Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Revealing the Nature of Photoluminescence Emission in Metal-Halide Double Perovskite - $Cs_2AgBiBr_6$

# Supporting Information

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## Comparison of PLE and R spectra with literature absorption data

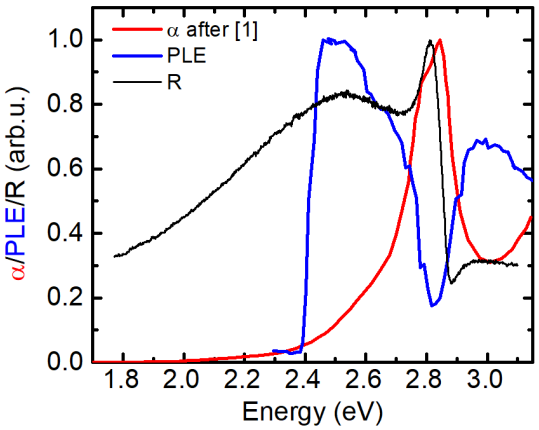


Figure S1: Comparison of measured at 5K PLE and R spectra with 80K absorption spectrum taken after ref.[1] The clear discrepancy between absorption and PLE spectrum can be observed.

## Estimation of indirect bandgap position

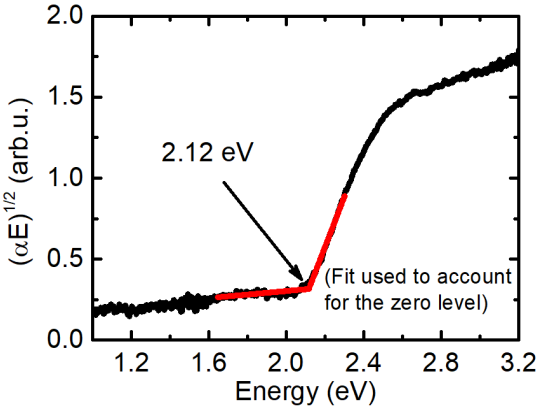


Figure S2: Tauc plot of photoacoustic signal (PAS). The PAS signal is proportional to absorption. In order to take in to account some residual signal below 2.1 eV related to background level of our setup and possible tail density of states absorption we use bimodal linear regression. As a bandgap value we take cross of two straight lines (red) which gives value of 2.12 eV in good agreement with literature reports.[1–4]

**Simulations of phonon and Raman Spectra**

The simulated phonon dispersion plots of cubic and tetragonal $Cs_2AgBiBr_6$ are shown in Fig. S3.

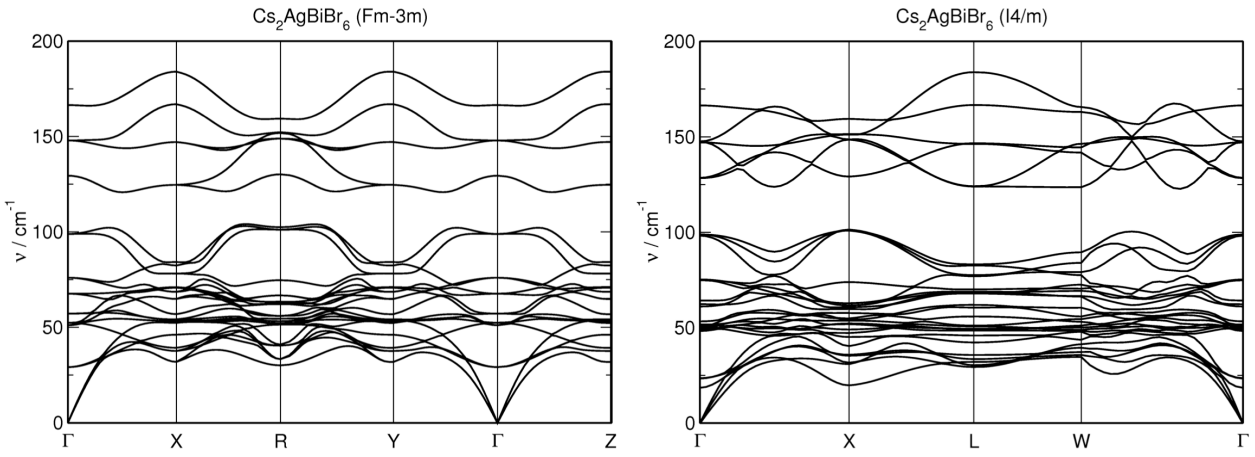


Figure S3: Phonon dispersion curves simulated for cubic (left) and tetragonal (right) forms of $Cs_2AgBiBr_6$. Due to very heavy elements, the normal modes are very soft, below 200 $cm^{-1}$.

We have simulated the Raman spectra of optimized cubic and tetragonal $Cs_2AgBiBr_6$ system (blue and red in Fig. S4). The $A_{1_g}$ mode is not affected by the crystal phase, however, the $E_g$ and $T_{2_g}$ modes have small shifts towards smaller wavenumbers in the tetragonal form. Also, the intensities of these two modes change when changing phase, especially strong for $E_g$, while $A_{1_g}$ intensity stays the same. Moreover, we have calculated the Raman shift for a cubic form with lattice vectors taken from experiment (black in Fig. S4).[3] The experimental value of the lattice vector is by about 2.4% smaller than our optimized value, showing the effect of the tensile strain or compression on the Raman shifts. Upon strain, the Raman peaks shift toward lower wavenumbers and the strongest effect is observed for the $E_g$ (from 191 to 167 $cm^{-1}$) and $A_{1_g}$ (from 154 to 130 $cm^{-1}$) modes. The $T_{2_g}$ mode shifts down by about 12 $cm^{-1}$ (from 88 to 76 $cm^{-1}$).

