Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Multimode Luminescence and Highly Anti-Thermal Quenching in $Sb^{3+}/Yb^{3+}/Pr^{3+}$ Co-Doped Cs_2NaYCl_6 Double Perovskites

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1. Experiment

1.1 Materials

Cesium chloride (CsCl, 99.99%), sodium chloride (NaCl, 99.8%), yttrium oxide (Y_2O_3,99.99%), Ytterbium oxide (Yb_2O_3, 99.99%), praseodymium oxide (Pr_6O_{11}, 99.99%) and antimony chloride ($SbCl_3$, 99.99%) were purchased from Macklin. Hydrochloric acid (HCl, 37 wt% in water) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol anhydrous (CH_3CH_2OH, 99.9%) was purchased from Nanning Blue Sky Experimental Equipment Co., Ltd. All of these chemical agents were used as received without further purification.

1.2 Synthesis

$Sb^{3+}/Yb^{3+}/Pr^{3+}$ co-doped Cs_2NaYCl_6 double perovskites were synthesized by a typical solvothermal method. In 25.0-mL Teflon liner, 2.00 mmol of CsCl, 1.00 mmol of NaCl, (1-x)/2 mmol of Y_2O_3, 0.01 mmol of $SbCl_3$, 0.015 mmol of Yb_2O_3, x/6 (x=0.1, 1, 3, 5 and 10) mmol of Pr_6O_{11} and were pre-dissolved in 2.00 mL of HCl by ultrasonication. Then, the mixture was transferred into a stainless steel autoclave and kept at 180 °C for 10 h. The $Sb^{3+}/Yb^{3+}/Pr^{3+}$ co-doped Cs_2NaYCl_6 crystal were precipitated and washed three times with ethanol and then dried in an oven at 60 °C for 12 h.

2. Characterizations

The crystal structure was characterized by X-ray powder diffraction (XRD, Bruker D8 Discover). The elemental composition and chemical state were identified by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The scanning electron microscopy (SEM, Zeiss Sigma 500) was used to observe the morphology. The energy-dispersive spectrometry (EDS, Oxford X-Max Aztec) was used to collect the element composition and distribution. The steady-state PL spectra, photoluminescence quantum yields (PLQY), temperature-dependent PL spectra and temperature-dependent time-resolved PL (TRPL) were measured with a Horiba Jobin Yvon Fluorolog-3 spectrometer. The absorption spectra were measured using a UV-VIS-NIR spectrophotometer (PerkinElmer Instruments, Lambda 750). The OHSP-350M LED Fast-Scan Spectrophotometer was used to evaluate the pc-LED under different drive currents (Hangzhou Hopoo Light&Color Technology Co., Ltd., China). A NIR camera captured the images (EOS 200D, Canon, China). The RL spectra were measured using a Zolix OmniFluo 960SP spectrometer.

3. Computational Methods

All calculations using density functional theory (DFT) were carried out using the Vienna Ab initio simulation package (VASP).[1] The generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) parameterization with projector-augmented wave (PAW) method was performed for the exchange and correlation functional.[2-4] The plane-wave cutoff energy was set to 450.0 eV and the total energy and relaxation were calculated using a single *k*-point. In this work, the lattice parameters and atomic positions were all allowed to relax to minimize the internal forces, until the force on each atom was smaller than 0.05 $eV \cdot Å^{-1}$, and the convergence threshold of energy for the self-consistent was 1.0×10^{-5} eV. All atomic positions and lattice vectors are fully optimized using the conjugate gradient algorithm with relaxed cell parameters and atomic positions.

4. Fabrication of LED devices

LED devices were fabricated using 365 nm NUV-LED chips. We mixed the powders of 1% Sb^{3+}, 3% Yb^{3+}, 1% Pr^{3+} co-doped Cs_2NaYCl_6 well with epoxy resin respectively. Then, the mixtures are coated on the surface of the LED chip. Finally, the mixture covering the LED chips was put into an oven and dried at 60 °C for 72 h to obtain the device.

