SUPPORTING INFORMATION

Compositional tuning of carrier dynamics in Cs₂Na_{1-x}Ag_xBiCl₆ double perovskite nanocrystals

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METHODS/EXPERIMENTAL

Chemicals. Cesium carbonate (Cs_2CO_3 , 99%), silver acetate (Ag(ac) 99.99%), sodium acetate (Na(ac), 99%), bismuth acetate (Bi(ac)_3, 99.99%), benzoyl chloride (Bz-Cl, 98%), dioctyl ether (DOE, 99%), oleic acid (OA, 90%), oleylamine (OLAM, 70%), hexane (anhydrous) ethyl acetate (99.8%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Synthesis of Cs₂Na_{1-x}Ag_xBiCl₆ NCs. Cs₂Na_{1-x}Ag_xBiCl₆ NCs were synthesized following our previous works on DPs with minor modifications.¹ In detail, Cs₂CO₃ (0.25 mmol), Ag(ac) ((1-*x*) × 0.25 mmol), Na(ac) (x × 0.25 mmol), Bi(ac)₃ (0.25 mmol), 0.6 ml OLAM, 1.2 ml OA, and 4 ml DOE were mixed in a vial under N₂. Then, the system was heated on a hotplate up to 140 °C and at that temperature a solution of 220 µl Bz-Cl in 0.5 ml of degassed DOE was swiftly injected into the vial. Immediately after the injection, the reaction was cooled down by an ice-water bath. Finally, 6 ml of hexane was added to the crude NCs solution, and the resulting mixture was centrifuged at 6000 rpm for 5 min. The supernatant was discarded, and the precipitate was redispersed in 2 ml hexane. The solution was centrifuged again at 6000 rpm for 5 min and the precipitate was discarded. The NCs in the supernatant were precipitated by the addition of 2 ml of ethyl acetate and centrifuged at 6000 rpm for 5 min. The final precipitate was redispersed in 2 ml of hexane and stored in a N₂ filled glovebox for further use.

UV-vis Absorption, PL and PL Quantum Yield (QY) Measurements. The UV-visible absorption spectra were recorded using a Varian Cary 300 UV-vis absorption spectrophotometer. The PL spectra were measured by exciting the samples with a frequency tripled pulsed Nd:YAG laser at 3.49 eV with a 140 Hz repetition rate (pulse duration, 5 ns) and the emitted light was acquired with a Horiba Scientific Triax 180 1/2 m spectrograph and detected with an Instruments SA Spectrum One liquid-nitrogen-cooled charge-coupled device. The PL excitation (PLE) spectra were measured on a Varian Cary Eclipse spectrophotometer. The PL efficiencies were measured at room temperature on hexane dispersions of nanocrystals using a Nd:YAG laser as excitation source coupled with an integrating sphere. The emitted light was collected with a TM-C10083CA Hamamatsu Spectrometer. Time-resolved PL experiments were conducted using the same excitation source and collecting with a Hamamatsu R943-02 time-correlated single-photon counting unit coupled to an Oriel Instruments Cornerstone 260 monochromator. For low temperature measurements, the double perovskite NC were drop-cast onto glass substrates and the samples were placed in a variable-temperature insert of a closed-cycle helium cryostat (T=3.5 – 300 K) with direct optical access.

Transmission Electron Microscopy (TEM). The samples were prepared by dropping dilute nanocrystal solutions on 200 mesh carbon-coated copper grids for low-resolution TEM measurements which were performed on a JEOL JEM-1400Plus microscope with a thermionic gun (W filament) operated at an acceleration voltage of 120 kV. Dilute nanocrystal solutions were drop-cast on 400 mesh ultrathin carbon/holey carbon-coated 400 mesh copper grids for high-resolution TEM (HRTEM) imaging and high-angle annular dark-field (HAADF)-scanning TEM (STEM) imaging. For this purpose, a JEOL JEM-2200FS microscope equipped with a Schottky emitter working at an accelerating voltage of 200 kV, a CEOS spherical aberration corrector for the objective lens and an in-column image filter was used. STEM-energy-dispersive X-ray spectroscopy (EDS) elemental mapping was also conducted on this microscope equipped with a Bruker Quantax 400 EDX system with a 60 mm² XFlash 6T silicon drift detector (SDD).

X-ray Diffraction (XRD) Characterization. XRD analysis was carried out on PANanalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and a PIXcel^{3D} 2x2 area detector, operating at 45 kV and 40 mA. Specimens for the XRD measurements were prepared by dropping a concentrated NCs solution onto a silicon zero-diffraction single crystal substrate. The diffraction patterns were collected under ambient conditions using a parallel beam geometry and the symmetric reflection mode. XRD data analysis was conducted using the HighScore 4.1 software from PANalytical.

