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Supporting Information

Phase-structure Dependent Na Ion Transport in Yttrium-Iodide Sodium Superionic Conductor Na_3YI_6

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Table 1. Structure information of the *c2m*-Na_3YI_6, *p3m1*-Na_3YI_6, and *p31c*-Na_3YI_6 with corresponding atomic coordinates.

c2m-Na_3YI_6	*p3m1*-Na_3YI_6	*p31c*-Na_3YI_6
a: 8.04 Å, b: 13.62 Å, c: 8.00 Å	a: 13.49 Å, b: 13.49 Å, c: 7.57 Å	a: 8.04 Å, b: 8.04 Å, c: 14.66 Å
α = 90.0°, β = 109.5°, γ = 90.0°	α = 90.0°, β = 90.0°, γ = 60.0°	α = 90.0°, β = 90.0°, γ = 120.0°
Unit-cell Vol = 824.87 Å^3	Unit-cell Vol = 1192.96 Å^3	Unit-cell Vol = 821.11 Å^3
Na1 (0.000, 0.667, 0.000)	Na1 (0.000, 0.664, 0.000)	Na1 (0.333, 0.667, 0.471)
Na2 (0.000, 0.167, 0.000)	Na2 (0.000, 0.343, 0.000)	Na2 (0.333, 0.667, 0.029)
Na3 (0.000, 0.832, 0.000)	Na3 (0.343, 0.657, 0.000)	Na3 (0.667, 0.333, 0.529)
Na4 (0.000, 0.332, 0.000)	Na4 (0.664, 0.335, 0.000)	Na4 (0.000, 0.000, 0.250)
Na5 (0.500, 0.167, 0.000)	Na5 (0.336, 0.000, 0.000)	Na5 (0.667, 0.333, 0.971)
Na6 (0.500, 0.667, 0.500)	Na6 (0.657, 0.000, 0.000)	Na6 (0.000, 0.000, 0.750)
Y1 (0.000, 0.997, 0.000)	Na7 (0.000, 0.678, 0.500)	Y1 (0.333, 0.667, 0.750)
Y2 (0.000, 0.497, 0.500)	Na8 (0.678, 0.322, 0.500)	Y2 (0.667, 0.333, 0.250)
I1 (0.239, 0.155, 0.230)	Na9 (0.322, 0.000, 0.500)	I1 (0.036, 0.681, 0.873)
I2 (0.761, 0.155, 0.770)	Y1 (0.000, 0.000, 0.000)	I2 (0.319, 0.964, 0.627)
I3 (0.239, 0.655, 0.730)	Y2 (0.333, 0.333, 0.503)	I3 (0.036, 0.355, 0.627)
I4 (0.761, 0.655, 0.270)	Y3 (0.667, 0.667, 0.497)	I4 (0.319, 0.355, 0.873)
I5 (0.768, 0.839, 0.762)	I1 (0.120, 0.446, 0.738)	I5 (0.645, 0.964, 0.873)
I6 (0.232, 0.839, 0.238)	I2 (0.446, 0.434, 0.738)	I6 (0.355, 0.319, 0.373)
I7 (0.768, 0.339, 0.262)	I3(0.434, 0.120, 0.738)	I7 (0.645, 0.681, 0.627)
I8 (0.232, 0.339, 0.738)	I4(0.554, 0.880, 0.262)	I8 (0.355, 0.036, 0.127)
I9 (0.769, 0.001, 0.235)	I5(0.566, 0.554, 0.262)	I9 (0.681, 0.645, 0.127)
I10 (0.231, 0.001, 0.765)	I6 (0.880, 0.566, 0.262)	I10 (0.964, 0.645, 0.373)
I11 (0.769, 0.501, 0.735)	I7 (0.453, 0.774, 0.730)	I11 (0.681, 0.036, 0.373)
I12 (0.231, 0.501, 0.265)	I8 (0.774, 0.772, 0.730)	I12 (0.964, 0.319, 0.127)
	I9 (0.772, 0.453, 0.730)	
	I10 (0.226, 0.547, 0.270)	
	I11 (0.228, 0.226, 0.270)	
	I12 (0.547, 0.228, 0.270)	
	I13 (0.110, 0.785, 0.771)	
	I14 (0.104, 0.110, 0.771)	
	I15 (0.785, 0.104, 0.771)	
	I16 (0.215, 0.890, 0.229)	
	I17 (0.890, 0.896, 0.229)	
	I18 (0.896, 0.215, 0.229)	

