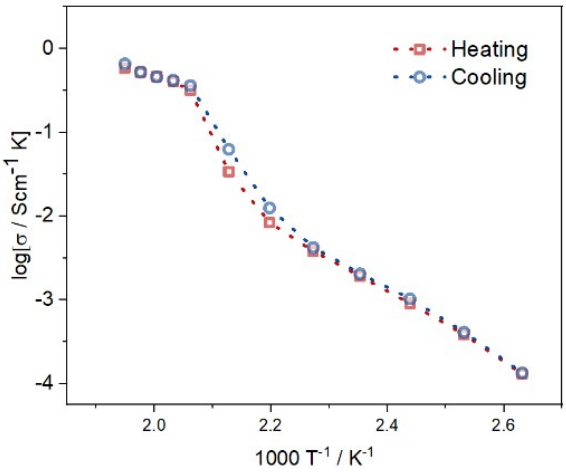

Fig. S3 Arrhenius conductivity plot of Na_3ONO_2 during heating and cooling.

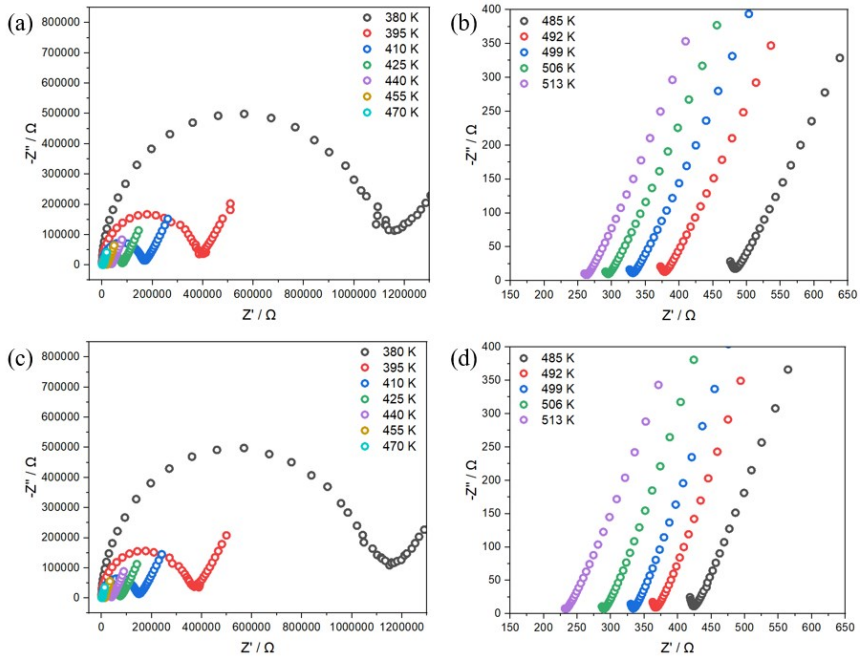

Fig. S4 (a), (b) Nyquist curves of Na_3ONO_2 during heating. (c), (d) Nyquist curves of Na_3ONO_2 during cooling.

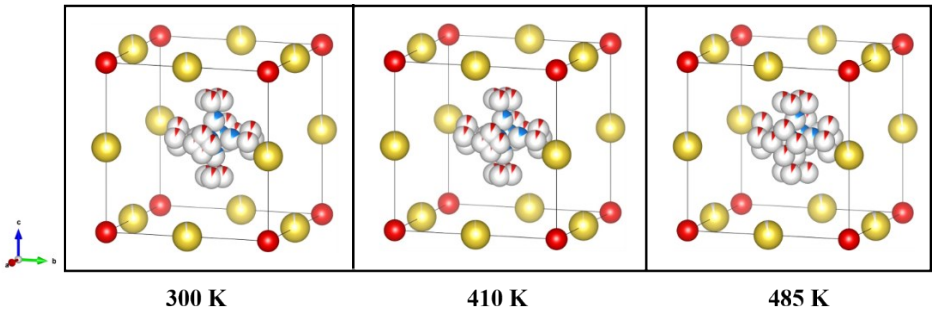

Fig. S5 Crystal model of Na_3ONO_2 after refinement based on neutron powder diffraction (NPD) at selected temperature.

Table S1. Refined Crystal Parameters Based on NPD for Na3ONO2 at 300, 410, and 485 K.

