**Computational predictions of stable phase for antiperovskite Na**3**OCl via rotation of ONa**6 **octahedra**

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Antiperovskite Na3OCl has been considered as a candidate material for solid elec- trolyte. Hippler *et al*. reported Na3OCl in cubic phase Pm3¯m [1] but Zinenko *et al*. showed unstable phonon modes at the R and M points for cubic Na3OCl [2]. In this work, we study the structural stability of Na3OCl in terms of energy landscapes and phonon spectra with the rotation of ONa6 octahedra. We prove that the cubic Na3OCl can be energetically stabilized through octahedral tilts among 15 possible tilted systems consistent with Howard and Stokes’ group-theoretical analysis of octahedral tilting in perovskites [3]. We find that all 14 tilted structures of Na3OCl are more stable than the cubic Pm3¯m by 11-16 meV per five-atom unit cell. The tilt angles along the pseudocu- bic [100], [010], and [001] directions vary in the range of 2.6–9.3◦. While the Pnma and P21/m structures of Na3OCl are found as the two most stable ones, only the P21/m phase has stable phonon vibrations with a direct band gap of 3.38 eV at the Γ point.

**References**

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14

14

12

10

8

6

4

(c)

(d)

Total Na Cl O

0

−

X S Y Z U A B Z Y B U X S A Density of States

(a)

(b) Total

Na Cl O

X M

R X M R Density of States

12

10

Frequency (THz)

Frequency (THz)

8

6

4

2

0

2

Figure 1: (a) Phonon band structure and (b) density of states of the cubic Pm3¯m phase. The soft modes at M and R points in the phonon band structure indicate that the cubic Pm3¯m phase is dynamically unstable. (c) Phonon dispersion curves and (d) densities of states of monoclinic P21/m. The phonon dispersion curves and the total density of states show no negative modes, which proves the monoclinic P21/m is dynamically stable.