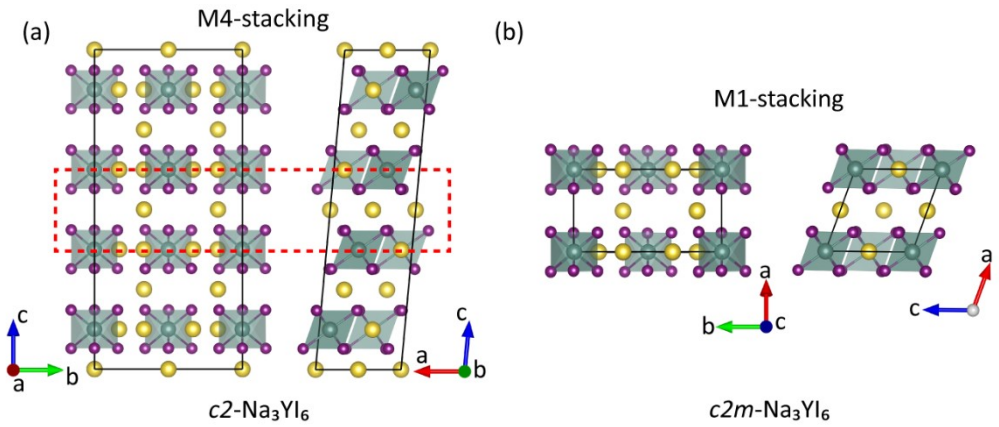

Figure S1. Crystal information of the *c2*-Na_3YI_6 and the *c2m*-Na_3YI_6. The yellow, cyan, and purple balls represent the Na, Y and I atoms, respectively. The cyan polyhedra represent the YI_6 octahedra.