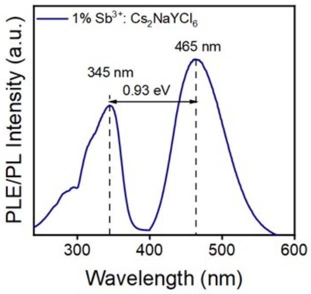

Figure S1. The PLE and PL spectra of 1% Sb^{3+} doped Cs_2NaYCl_6 double perovskites.

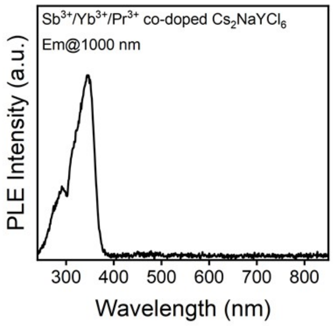

Figure S2. The PLE spectra of 1% Sb^{3+}/3% Yb^{3+}/1% Pr^{3+} Cs_2NaYCl_6 double perovskites (Em@1000 nm).

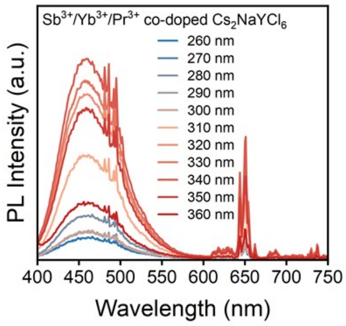

Figure S3. The PL spectra of 1% Sb^{3+}/3% Yb^{3+}/1% Pr^{3+} co-doped Cs_2NaYCl_6 double perovskites at different excitation wavelength.

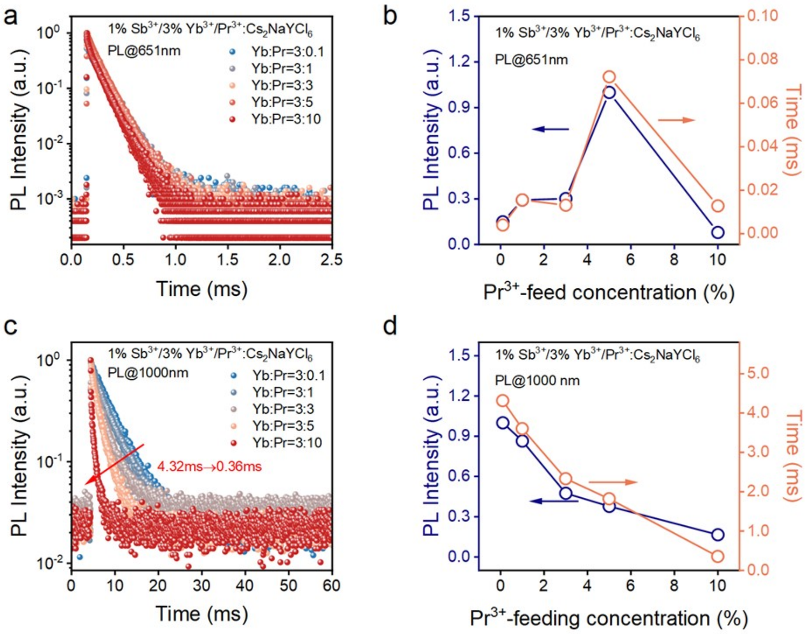

Figure S4. (a) The PL decay curves monitored at 651 nm of 1% Sb^{3+}/3% Yb^{3+}/x% (x = 0.1, 1, 3, 5, 10) Pr^{3+} co-doped Cs_2NaYCl_6 double perovskites. (b) Trend chart of integrated area and PL lifetime with different Pr^{3+} ion feeding concentrations (Em@651 nm). (c) The PL decay curves monitored at 1000 nm of 1% Sb^{3+}/3% Yb^{3+}/x% Pr^{3+} Cs_2NaYCl_6 double perovskites (x = 0.1, 1, 3, 5, 10). (d) Trend chart of integrated area and PL lifetime with different Pr^{3+} ion feeding concentrations (Em @1000 nm).

