A New 12L-Hexagonal Perovskite Cs$_4$Mg$_3$CaF$_{12}$: Structural Transition Derived from the Partial Substitution of Mg$^{2+}$ with Ca$^{2+}$

Zheng Wang,$^{ab}$ Qun Jing,$^{ab}$ Min Zhang,*$^a$ Xiaoyu Dong,$^{ab}$ Shilie Pan,*$^a$ Zhihua Yang$^a$

$^a$Key Laboratory of Functional Materials and Devices for Special Environments of CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices; Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China

$^b$University of Chinese Academy of Sciences, Beijing 100049, China

* To whom correspondence should be addressed. E-mail: zhangmin@ms.xjb.ac.cn (M. Zhang); E-mail: slpan@ms.xjb.ac.cn (S. Pan)
**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.

<table>
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<tr>
<th>Atoms</th>
<th>Site</th>
<th>S.O.F</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U(eq)$</th>
<th>BVS</th>
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<td>0</td>
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<td>Cs(2)</td>
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<tr>
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<td>1</td>
<td>3333</td>
<td>6667</td>
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Table S2 Selected bond lengths (Å) for CMCF<sup>a</sup>.

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<th>Length (Å)</th>
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<sup>a</sup> 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.