Scanning Electron Microscopy (SEM). SEM analysis was obtained by HRSEM JEOL JSM-7500LA microscope with a cold field-emission gun (FEG), operating at 15 kV acceleration voltage. Energy-dispersive spectroscopy (EDS, Oxford instrument, X-Max, 80 mm²) was used to evaluate the elemental ratios. All experiments were done at 8 mm working distance, 15 kV acceleration voltage and 15 sweep count for each sample.

X-ray Photoelectron Spectroscopy (XPS) Characterization. XPS analyses were carried out with a Kratos Axis UltraDLD spectrometer using a monochromatic Al K α source, operated at 20 mA and 15 kV. Specimens for the XPS measurements were prepared by dropping a concentrated NC solution onto freshly cleaved highly oriented pyrolytic graphite substrates. Survey scan analyses were carried out with an analysis area of $300 \times 700 \mu$ m and a pass energy of 160 eV. High resolution analyses were carried out over the same analysis area and a pass energy of 10 eV. The Kratos charge neutralizer system was used on all specimens. Spectra were charge-corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV. Spectra were analyzed using CasaXPS software (version 2.3.17).

Computational Methodology. The study on the emission mechanism was performed on 2x2x2 supercells at the gamma point. Both atomic positions and cell parameters were relaxed at the density functional theory (DFT) level using the PBE exchange–correlation functional² and a double- ζ basis set plus polarization functions (DZVP) on all atoms³ as implemented in the CP2K 5.1 package.⁴ Scalar relativistic effects were incorporated as effective core potentials. The same level of theory was used to compute transition dipole moments, which, in the approximation of one-electron transition, are evaluated using the Fermi's golden rule. The role of surface defect was probed by modeling explicit cubic Cs₂Na_{1-x}Ag_xBiCl₆ nanocrystals of about 3.0 nm. NCs models were created by cutting the corresponding cubic bulk structures along the (100) facets, leaving Cs and Cl on the surface. As-cut, these nanostructures present a stoichiometry of Cs₃₄₃Na_{108-x}Ag_xBi₁₀₈Cl₇₅₆ respectively, corresponding to an excess of positive charge when each ion is considered in its more stable thermodynamic electronic configuration (i.e. Cs⁺, Na⁺ and Ag⁺, Bi³⁺ and Cl⁻). This excess was compensated by removing 19 Cs ions from the surface, leading to a charge balanced Cs₃₂₄Na_{108-x}Ag_xBi₁₀₈Cl₇₅₆ stoichiometry.⁵ Structural relaxation and analysis of the electronic structure was carried out at the DFT/PBE/DZVP level of theory with CP2k.

Table S1. Compositions of Bi-doped $Cs_2Na_{1-x}Ag_xBiCl_6NC$ samples measured by both XPS and SEM-EDS instruments. For the sake of simplicity, the amounts of the different elements were expressed relative to that of Bi, which was assumed to be 1.

Na/Ag precursors	SEM-EDS	XPS
ratio	Composition	Composition
100/0	Cs _{1.86} Na _{0.85} BiCl _{5.53}	$Cs_{1.91}Na_{1.26}BiCl_{4.98}$
95/5	$Cs_{1.85}Na_{0.92}Ag_{0.09}BiCl_{5.52}$	$Cs_{1.94}Na_{1.19}Ag_{0.06}BiCl_{5.08}$
90/10	$Cs_{2.00}Na_{0.78}Ag_{0.12}BiCl_{5.61}$	$Cs_{2.00}Na_{0.96}Ag_{0.08}BiCl_{5.12}$
80/20	$Cs_{1.69}Na_{0.73}Ag_{0.23}BiCl_{5.46}$	$Cs_{1.82}Na_{0.99}Ag_{0.18}BiCl_{5.13}$
60/40	$Cs_{1.73}Na_{0.61}Ag_{0.46}BiCl_{5.49}$	$Cs_{1.83}Na_{0.74}Ag_{0.36}BiCl_{5.04}$
40/60	$Cs_{1.99}Na_{0.45}Ag_{0.66}BiCl_{5.70}$	$Cs_{1.93}Na_{0.33}Ag_{0.54}BiCl_{4.96}$
20/80	$Cs_{1.91}Na_{0.16}Ag_{0.82}BiCl_{5.47}$	$Cs_{1.97}Na_{0.16}Ag_{0.75}BiCl_{4.98}$
0/100	Cs _{1.88} Ag _{1.09} BiCl _{5.64}	$Cs_{1.88}Ag_{0.89}BiCl_{5.11}$