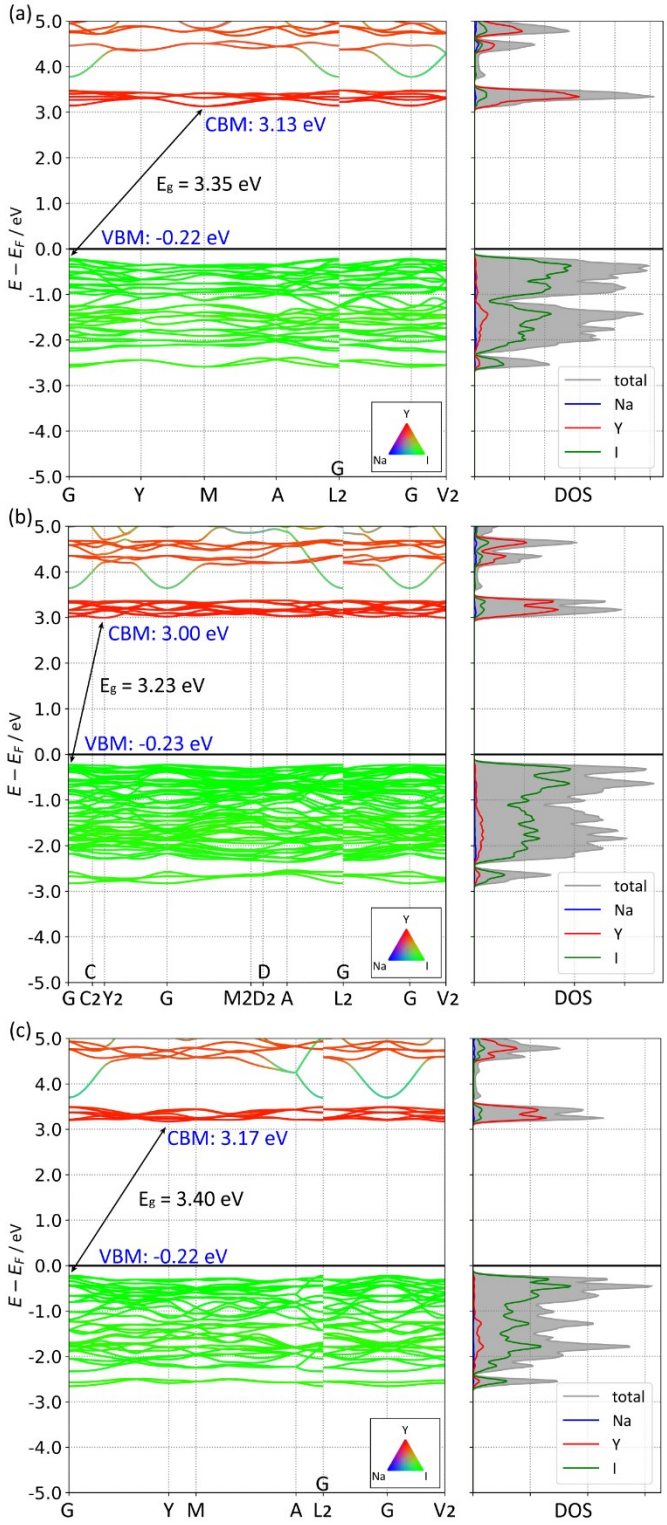

Figure S2. Element weighted electronic band structures of (a) c2m-Na_3YI_6, (b) p3m1-Na_3YI_6, and (c) p31c-Na_3YI_6 calculated by PBE functional.

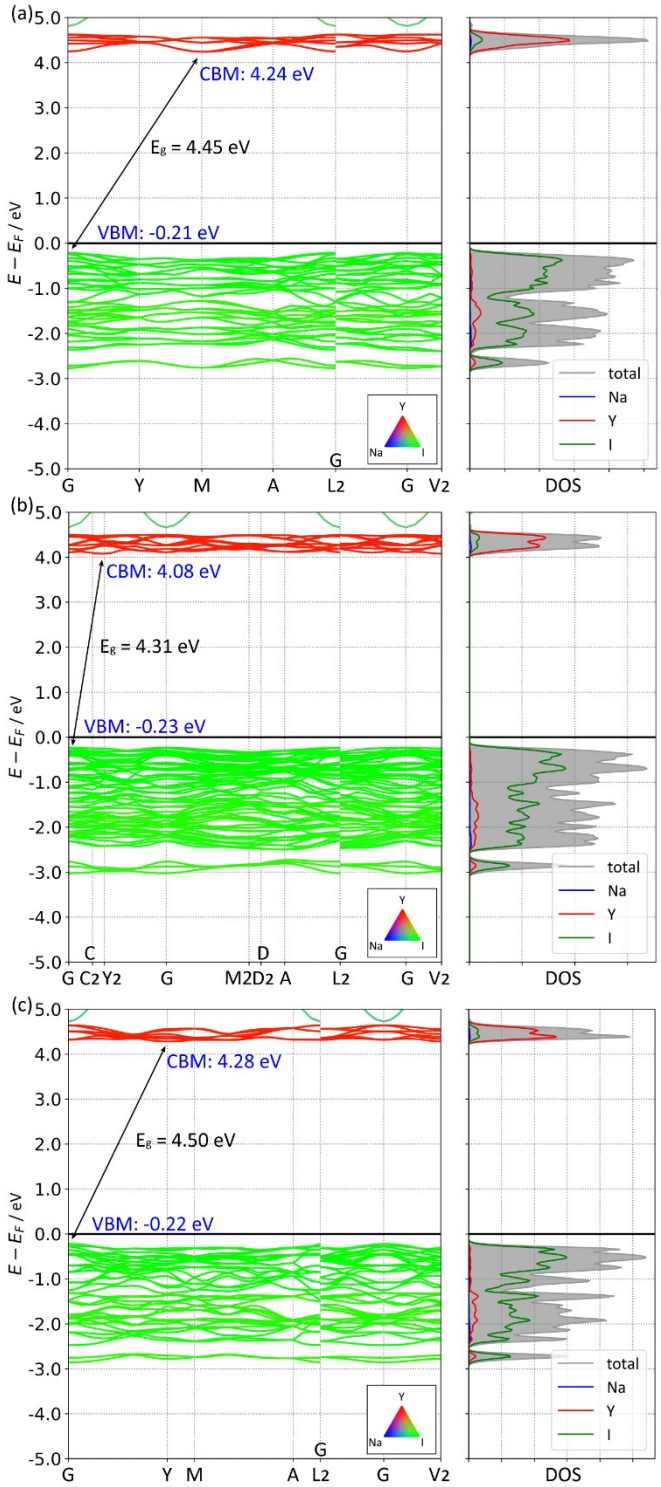

Figure S3. Element weighted electronic band structures of (a) c2m-Na_3YI_6, (b) p3m1-Na_3YI_6, and (c) p31c-Na_3YI_6 calculated by HSE06 functional.