The simulated Raman modes suggest that the investigated experimental structure is not perfectly cubic and some parts might be Ag or Bi dominant. Raman modes are schematically shown in Fig. S5.

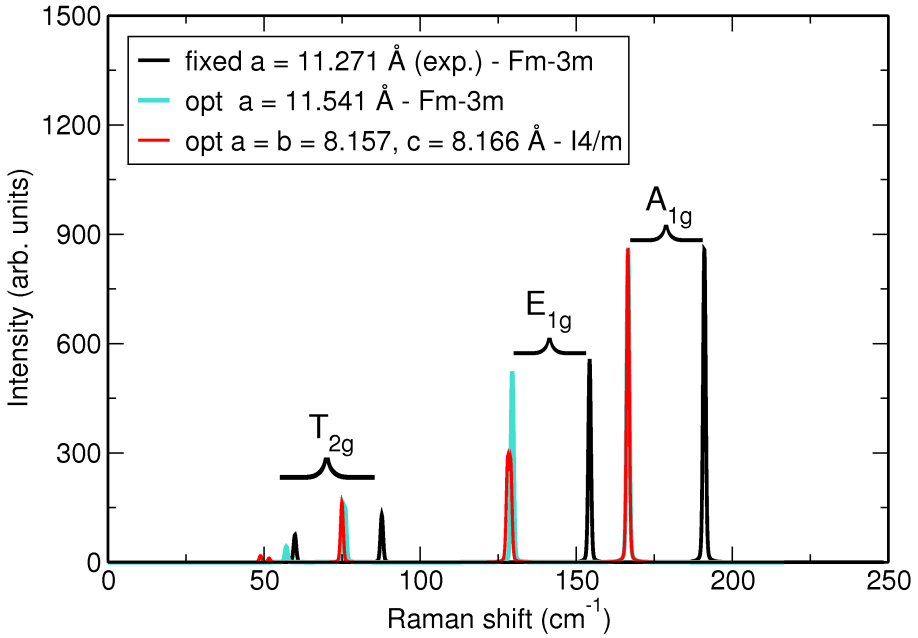


Figure S4: Simulated Raman spectra of $Cs_2AgBiBr_6$ in cubic (blue and black) and tetragonal forms (red). For the cubic phase, two lattice vectors are used: experimental (black)[3] and fully relaxed at the PBE level (blue). The symmetries of modes are shown. Corresponding normal modes are sketched in Fig. S5.

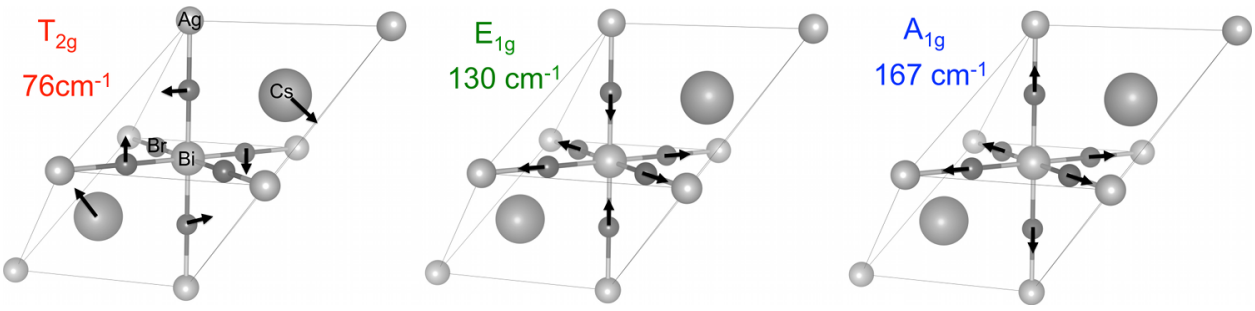


Figure S5: Schematic representation of normal modes observed in the cubic $Cs_2AgBiBr_6$ phase. $T_{2_g}$ mode consists of collective motion of Cs atoms and scissoring of Br atoms, which are around Bi; $E_g$ and $A_{1_g}$ modes are the asymmetric and symmetric stretching of Br atoms in the octahedra formed with Bi atoms in the middle, respectively.

# References


(1) Bartesaghi, D.; Slavney, A. H.; Gelvez-Rueda, M. C.; Connor, B. A.; Grozema, F. C.; Karunadasa, H. I.; Savenije, T. J. Charge Carrier Dynamics in Cs2AgBiBr6 Double Perovskite. *The Journal of Physical Chemistry C* **2018**, *122*, 4809–4816.

(2) Slavney, A. H.; Hu, T.; Lindenberg, A. M.; Karunadasa, H. I. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. *Journal of the American Chemical Society* **2016**, *138*, 2138–2141.

(3) McClure, E. T.; Ball, M. R.; Windl, W.; Woodward, P. M. Cs2AgBiX6 (X= Br, Cl): new visible light absorbing, lead-free halide perovskite semiconductors. *Chemistry of Materials* **2016**, *28*, 1348–1354.

(4) Filip, M. R.; Hillman, S.; Haghighirad, A. A.; Snaith, H. J.; Giustino, F. Band gaps of the lead-free halide double perovskites Cs2BiAgCl6 and Cs2BiAgBr6 from theory and experiment. *The journal of physical chemistry letters* **2016**, *7*, 2579–2585.