Formula	Lattice params(Å)	Coordinates				Occupancy	Thermal Params		
		Atom	x	y	z		U_{11}	U_{22}	U_{33}
Na_3ONO_2	a=4.594(4) 300 K					0.972	0.007	0.025	0.025
	a=4.616(6) 410 K	Na	0.5	0	0	0.988	0.006	0.033	0.033
	a=4.630(9) 485 K					0.958	0.019	0.049	0.049
	a=4.594(4) 300 K						U_{iso} = 0.01130		
	a=4.616(6) 410 K	O1	0	0	0	1	U_{iso} = 0.00980		
	a=4.630(9) 485 K						U_{iso} = 0.0229		
	a=4.594(4) 300 K		0.397				0.012	0.023	0.023
	a=4.616(6) 410 K	N	0.401	0.5	0.5	1/6	0.023	0.038	0.038
	a=4.630(9) 485 K		0.395				0.059	0.031	0.031
	a=4.594(4) 300 K	O2 (NO_2^-)		0.552	0.725		0.053	0.023	0.041
	a=4.616(6) 410 K		0.5	0.554	0.722	2/24	0.058	0.065	0.068
	a=4.630(9) 485 K			0.577	0.706		0.120	0.051	0.099
Na_3OBr	a=4.565(4) 300 K					0.956	0.003	0.011	0.011
	a=4.582(4) 410 K	Na	0.5	0	0	0.968	0.009	0.021	0.021
	a=4.584(6) 485 K					0.951	0.010	0.022	0.022
	a=4.565(4) 300 K						U_{iso} = 0.00934		
	a=4.582(4) 410 K	O1	0	0	0	1	U_{iso} = 0.01952		
	a=4.584(6) 485 K						U_{iso} = 0.02020		
	a=4.565(4) 300 K						U_{iso} = 0.0048		
	a=4.582(4) 410 K	Br	0.5	0.5	0.5	1	U_{iso} = 0.0092		
	a=4.584(6) 485 K						U_{iso} =0.0084		

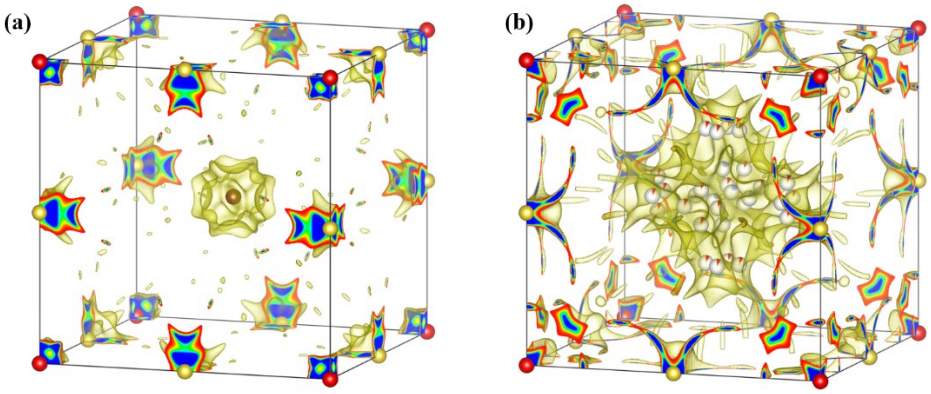

Fig. S6 (a) Nuclei density distribution of Na_3OBr from Maximum Entropy Method analysis based on NPD at 485 K. (b) Nuclei density distribution of Na_3ONO_2 from Maximum Entropy Method analysis based on NPD at 485 K.

