Electronic Supplementary Material (ESI) for RSC Advances.

A New 12L-Hexagonal Perovskite $Cs_4Mg_3CaF_{12}$: Structural Transition Derived from the Partial Substitution of Mg^{2+} with Ca^{2+}

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Table S1 Atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and bond valence sum (BVS) for CMCF. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Site	S.O.F	*x*	*y*	*z*	*U*(*eq*)	BVS
Cs(1)	4*e*	1	0	0	1315(1)	16(1)	1.14
Cs(2)	4*e*	1	6667	3333	503(1)	14(1)	1.31
Mg(1)	2*b*	1	3333	6667	1667	11(1)	2.46
Mg(2)	2*b*	1	3333	6667	751(1)	10(1)	2.20
Ca(1)	4*e*	1	0	0	0	11(1)	1.94
F(1)	4*e*	1	1752(2)	3505(3)	416(1)	17(1)	1.10
F(2)	4*e*	1	570(3)	5285(2)	1231(1)	15(1)	1.18

Table S2 Selected bond lengths (Å) for CMCF[a].

Mg(1)-F(2)	1.9747(16)	Cs(1)-F(2)#3	3.1349(5)
Mg(1)-F(2)#15	1.9747(16)	Cs(1)-F(2)#4	3.1349(5)
Mg(1)-F(2)#3	1.9747(16)	Cs(1)-F(2)#5	3.1349(5)
Mg(1)-F(2)#16	1.9747(16)	Cs(1)-F(2)#6	3.1503(17)
Mg(1)-F(2)#7	1.9747(16)	Cs(1)-F(2)#7	3.1503(17)
Mg(1)-F(2)#17	1.9748(16)	Cs(1)-F(2)#8	3.1503(17)
Mean	1.9747	Cs(1)-F(1)#1	3.2783(18)
Mg(2)-F(1)#15	1.9737(18)	Cs(1)-F(1)#2	3.2783(18)
Mg(2)-F(1)	1.9737(18)	Cs(1)-F(1)	3.2783(18)
Mg(2)-F(1)#3	1.9737(18)	Mean	3.1742
Mg(2)-F(2)#15	2.066(2)	Cs(2)-F(2)#9	3.0229(16)
Mg(2)-F(2)	2.066(2)	Cs(2)-F(2)#2	3.0229(16)
Mg(2)-F(2)#3	2.066(2)	Cs(2)-F(2)#3	3.0229(16)
Mean	2.0199	Cs(2)-F(1)#10	3.1219(5)
Ca(1)-F(1)#22	2.2589(16)	Cs(2)-F(1)#9	3.1219(5)
Ca(1)-F(1)	2.2589(16)	Cs(2)-F(1)#2	3.1219(5)
Ca(1)-F(1)#23	2.2589(16)	Cs(2)-F(1)#11	3.1219(5)
Ca(1)-F(1)#2	2.2589(16)	Cs(2)-F(1)	3.1219(5)
Ca(1)-F(1)#13	2.2589(16)	Cs(2)-F(1)#3	3.1219(5)
Ca(1)-F(1)#1	2.2589(16)	Cs(2)-F(1)#12	3.2256(18)
Mean	2.2589	Cs(2)-F(1)#13	3.2256(18)
Cs(1)-F(2)#1	3.1349(5)	Cs(2)-F(1)#14	3.2256(18)
Cs(1)-F(2)	3.1349(5)	Mean	3.1230
Cs(1)-F(2)#2	3.1349(5)		

[a] Note. Symmetry transformations used to generate equivalent atoms:

#1 -y,x-y,z #2 -x+y,-x,z #3 -y+1,x-y+1,z

#4 -x+y-1,-x,z #5 x,y-1,z #6 y-1/3,-x+y-2/3,-z+1/3

#7 x-y+2/3,x+1/3,-z+1/3 #8 -x-1/3,-y+1/3,-z+1/3

#9 x+1,y,z #10 -y+1,x-y,z #11 -x+y+1,-x+1,z

#12 x-y+1,x,-z #13 y,-x+y,-z #14 -x+1,-y+1,-z

#15 -x+y,-x+1,z #16 -x+2/3,-y+4/3,-z+1/3

#17 y-1/3,-x+y+1/3,-z+1/3 #18 -x+2/3,-y+1/3,-z+1/3

#19 x,y+1,z #20 x+1,y+1,z #21 x-1,y,z

#22 -x,-y,-z #23 x-y,x,-z #24 -x+1,-y,-z

#25 x-1,y-1,z

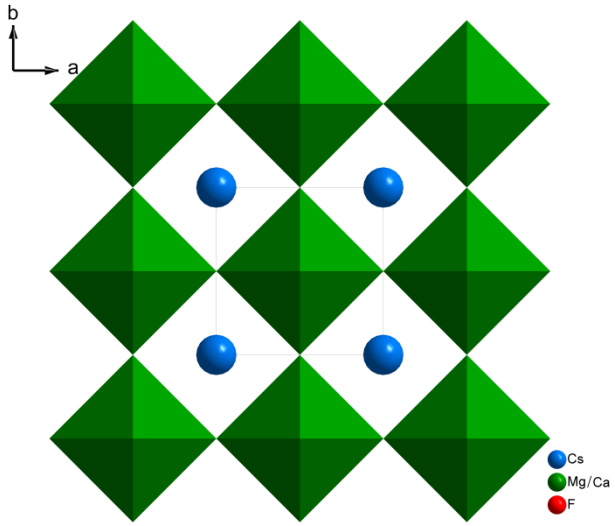

Figure S1. Structure of cubic $CsMF_3$ (M = Mg and Ca).

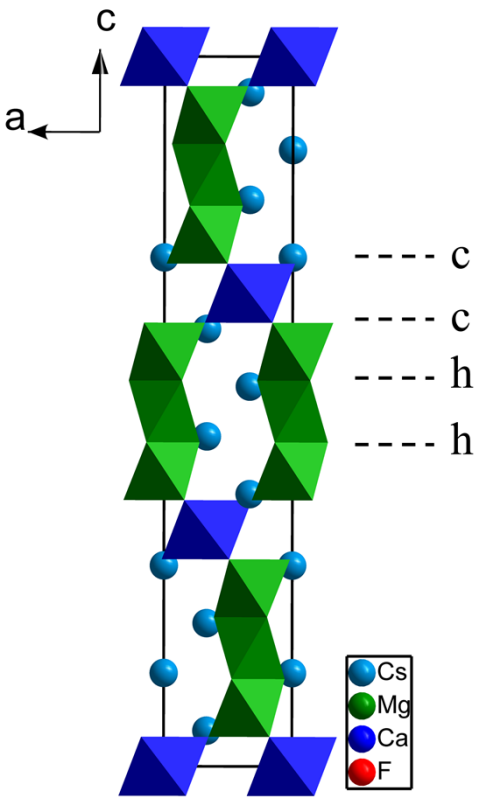

Figure S2. Crystal structure of CMCF.

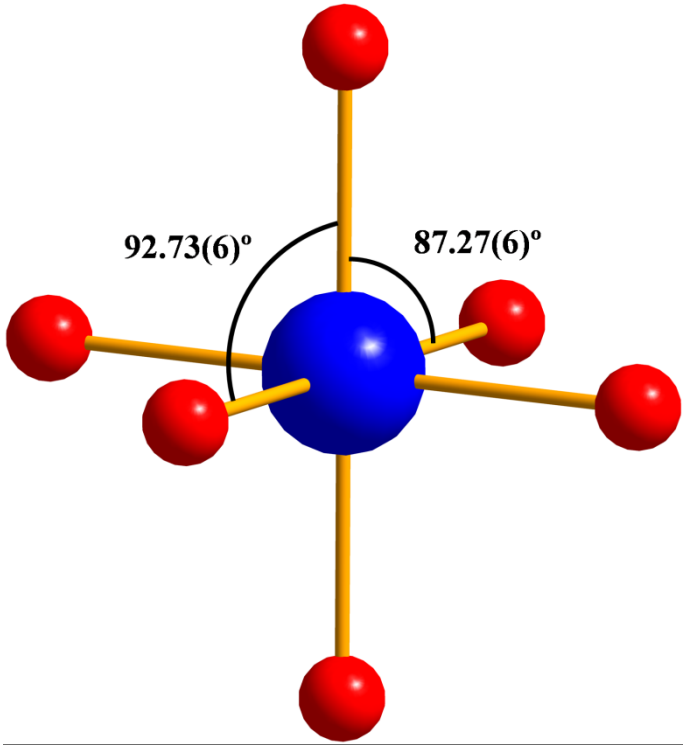

Figure S3. The bond angles of [CaF_6] octahedra.

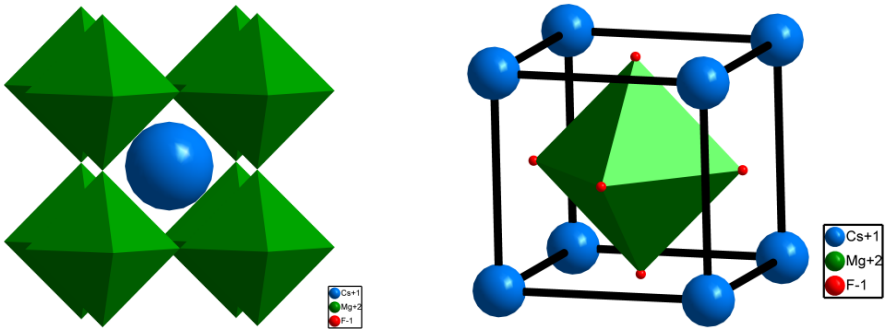

Figure S4. The typical perovskite model.