Figure S1. Representative XPS spectra of sample $Cs_2Na_{1-x}Ag_xBiCl_6 NCs$ (x=0.05). The spectra are shown over the energy regions typical for Cs 3*d*, Na 1*s*, Ag 3*d*, Bi 4*f* and Cl 2*p* peaks. Quantitative analysis (as reported in Table S1) were obtained by calculating the areas under these peaks after normalization to the corresponding relative factor. The position of the observed peaks are consistent with the expected oxidation states (Cs⁺, Na⁺, Ag⁺, Bi³⁺, Cl⁻) for the corresponding metal chlorides. [NIST X-ray Photoelectron Spectroscopy Database, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012); http://srdata.nist.gov/xps/]



Figure S2. (a) SEM-EDS spectrum and (b) SEM image of $Cs_2Na_{1-x}Ag_xBiCl_6 NCs$ (*x*=0.05). (c-g) The SEM-EDS elemental mapping of Cs, Na, Ag, Bi, Cl.



Figure S3. TEM images and corresponding size distribution histogram $Cs_2Na_{1-x}Ag_xBiCl_6$ NCs: (a) *x*=0; (b) *x*=0.05; (c) *x*=0.1; (d) *x*=0.2; (e) *x*=0.4; (f) *x*=0.6; (g) *x*=0.8; (h) *x*=1.



Figure S4. Electronic structures of four different $Cs_2Na_{1-x}Ag_xBiCl_6$ NC models featuring x=0, 0.05, 0.80 and 1 respectively, optimized at the DFT/PBE level of theory. The energy levels are aligned according to their computed vertical ionization potential, which corresponds to the correct position of the valence band edge.



Figure S5. (a) Optical absorption (circles) and PL peak energies (squares) extracted from panel data in **Figure 4a**. (b) PL FWHM (rhombi) and Stokes shift (Δ_{SS} , triangles) as a function of *x*.



Figure S6. (a) Photoluminescence excitation (PLE) spectra of $Cs_2Na_{1-x}Ag_xBiCl_6$ NCs (continuous lines) and respective fitting with two gaussian curves corresponding to the PLE peaks of pure $Cs_2NaBiCl_6$ and $Cs_2AgBiCl_6$ NCs (red and blue dashed curves, respectively). (b) Relative weights of the pure $Cs_2NaBiCl_6$ (triangles) and $Cs_2AgBiCl_6$ (squares) NCs components as a function of *x*.



Figure S7. PL lifetime, τ , of the samples featuring *x*=0.05 (red squares), *x*=0.4 (purple triangles) and *x*=0.8 (blue circles) as obtained by the fitting procedure of the PL decay traces with a stretched exponential decay function as a function of temperature, T, from T=300K down to T=50K. The grey shading highlights the temperature regime where phonon-mediated processes have been effectively suppressed.



Figure S8. Dependence of the stretching factor, β , on the Ag concentration as obtained by the fitting procedure reported in **Figure 5a**, showing nearly invariance.



Figure S9. Computed oscillator strength for TE transitions (CBM \rightarrow VBM transitions) at the DFT/PBE level as a function of the number of Ag⁺ cations surrounding a central BiCl₆ octahedron in a Cs₂NaBiCl₆ 2 × 2× 2 supercell. Given the octahedral disposition around the Bi center in the DP lattice, the substitution of Na⁺ ions either with 2 Ag⁺ or with 4 Ag⁺ (i.e. 2 remaining Na⁺) led to two possible configurations, *cis* or *trans*. In a random distribution of Na⁺ and Ag⁺ ions, the *cis* configurations are statistically the most probable and are thus the only ones reported in **Figure 5c**. The oscillator strengths associated to 0 Ag⁺ and 6Ag⁺ around the BiCl₆ octahedron are not shown in **Figure 5c** as these points correspond to non-emissive compositions. The color scheme refers to the code in **Figure 4a**.



Figure S10. PL spectra of $Cs_2Na_{1-x}Ag_xBiCl_6$ NCs at T=300 K (dark continuous lines) and T=77 K (light dashed lines). The black arrows highlight the effect of lowering the temperature on the PL intensity for each sample.



Figure S11. PL spectra of $Cs_2Na_{1-x}Ag_xBiCl_6$ NCs featured by (a) x=0.05 and (b) x=0.8 upon lowering the temperature from T=300K down to T=3.5K.