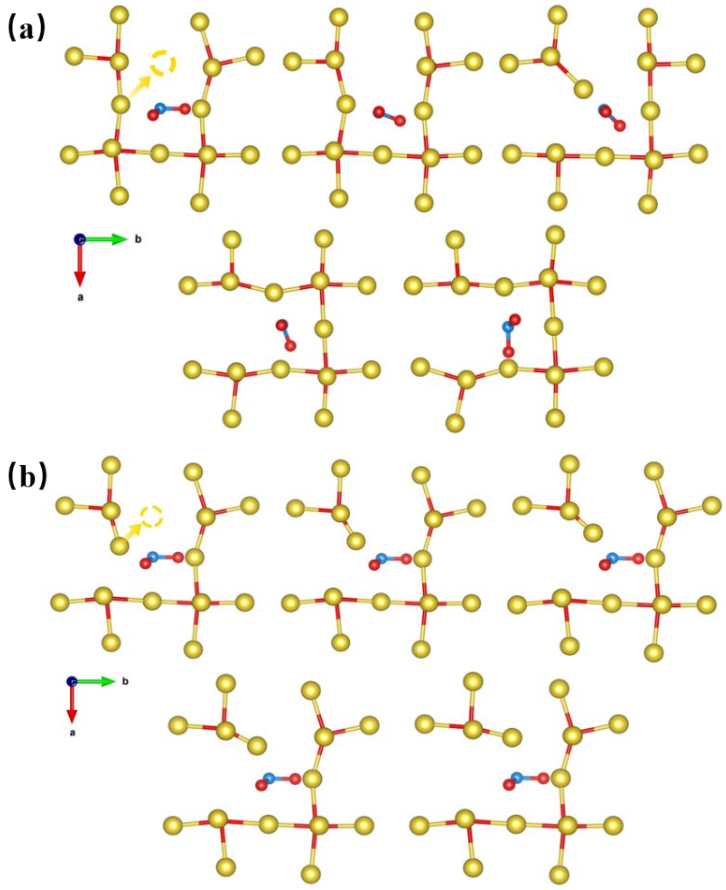

Fig. S7 Yellow sphere is Na, Red sphere is O, blue sphere is N. (a) Schematic diagram of the migration process when NO_2^- group is restrained in the Na_3ONO_2 lattice. Its N-O bond is nearly kept vertical to the x-y plane around the migrating Na^+ so that the group rotation would be limited. The energy barrier is 0.79 eV. (b) Schematic diagram of the migration process when NO_2^- group is totally fixed in the Na_3ONO_2 lattice. The energy barrier is 1.37eV.

