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Regulation of the order–disorder phase transition in a $Cs_2NaFeCl_6$ double perovskite towards reversible thermochromic application

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Abstract: Multifunctional lead-free double perovskites demonstrate remarkable potential towards applications in various fields. Herein, an environmentally-friendly, low-cost, high-throughput $Cs_2NaFeCl_6$ single crystal with exceedingly high thermal stability is designed and grown. It obtains a cubic lattice system in the temperature range of 80–500 K, accompanied by a completely reversible chromatic variation ranging from yellow to black. Importantly, the intriguing thermochromism is proved to own extremely high reproducibility (over 1000 cycles) without a hysteretic effect, originating from its structural flexibility that including (i) the noteworthy distortion/deformation of $[NaCl_6]^{5-}$ and $[FeCl_6]^{3-}$ octahedra; (ii) order–disorder arrangement transition of $[NaCl_6]^{5-}$ and $[FeCl_6]^{3-}$ octahedra as the function of temperature. This study paves the way towards a new class of smart windows and camouflage coatings with an unprecedented colour range based on a $Cs_2NaFeCl_6$ perovskite.

Key words: lead-free perovskite; $Cs_2NaFeCl_6$ single crystal; thermochromism; crystallographic structure; order-disorder phase transition

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Supporting Information

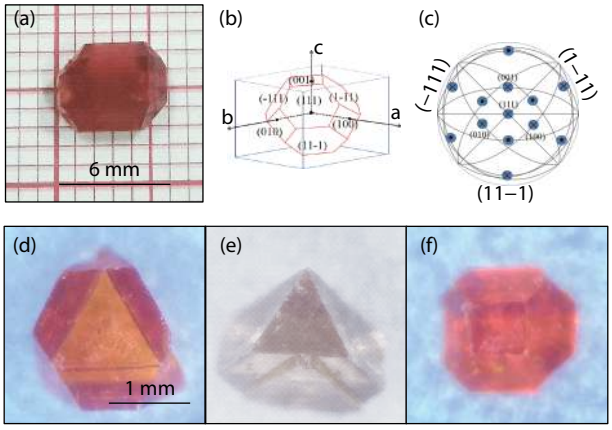

Fig. S1. (Color online) (a) is the as-grown $Cs_2NaFeCl_6$ perovskite single crystal with a length of 6 mm. (b) Schematic view of the planes in fcc crystal. (c) Schematic representation of the stereographic projection. (d–f) are the single crystals with different morphology.

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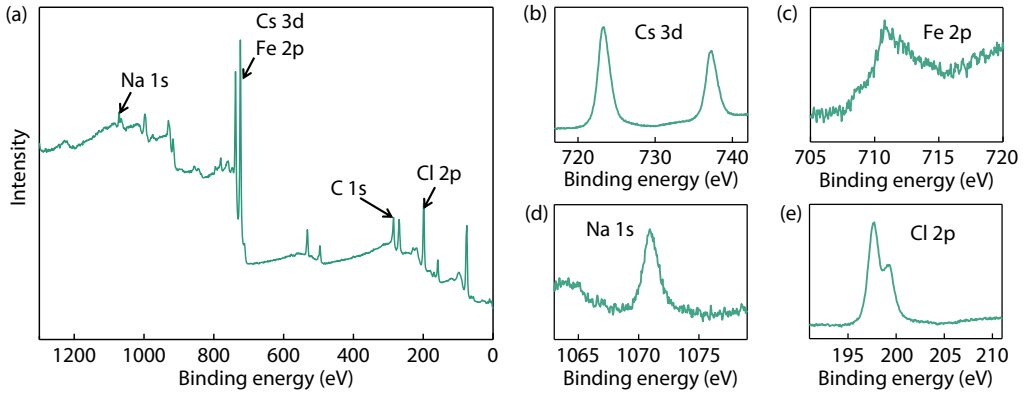

Fig. S2. XPS of the $Cs_2NaFeCl_6$ perovskite single crystal. (a) Total survey spectrum with the binding energy in the range of 0–1300 eV. (b) Cs-3d. (c) Fe-2p. (d) Na-1s. (e) Cl-2p.