Figure S12. (a) Energy position of the PL peak maximum of $Cs_2Na_{0.95}Ag_{0.05}InCl_6$ (blue triangles) and $Cs_2Na_{0.2}Ag_{0.8}InCl_6 NCs$ (red circles) as a function of temperature. (b) Full width at half maximum (FWHM) of the PL peak of $Cs_2Na_{0.95}Ag_{0.05}InCl_6$ (blue triangles) and $Cs_2Na_{0.2}Ag_{0.8}InCl_6 NCs$ (red circles) as a function of temperature. The black lines are the results of the fitting procedure of the experimental data with equation $FWHM = 2.36\sqrt{S}E_{ph}$ $\sqrt{\operatorname{coth}(\frac{E_{ph}/2k_BT})}$ where *S* is the Huang-Rhys factor, E_{ph} the energy of the phonon involved in the PL broadening and k_B the Boltzmann constant. The fitting procedure gives *S*=37.7 (*S*=50.1) and E_p =23.8 meV (E_p =23.3 meV) for *x*=0.05 (*x*=0.8), in agreement with previous results.⁶



Figure S13. Time-resolved PL decay curves of $Cs_2Na_{1-x}Ag_xBiCl_6 NCs$ (x=0.05 and x=0.8, upper and lower panels, respectively) upon lowering the temperature from T=300 K down to T=3.5 K (dark and light colors, respectively). Left panels report the whole decay traces, whereas right panels highlight the fast component from which the fraction of bright (*B*) NCs reported in **Figure S14** have been extracted.



Figure S14. (a) Integrated PL intensity of the samples featuring x = 0.05 (blue triangles) and x = 0.8 (red circles) as a function of temperature. (b) Temperature dependence of the fraction of bright NCs, *B*, of Cs₂Na_{0.95}Ag_{0.05}InCl₆ and Cs₂Na_{0.2}Ag_{0.8}InCl₆ NCs (blue triangles and red circles, respectively). Notice that for T > 200 K the evaluation of *B* of the sample with x = 0.8 is difficult due to the strong contribution by multi-phonon nonradiative decay. The black lines are the fitting curves to **Equation S1**.

Supplementary Discussion 1

Consistent with our model described in the main text and depicted in Figure 5e, the NC systems featured by x=0.05 (Cs₂Na_{0.95}Ag_{0.05}InCl₆) and x=0.8 (Cs₂Na_{0.2}Ag_{0.8}InCl₆) showed markedly different trends of their integrated PL intensity vs. T (Figure S12). Specifically, the NCs having x=0.05 showed a mild PL brightening for T \sim 180 K, followed by a dramatic drop to \sim 5% of the maximum value at T=3.5 K. In contrast, the PL intensity of NCs with x=0.8 underwent a >25-fold enhancement that remained nearly constant down to T~20 K, below which temperature it gradually decreased by $\sim 30\%$ of its maximum value. Despite this difference, the two systems showed very similar evolution of their PL dynamics with temperature (Figure S14). Specifically, for 300 K≥T≥180 K, the PL kinetics lengthened, accompanied by the intensification of the PL intensity, in agreement with the progressive suppression of thermally-assisted nonradiative channels (grey shading in Figure S15). This is corroborated by the Huang-Rhys factor extracted by the fitting of the T-dependence of the PL full width at half maximum, showing a stronger phonon-coupling for the x=0.8 sample with respect to the x=0.05 one (Figure S13). On the other hand, for T<180 K, both samples showed dimming of the PL intensity at constant PL lifetime, which strongly indicated that the fraction of emissive NCs in the two ensembles was progressively diminishing. This was confirmed by the analysis of the early-time PL intensity as a function of temperature (Figure S14) that revealed the substantially different steepness of the *B* vs. T trend for the two NC systems. This corroborated our model that the branching ratio between emissive and non-emissive NCs in the ensembles was dictated by the thermal equilibrium between electron trapping and de-trapping in a defect state whose depth in the forbidden gap decreased with increasing Ag⁺ content, as depicted in **Figure 5e**. Accordingly, the fit of *B* vs. T using the expression:

$$B = B_0 e^{-\frac{\Delta E_{DT}}{k_B T}}$$
(S1)

for NCs with x=0.05 yielded an activation energy for detrapping $\Delta E_{DT} = 102$ meV, nearly fifty-fold larger than the value found for NCs featuring for x=0.8 ($\Delta E_{DT} = 2$ meV, **Figure S15**).

Supporting References

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