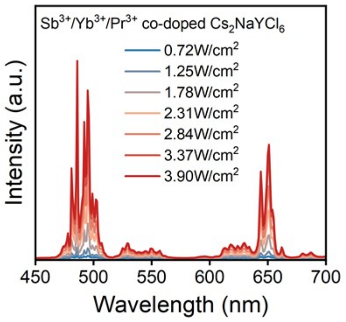

Figure S5. The UC PL spectra of 1% Sb^{3+}/3% Yb^{3+}/1% Pr^{3+} co-doped Cs_2NaYCl_6 double perovskites with different excitation power density.

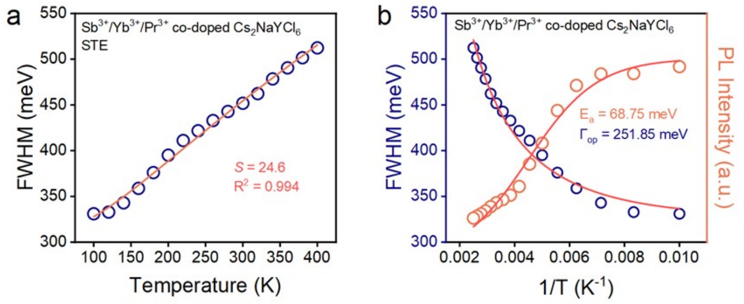

Figure S6. Dependence of (a) FWHM and (b) Γ_{op} on temperature of 1% Sb^{3+}/3% Yb^{3+}/1% Pr^{3+} co-doped Cs_2NaYCl_6 double perovskites.

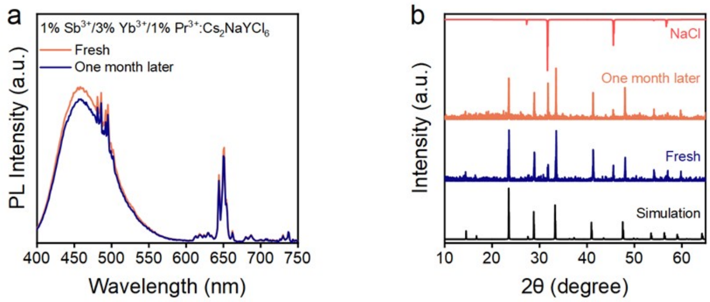

Figure S7. (a) PL spectra and (b) XRD of pristine and one months later for 1% Sb^{3+}/3% Yb^{3+}/1% Pr^{3+} co-doped Cs_2NaYCl_6 double perovskites.

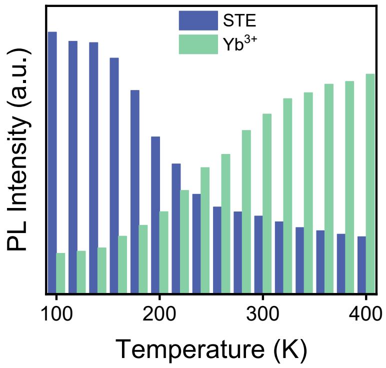

Figure S8. PL intensity of STE emission and Yb^{3+} emission with increasing temperature.

Table S1 The absolute sensitivity (S_a) and relative sensitivity (S_r) values of previously reported materials.

Materials	S_a (K^{-1})	S_r (% K^{-1})	Temperature range(K)	Ref.
$Tm^{3+}/Yb^{3+}:Ba_5Gd_8Zn_4O_{21}$	0.013	1.94	303-573	[5]
$Bi^{3+}/Sm^{3+}:Sr_3Y_2Ge_3O_{12}$	0.0017	0.38	298-498	[6]
$Cs_2NaHo_{0.99}Yb_{0.01}Cl_6$	—	0.68	300-900	[7]
$Er^{3+}:NaLaMgWO_6$	0.0223	1.04	303-483	[8]
$Sb^{3+}/Sm^{3+}:Cs_2NaInCl_6$	0.00173	0.75	140-280	[9]
$Sb^{3+}:Cs_2NaHoCl_6$	1.1	3.60	80-550	[10]
$Sb^{3+}/Yb^{3+}/Pr^{3+}:Cs_2NaYCl_6$	0.0183	6.72	100-400	This work

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