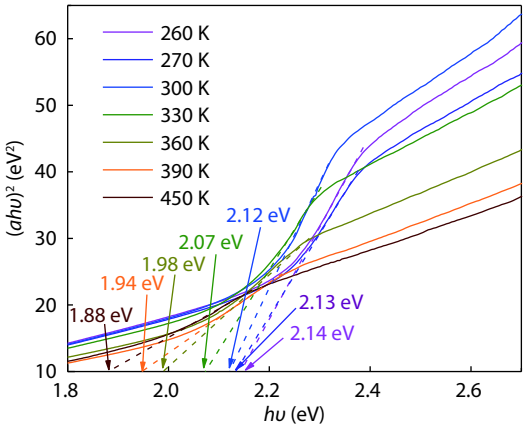

Fig. S3. $(ahv)^2$ vs hv curves calculated from UV–vis spectra.

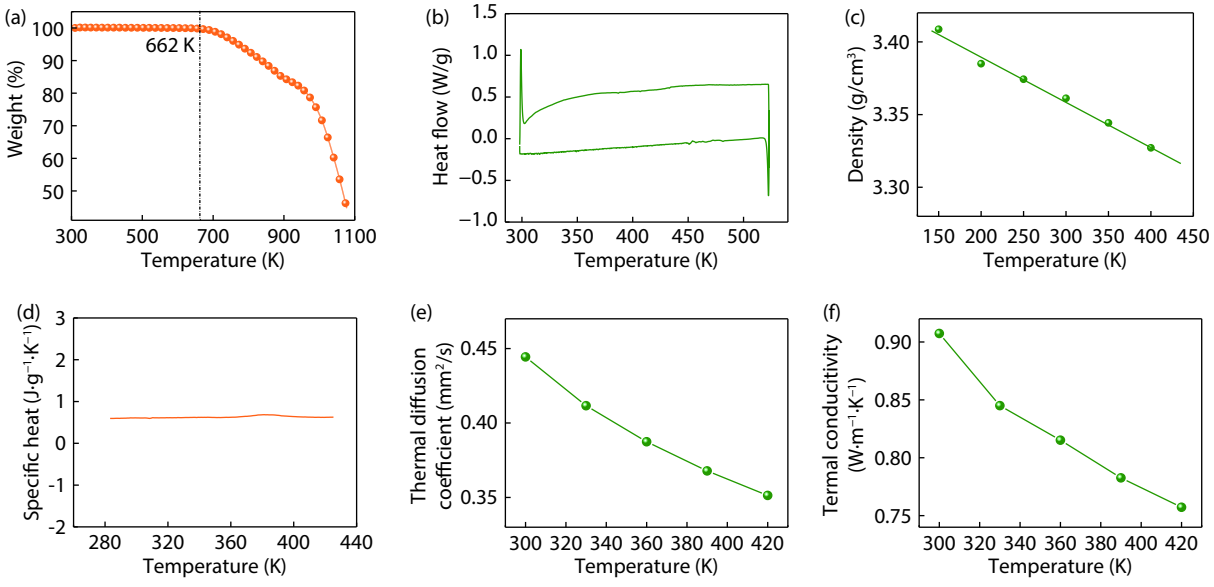

Fig. S4. Thermal properties of $Cs_2NaFeCl_6$ perovskite single crystal. (a) TGA curve. (b) DSC curve. (c) Density as the function of temperature. (d) Specific-heat curve. (e) Thermal diffusion coefficient. (f) Thermal conductivity curve.

