Please put this in the Supplementary Information

**Raman spectroscopy**



**Fig. SX** Raman spectra of the all-inorganic copper halide perovskites (CHPs). Notable Raman shifts are marked with dashed lines.

Fig. SX shows the Raman spectra of the CHPs. We observed a main peak at ~108 cm-1, which can be attributed to the Br-Cu-Br vibration mode, as the metal-halide bending or stretching mode are typically observed in this range.1,2 Shoulder peaks observed at ~52, ~64, and ~162 cm-1 may correspond to the lattice vibration of the entire [CuBr3]2- network, Cu-Br bonding vibration or combination of both ions, and the symmetric/ asymmetric stretching of the Cu-Br bonds in the internal modes of [CuBr3]2- units.3–6

**References**

1 Z. Guo, J. Li, Y. Gao, J. Cheng, W. Zhang, R. Pan, R. Chen and T. He, Multiphoton absorption in low-dimensional cesium copper iodide single crystals, *J. Mater. Chem. C*, 2020, **8**, 16923–16929.

2 T. Haposan, A. Arramel, P. Y. D. Maulida, S. Hartati, A. A. Afkauni, M. H. Mahyuddin, L. Zhang, D. Kowal, M. E. Witkowski, K. J. Drozdowski, M. Makowski, W. Drozdowski, L. J. Diguna and M. D. Birowosuto, All-inorganic copper-halide perovskites for large-Stokes shift and ten-nanosecond-emission scintillators, *J. Mater. Chem. C*, 2024, **12**, 2398–2409.

3 Y. Yang, J. P. Robbins, L. Ezeonu, Y. Ma, N. Sparta, X. Kong, S. Strauf, S. G. Podkolzin and S. S. Lee, Probing lattice vibrations of stabilized CsPbI3 polymorphs *via* low-frequency Raman spectroscopy, *J. Mater. Chem. C*, 2020, **8**, 8896–8903.

4 J. Li, X. Liu, P. Cui, J. Li, T. Ye, X. Wang, C. Zhang and Y. S. Zhao, Lead-free thermochromic perovskites with tunable transition temperatures for smart window applications, *Sci. China Chem.*, 2019, **62**, 1257–1262.

5 M. A. Pérez-Osorio, Q. Lin, R. T. Phillips, R. L. Milot, L. M. Herz, M. B. Johnston and F. Giustino, Raman Spectrum of the Organic–Inorganic Halide Perovskite CH 3 NH 3 PbI 3 from First Principles and High-Resolution Low-Temperature Raman Measurements, *J. Phys. Chem. C*, 2018, **122**, 21703–21717.

6 A. Kaiba, M. H. Geesi, P. Guionneau, T. A. Aljohani, L. Bih, H. Bih and S. Kassou, Synthesis, structural and Raman spectroscopic in organic−inorganic halide perovskites based on β-Alanine, *J. Mol. Struct.*, 2020, **1204**, 127380.