Supporting Information

High Quality Lead-Free Perovskites toward White Light Emitting

Diodes and X-ray Imaging

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Supporting Information

Table S1. Lead-free perovskites are used in WLEDs.

Phosphors	λ_{ex}	λ_{em}	Excitation chip	Mixed commercial powder
Cs ₂ Ag _{0.4} Na _{0.6} InCl ₆ : Bi ³⁺ , Ce ³⁺	350 nm	570 nm	365 nm UV chip	BaMgAl ₁₀ O ₁₇ : Eu ²⁺
Cs ₂ InCl ₅ ·H ₂ O: Sb ³⁺	340 nm	580 nm	365 nm UV chip	BaMgAl ₁₀ O ₁₇ : Eu ²⁺
Cs ₃ InBr ₆	370 nm	440 nm	365 nm UV chip	(Ba, Sr) ₂ SiO ₄ : Eu ²⁺
Cs ₃ Cu ₂ I ₅	313 nm	445 nm	310 nm UV chip	CaAlSiN ₃ : Eu ²⁺ , (Ba, Sr) ₂ SiO ₄ : Eu ²⁺
Cs₃Bi₂Br ₉ ^[1]	332 nm	410 nm	violet-emissive	Y ₃ Al ₅ O ₁₂

			GaN chips	
Cs ₂ NaInCl ₆ : Sb ^{3+ [2]}	317 nm	445 nm	370 nm UV chip	$Sr_2Si_5N_8$: Eu^{2+}
				β-SiAlON: Eu ²⁺
Rb ₃ (Cd _{0.8} Mn _{0.2}) ₂ Cl ₇	280 nm	575 nm	254 nm	Sr ₃ MgSi ₂ O ₈ : Eu ²⁺
[3]				$Lu_{3}Al_{5}O_{12}$: Ce ³⁺

 Table S2. Lead-free perovskites are used in scintillators.

Scintillator	Stokes shift (nm)	steady-state X-ray light yields (MeV ⁻¹)	detection limit (nGy s ⁻¹)	Spatial resolution (lp mm ⁻¹)
Cs ₂ Ag _{0.6} Na _{0.4} - In _{0.85} Bi _{0.15} Cl ₆	242	39000	19	4.3
Cs ₂ NaLnCl ₆ : (Ln: Tb, Eu)	170, 199	46600, 1250	-	-
Cs ₂ ZnBr ₄ : Cu	200	9987	57	9
Rb ₂ AgBr ₃	214	25600	19	10.2
Rb ₂ CuBr ₃ ^[4]	85	91056	121.5	
CsCu₂I₃ ^[5]	219	21580	-	7.5
Cs ₂ AgBiBr ₆ ^[6]	177		59.7	4.9



Figure S1. a) Crystal structure diagram of Cs_2HfCl_6 .



Figure S2. a) Energy disperse spectrum of Cs_2HfCl_6 : 3% Te⁴⁺. b) and c) SEM and EDS-mapping of selected area for Cs_2HfCl_6 : 3% Te⁴⁺.



Figure S3. The High-resolution XPS spectra of Cs_2HfCl_6 : 3% Te⁴⁺ corresponding to a) Cs 3d, b) Cl 2P and c) Hf 4f respectively. In Figure S3a and S3b, peak positions of Cs 3d and Cl 2p corresponding to different binding energy manifest the Cs and Cl elements of sample powder are presented in the form of +1 and -1 oxidation state respectively.



Figure S4. a) PL decay curves of Cs₂HfCl₆.



Figure S5. a) PLQY result of the as-obtained Cs₂HfCl₆: 3% Te⁴⁺.



Figure S6. a) The Tauc plots of Cs_2HfCl_6 : x% Te⁴⁺ crystals (x = 0, 1, 2, 3, 4, 5 and 10).

The optical bandgap can be calculated by the following formula:^[7]

$$\left[F(R_{\infty})hv\right]^{n} = A(hv - E_{g}) \tag{1}$$

where hv is the photon energy, A is the proportional constant and E_g is the optical bandgap value. Considering the direct bandgap of Cs₂HfCl₆:Te⁴⁺,^[8] n = 2 is used to reckoning. $F(R_{\infty})$ is the Kubelka–Munk function defined as:

$$F(R_{\infty}) = (1 - R)^2 / 2R = K/S$$
 (2)

Where *R*, *K*, and *S* are the reflection, absorption, and scattering coefficient, respectively. From the linear extrapolation of $[F(R_{\infty})hv]^2 = 0$ in **Figure S6a**, the bandgap of Cs₂HfCl₆ and Cs₂HfCl₆: 3% Te⁴⁺ is calculated to be 4.67 and 4.13 eV respectively.