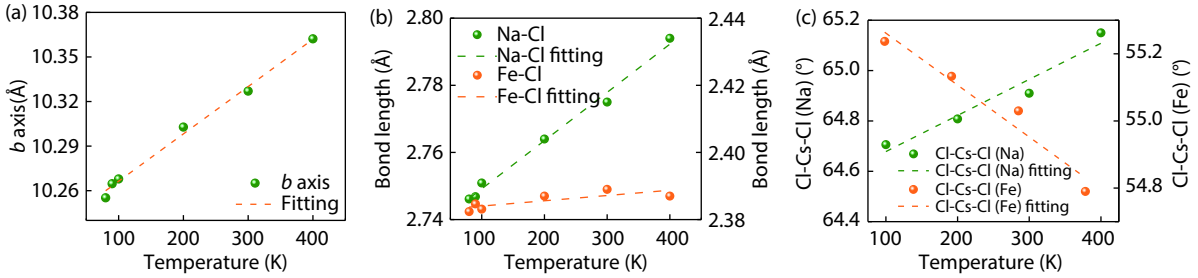

Fig. S5. (a) *b*-axis length evolution as the function of temperature. (b) Bonds length evolution of Fe-Cl and Na-Cl as the function of temperature. (c) Bonds angle evolution of Cs-Cl-Cs (Na) and Cs-Cl-Cs (Fe) evolution as the function of temperature.

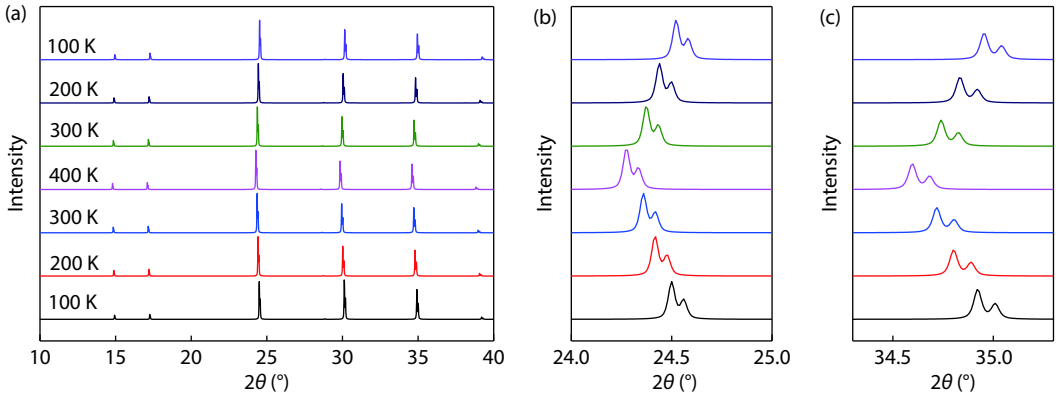

Fig. S6. (a) XRD patterns in the diffraction range of 10°–40°. The corresponding detail XRD peaks for (b) (111) plane and (c) (220) plane.

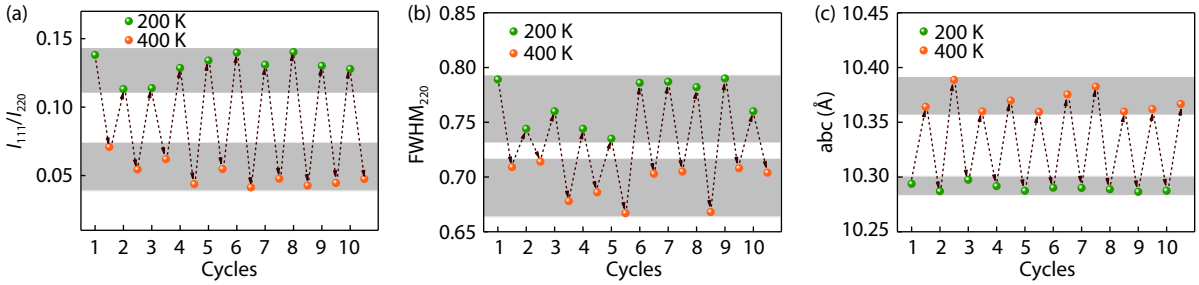

Fig. S7. (Color online) Reversible test for the crystallographic structure in $Cs_2NaFeCl_6$ perovskite from 200 to 400 K with 10 cycles. (a) I_{111}/I_{220}. (b) FWHM. (c) Unit cell length.