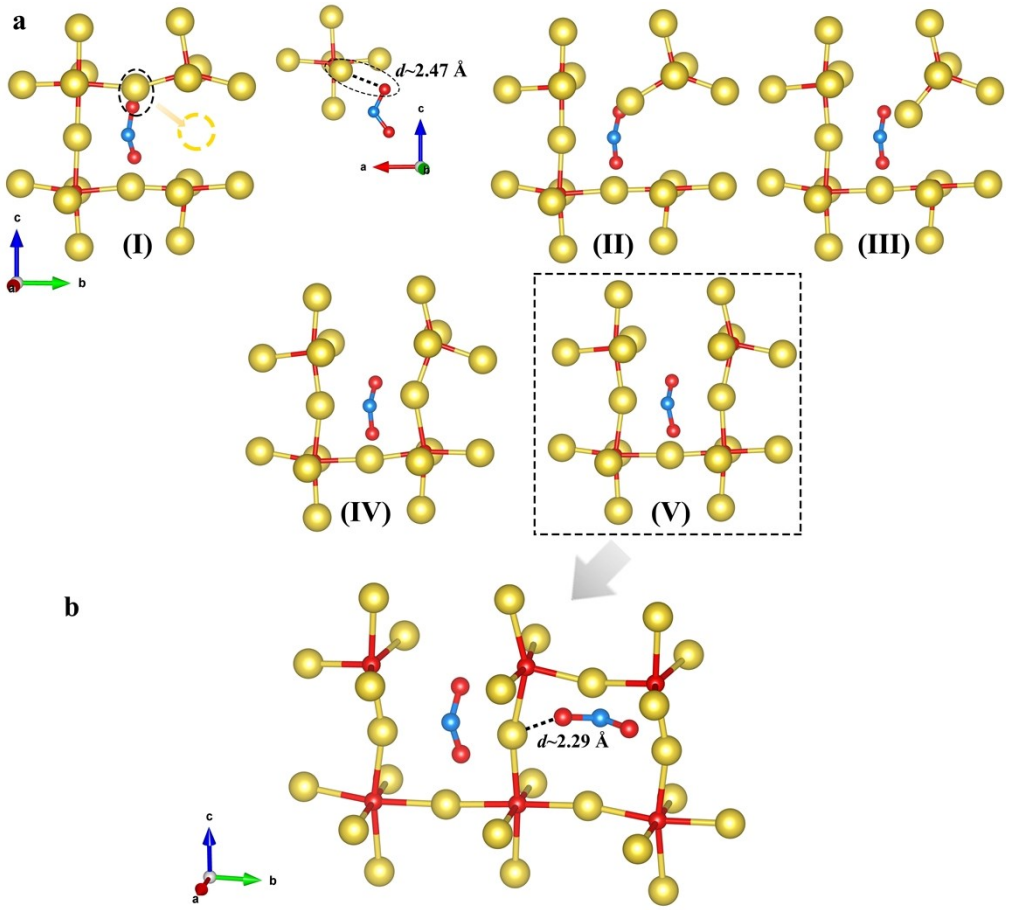

Fig. S8 Yellow sphere is Na, Red sphere is O, blue sphere is N. (a) Calculated pathway staring from an initial model in which Na^+ is away from O^{2-}. (I) represents the initial state, (V) is the final state, (II-IV) are intermediate states. The NO_2^- group points its O^{2-} inside the paper plane. In (I), the migrating Na^+ we examine is about 2.47Å far from O^{2-}, as marked in black circle. The right side image from b-axis clearly shows that Na^+ is not pointed by O^{2-}. During the whole process, this Na^+ is not pointed by the $O^{2-}(NO_2^-)$ in its own cell. (b) Carefully check the final state (V), we find that the Na^+ is actually pointed again by the neighboring NO_2^- from the right cell.

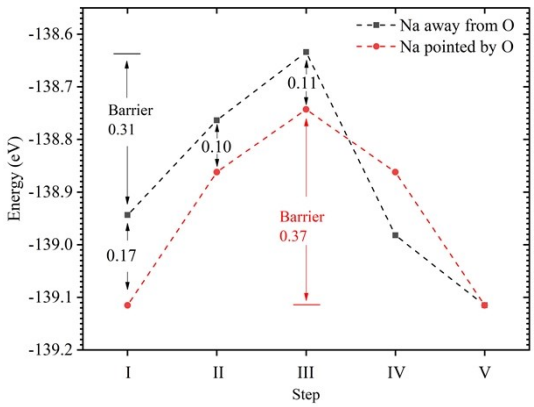

Fig. S9 Calculated energy of each step for two models. Red line is the stable model where Na is pointed by O, while black line is a metastable model where Na^+ is away from O^{2-} in its initial states.

During the calculation in our manuscript, the initial and final models have energy degeneracy.

When we are trying to specifically investigate the Na^+ ions that are away from O^{2-} (of NO_2^-), we find an initial structure in which its migrating Na^+ is not pointed by the O^{2-} (of NO_2^-), with distance ~ 2.473 Å, as shown in the following Fig. S8(a). We also perform NEB calculation of the migration of Na^+. Several intermediate steps and final state are illustrated in Fig. S8(a) (II)-(V).

As you can see from Fig. S9, the first result is that the initial structure (I), intermediates (II)(III) (black line) all have higher energy compared to the model with Na^+ pointed by O^{2-}(red line), especially the initial structure with ~0.17 eV higher energy, indicating a metastable state. Although the energy barrier has a little decrease to 0.31 eV, it is actually compensated by the energy increase on initial state. Therefore, we think this metastable pathway (Na^+ away from O^{2-}) is not as efficient as the stable one (Na^+ pointed by O^{2-}) discussed in the manuscript, and we chose the stable one for further discussion.

The second result is that, in the final state(V), as shown in Fig. S8(b), the Na^+ is actually pointed again by the O^{2-}(of NO_2^-) but from the neighboring cell. This is intriguing because even though we set Na^+ away from O^{2-} in the starting model, its neighboring NO_2^- would try to rotate to "host" the Na^+ in its final stage. This make its lattice energy decrease fast from step (III) to step (V) and finally almost equal to that of stable model (Na^+ pointed by O^{2-}), as shown in Fig. S9.

So based on above, it is clear that Na-O interaction can help stabilize the lattice in the whole process. The migration pathway with Na-O close interaction is more energetically favorable. In our work, it is possibly the Na-O interaction that plays a predominant role in boosting conductivity, rather than the volume effect.