Figure S7. a) Temperature-dependent PL of Cs₂HfCl₆: 3% Te⁴⁺.



Figure S8. a) and b) Emission spectra and excitation spectra of Cs_2HfCl_6 : 3% Te⁴⁺ are monitored at different excitation and emission wavelengths, respectively. c) The PL decay curves of Cs_2HfCl_6 : 3% Te⁴⁺.



Figure S9. a) and b) PL and RL spectra of Cs_2HfCl_6 : x% Te⁴⁺ (x = 1, 2, 3, 4, 5 and 10)

respectively.



Figure S10. a) and c) The band structures of Cs_2HfCl_6 and Cs_2HfCl_6 : 3% Te⁴⁺ calculated with the DFT method respectively. b) and d) The total and partial density of states of Cs_2HfCl_6 and Cs_2HfCl_6 : 3% Te⁴⁺ based on the DFT method.



Figure S11. a) PL curves of Cs₂HfCl₆: x% Te⁴⁺ (x=0, 1, 2, 3, 4, 5 and 10) crystals.



Figure S12. a), b) and c) are the tests of thermal stability, water stability and air stability, respectively. As shown in **Figure S12a**, the thermogravimetry analysis (TGA) is carried out for Cs_2HfCl_6 : 3% Te⁴⁺ at the nitrogen atmosphere. It can be clearly observed that the structure still maintains integrality up to 400 °C, which much superior to most lead-based perovskites.

Furthermore, the powder is put into a cuvette with deionized water to measure stability against water in **Figure S12b**. The PL intensity of the sample completely immersed in deionized water remain the original 85% after 180 minutes, which indicates that the sample has good resistance for water. Meanwhile, we also put the prepared sample in the atmosphere. The PL intensity of the sample can still be kept at the original 97% after 10 days in **Figure S12c**, which suggest outstanding environmental stability.



Figure S13. a) Schematic of RL spectra measurement using an integrating sphere and a spectrometer. b) The variation of RL spectra intensity with irradiation at different times.

References

- [1] M. Leng, Y. Yang, K. Zeng, Z. Chen, Z. Tan, S. Li, J. Li, B. Xu, D. Li, M. P. Hautzinger, Y. Fu, T. Zhai, L. Xu, G. Niu, S. Jin, J. Tang, Adv. Funct. Mater. 2017, 28 (1), 1704446.
- [2] M. B. Gray, S. Hariyani, T. A. Strom, J. D. Majher, J. Brgoch, P. M. Woodward, J. Mater. Chem. C. 2020, 8 (20), 6797-6803.
- [3] J. H. Han, N. S. M. Viswanath, Y. M. Park, H. B. Cho, S. W. Jang, J. W. Min, W.

B. Im, Chem. Mater. 2022, 34, 5690.

- [4] B. Yang, L. Yin, G. Niu, J. H. Yuan, K. H. Xue, Z. Tan, X. S. Miao, M. Niu, X. Du,
 H. Song, E. Lifshitz, J. Tang, Adv. Mater. 2019, 31 (44), 1904711.
- [5] M. Zhang, J. Zhu, B. Yang, G. Niu, H. Wu, X. Zhao, L. Yin, T. Jin, X. Liang, J. Tang, Nano Lett. 2021, 21 (3), 1392-1399.
- [6] B. Yang, W. Pan, H. Wu, G. Niu, J. H. Yuan, K. H. Xue, L. Yin, X. Du, X. S. Miao,X. Yang, Q. Xie, J. Tang, Nat. Commun. 2019, 10 (1), 1-10.
- [7] J. Zhou, X. Rong, M. S. Molokeev, X. Zhang, Z. Xia, J. Mater. Chem. A. 2018, 6 (5), 2346-2352.
- [8] B. Kang, K. Biswas, J. Phys. Chem. C. 2016, 120 (22), 12187-12195.