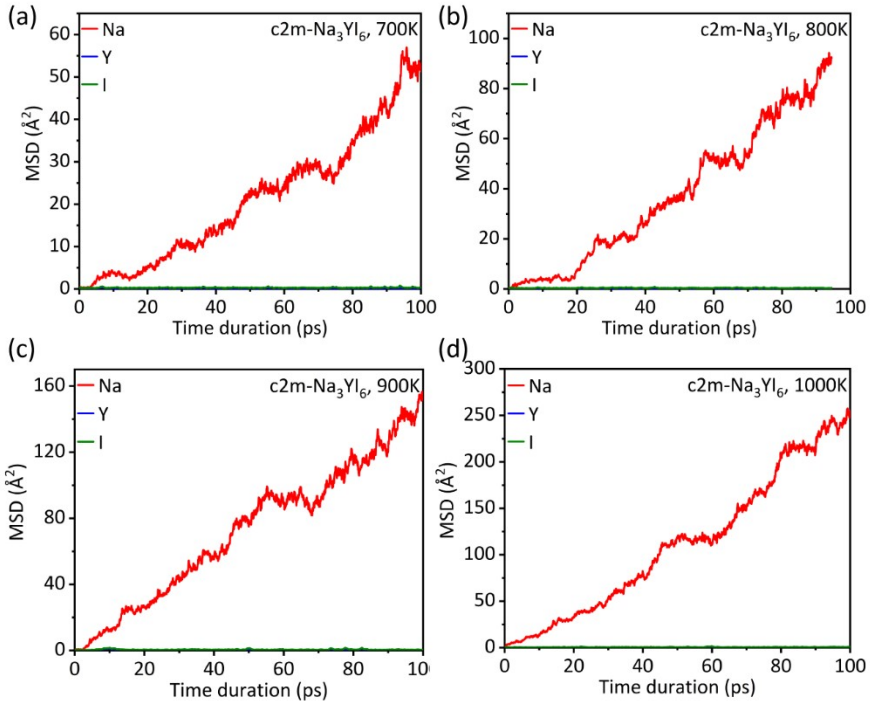

Figure S4. Mean square displacements of c2m-Na_3YI_6 at the temperature range from 700 K to 1000 K with the time duration of 100 ps.