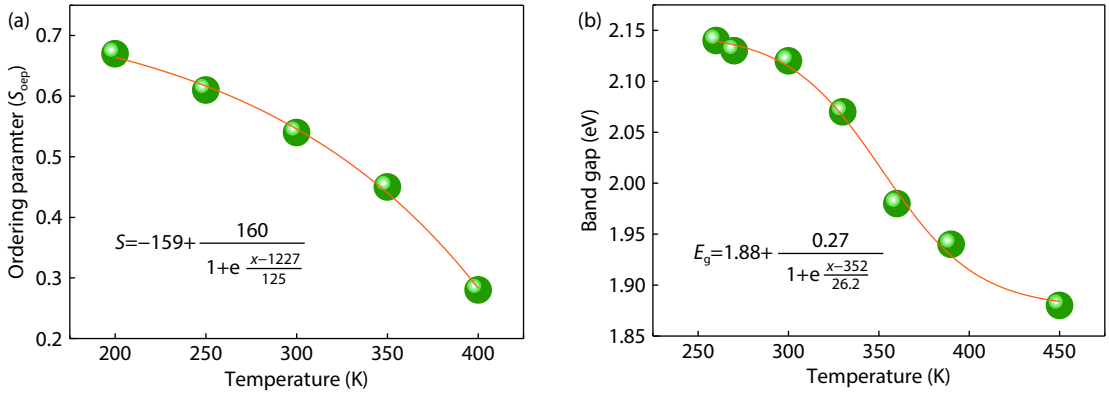

Fig. S8. (Color online) (a) Band gap evolution as the function of temperature. (b) Ordering parameter evolution as the function of temperature, both the curves are fitted by Bozeman equation as shown in inset of (a) and (b).

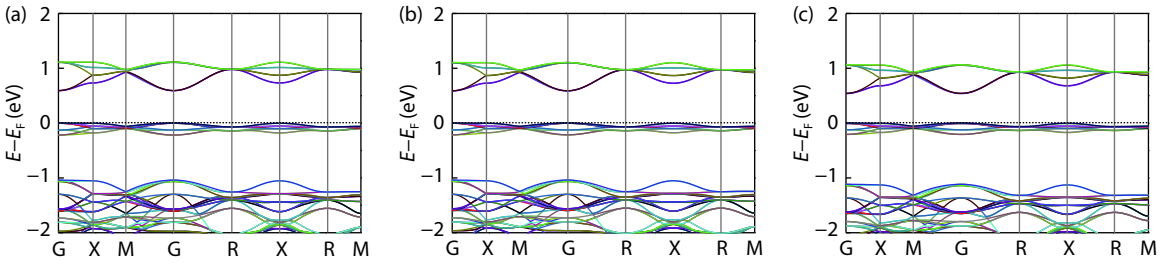

Fig. S9. (Color online) Calculated band structure by the GGA-PBE exchange-correlation functional of $Cs_2NaFeCl_6$ perovskite with thermal treatment at (a) 200 K, (b) 300 K, (c) 400 K.

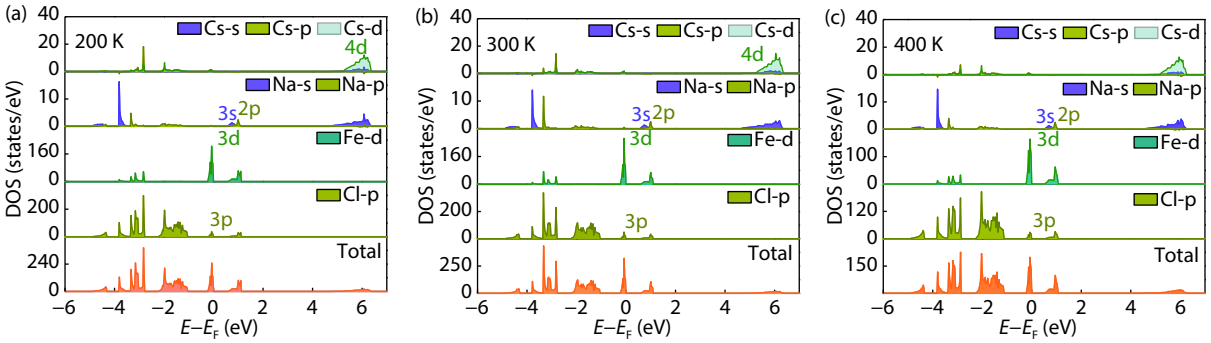

Fig. S10. (Color online) Total density of states (TDOS) and projected density of states (PDOS) of $Cs_2NaFeCl_6$ perovskite with thermal treatment at (a) 200 K, (b) 300 K, (c) 400 K.