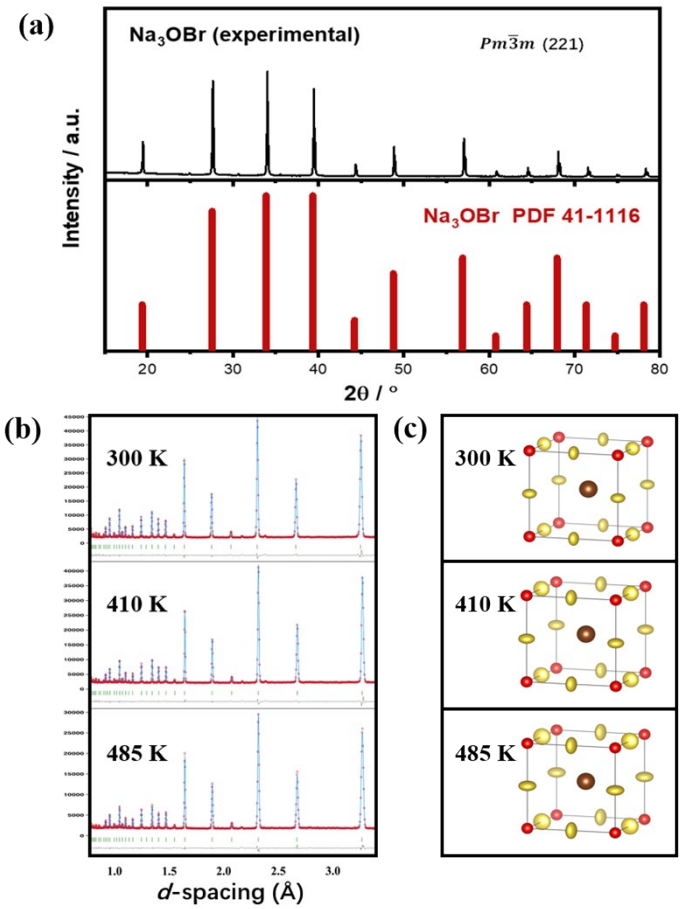

Fig. S10 (a) Powder XRD pattern of Na_3OBr at room temperature. (b) Rietveld refinement of Na_3OBr based on NPD at 300 K, 410 K and 485 K. (c) Schematic crystal structure of Na_3OBr at 300 K, 410 K and 485 K with anisotropic thermal displacements.

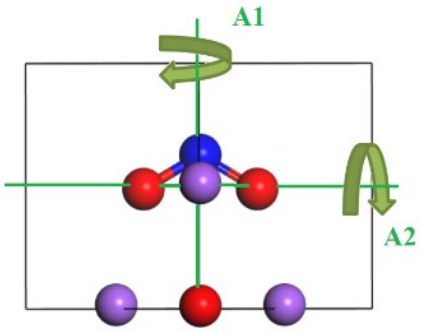

Fig. S11 Calculation about the rotation of NO_2^- group. Two representative rotation methods, that is around A1 and A2 axis, are carefully studied.

The calculation results of rotation barrier of NO_2^- shows that the rotation of NO_2^- has an anisotropy. If rotated around the A2 axis along O-O direction, the barrier is about 0.08 eV, otherwise it shows a much higher rotation barrier up to 1.7 eV when around A1 axis.

2. Computational details

In the calculation of transition state and barrier, a 2×2×1 supercell with a vacancy of Na on x-axis and a vacancy of Na on y-axis are constructed as the starting point of reactant and product respectively. Then the transition state of the migration of Na in xy-plane and the energy barrier are calculated through the CI-NEB approach. Two conformation of NO_2 are considered during the migration of Na, one with the O atoms in NO_2 almost pointing to lattice Na (P1), and the other with one O atom rotating during the migration (P2). The migration pathways are shown in Fig. S12.

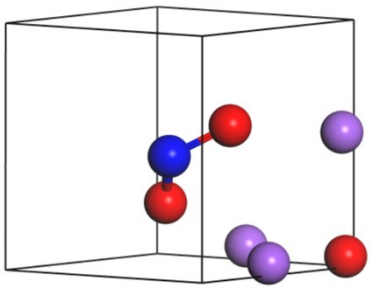

Fig. S12 Structure of Na_3ONO_2 after optimization, O in NO_2 pointing to lattice Na.

Table S2. The calculated barriers in eV of Na migration with lattice constants of different temperature.

	300 K	410 K	485 K
Na_3OBr	0.43	0.42	0.42
Na_3ONO_2 (P1)	0.39	0.37	0.37
Na_3ONO_2 (P2)	0.84	0.81	0.79