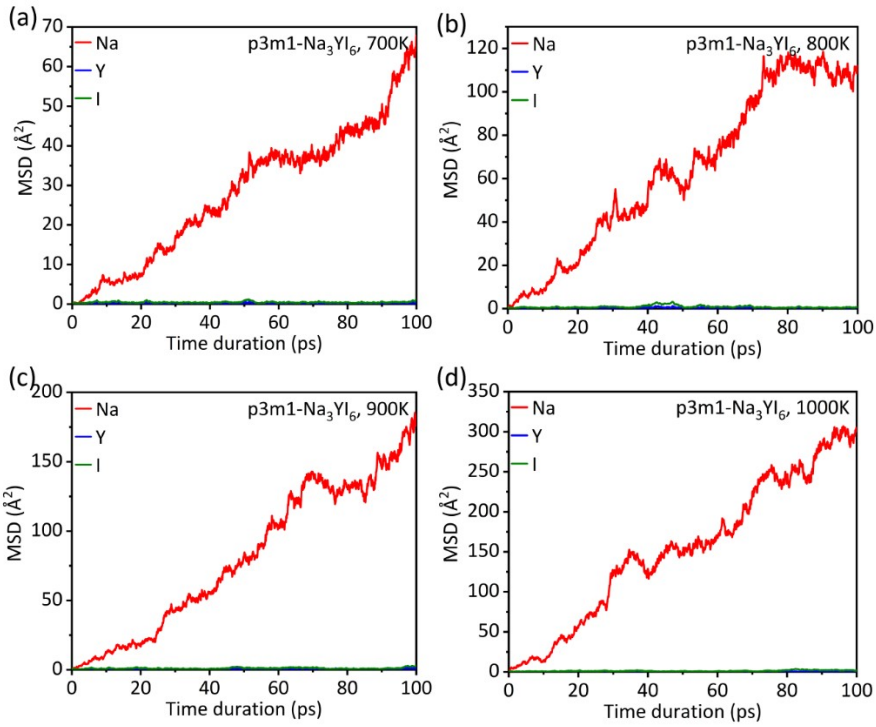

Figure S5. Mean square displacements of p3m1-Na_3YI_6 at the temperature range from 700 K to 1000 K with the time duration of 100 ps.

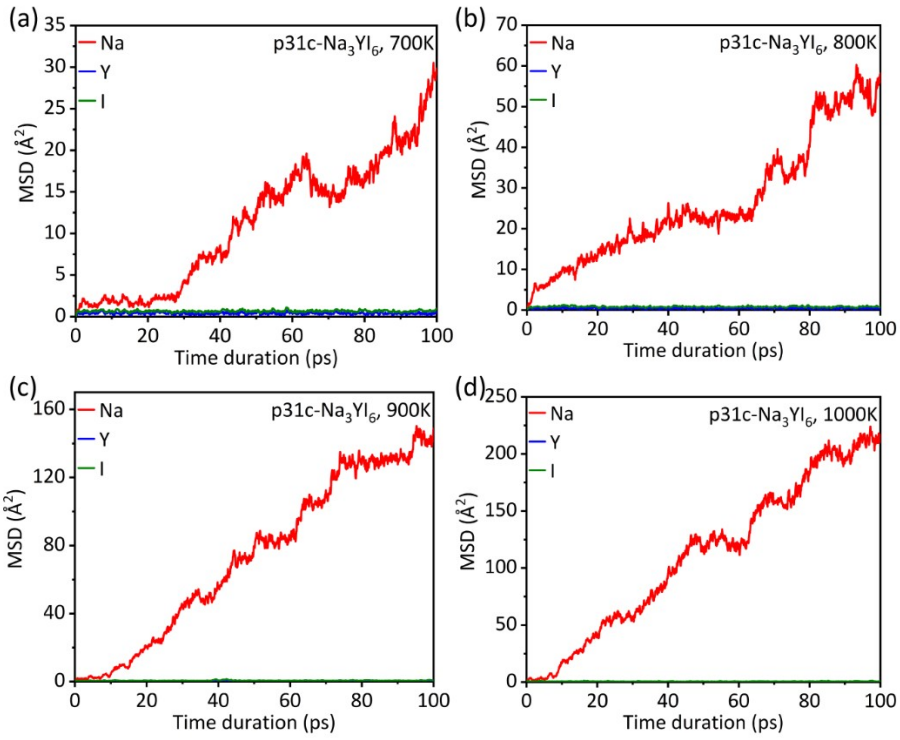

Figure S6. Mean square displacements of p3m1-Na_3YI_6 at the temperature range from 700 K to 1000 K with the time duration of 100 ps.