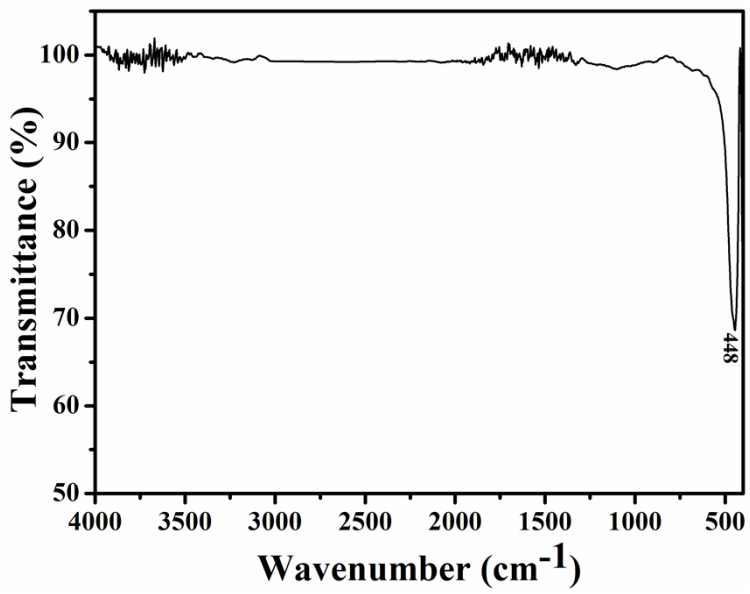

Figure S5. Infrared spectrum of CMCF.

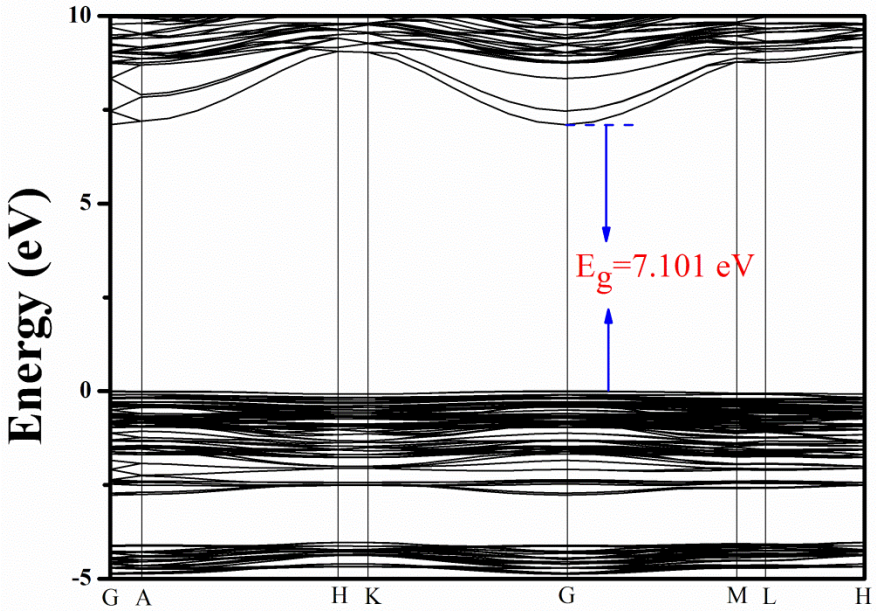

Figure S6. Band structure of CMCF.

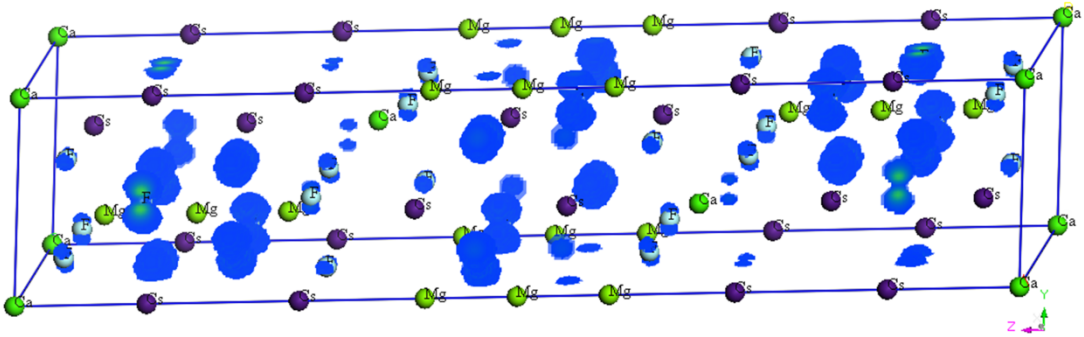

Figure S7. The map of charge density of CMCF.