Table S1. Summary of bond length and bond angle of $Cs_2NaFeCl_6$ single crystal forming in different temperature.

Bond length and angle (Å or °)	$Cs_2NaFeCl_6$ (80 K)	$Cs_2NaFeCl_6$ (90 K)	$Cs_2NaFeCl_6$ (100 K)	$Cs_2NaFeCl_6$ (200 K)	$Cs_2NaFeCl_6$ (300 K)	$Cs_2NaFeCl_6$ (400 K)
Fe-Cl	2.3832(10)*4	2.3832(11)*6	2.3830(10)*6	2.3852(12)*6	2.3866(17)*6	2.387(2)*6
Na-Cl	2.7463(9)	2.7493(11)	2.7509(10)	2.7662(12)	2.7769(17)	2.794(2)
Cl-Fe-Cl	180.0*3	180.0*3	180.0*3	180.0*3	180.0*3	180.0*3
Cl-Na-Cl	180.0*3	180.0*3	180.0*3	180.0*3	180.0*3	180.0*3
Fe-Cl-Na	180.0	180.0	180.0	180.0	180.0	180.0
Cl-Cs-Cl (Na)	64.65(2)	64.68(3)	64.71(3)	64.86(3)	64.96(4)	65.16(6)
Cl-Cs-Cl (Fe)	55.29(2)	55.26(3)	55.24(3)	55.08(3)	54.97(4)	54.77(6)

Table S2. Details of atoms occupation situation of $Cs_2NaFeCl_6$(80 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.75	0.75	0.75	1	0.00658(17)	8c	-43m
Fe02	0	0	0	1	0.0041(3)	4a	m-3m
Cl03	0	0	0.76769(9)	1	0.0075(3)	24e	4m.m
Na04	0	0	0.5	1	0.0072(8)	4b	m-3m

Table S3. Details of atoms occupation situation of $Cs_2NaFeCl_6$(90 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.75	0.75	0.75	1	0.0071(2)	8c	-43m
Fe02	0	0	0	1	0.0043(4)	4a	m-3m
Cl03	0.76783(11)	0	0	1	0.0083(3)	24e	4m.m
Na04	0.5	0	0	1	0.0062(9)	4b	m-3m

Table S4. Details of atoms occupation situation of $Cs_2NaFeCl_6$(100 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.75	0.75	0.75	1	0.0083(2)	8c	-43m
Fe02	0	0	0	1	0.0054(4)	4a	m-3m
Cl03	0.76791(10)	0	0	1	0.0092(3)	24e	4m.m
Na04	0.5	0	0	1	0.0079(9)	4b	m-3m

Table S5. Details of atoms occupation situation of $Cs_2NaFeCl_6$(200 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.75	0.75	0.75	1	0.0165(3)	8c	-43m
Fe02	0	0	0	1	0.0095(5)	4b	m-3m
Cl03	0.76849(12)	0	0	1	0.0168(4)	24e	4m.m
Na04	0.5	0	0	1	0.0134(12)	4a	m-3m

Table S6. Details of atoms occupation situation of $Cs_2NaFeCl_6$(300 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.25	0.25	0.25	1	0.0249(3)	8c	-43m
Fe02	0	0	0	1	0.0143(6)	4a	m-3m
Cl03	0.23110(16)	0	0	1	0.0246(5)	24e	4m.m
Na04	0.5	0	0	1	0.0218(16)	4b	m-3m

Table S7. Details of atoms occupation situation of $Cs_2NaFeCl_6$(400 K) single crystal.

Atom	*x*	*y*	*z*	Occ.	U	Site	Sym.
Cs01	0.25	0.25	0.25	1	0.0349(5)	8c	-43m
Fe02	0	0	0	1	0.0199(9)	4a	m-3m
Cl03	0	0.2303(2)	0	1	0.0341(8)	24e	4m.m
Na04	0	0.5	0	1	0.028(3)	4b	m-3m