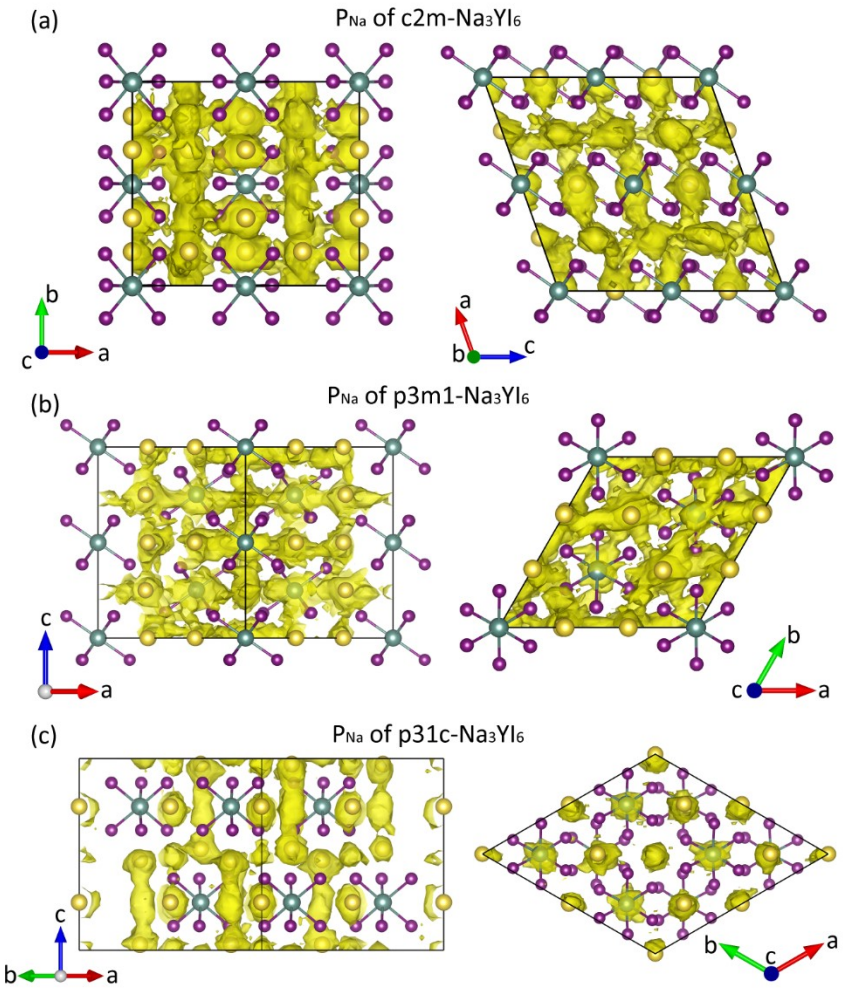

Figure S7. Na ion probability density distribution (yellow ribbon) in (a) c2m-Na_3YI_6, (b) p3m1-Na_3YI_6, and (c) p31c-Na_3YI_6 at 900 K, with the isosurface value of $^{1/32}\,P_{max}$.

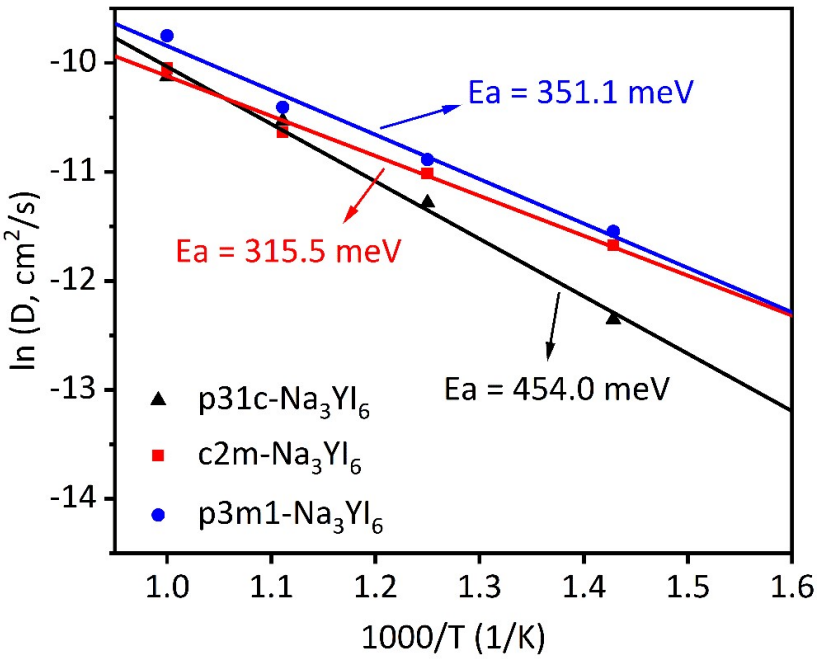

Figure S8. Arrhenius plot of the Na ionic diffusivities versus the inverse of the temperature of *c2m*-Na_3YI_6, *p3m1*-Na_3YI_6, and *p31c*-Na_3YI_6 obtained from the AIMD calculations. The corresponding fitted Na activation energy values are labeled.