Electronic Supporting Information (ESI)

Broadband Emission in Alkali Halides Triggered by Sb^{3+} Doping

Yanyan Li,[a,b] Mircea Cotlet,[c] Ido Hadar,[d] and Peijun Guo [a,b,*]

a. Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, New Haven, CT 06520, United States

b. Energy Sciences Institute, Yale University, 810 West Campus Drive, West Haven, CT 06516, United States

c. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, USA.

d. Institute of Chemistry, and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, 91904, Israel

Email: peijun.guo@yale.edu

Experimental Section

Materials. Sodium chloride (NaCl, >99.5%, TCl), potassium chloride (KCl, ACS reagent, 99.0-100.5%, Sigma-Aldrich), rubidium chloride (RbCl, 99.8% trace metals basis, Sigma-Aldrich), Antimony(III) chloride ($SbCl_3$, ≥99.95% trace metals basis, Sigma-Aldrich), formic acid (88%, Sigma-Aldrich), dimethyl sulfoxide (99.9%, SuperDry, J&K Scientific), and toluene (anhydrous, 99.8%, Sigma-Aldrich) were all procured from commercial venders and used without further purification.

Synthesis of Sb^{3+}-doped NaCl, KCl, and RbCl single crystals. Sb^{3+}-doped NaCl single crystals were synthesized using a slow evaporation technique. Typically, 0.6 mmol NaCl and 0.18 mmol $SbCl_3$ were dissolved in a mixture of formic acid and dimethyl sulfoxide, and the solution was stirred at 100 °C until it became clear. Then, the solution was filtered with a 0.22 μm polytetrafluoroethylene (PTFE) syringe, and the filtered solution was injected into vials and sealed with a paraffin film with small holes. The solution was then filtered using a 0.22 μm polytetrafluoroethylene (PTFE) filter. The filtered solution was injected into vials, sealed with paraffin film with small holes, and placed in a sealed container with dimethyl sulfoxide. Single crystals were obtained by maintaining the solution at 100 °C for 48 hours. The preparation of Sb^{3+}-doped KCl and RbCl single crystals followed the same procedures, with KCl and RbCl substituting NaCl. To synthesize different dopant ratios of 10%, 20%, and 40% Sb^{3+}-doped NaCl crystals, 0.06, 0.12, and 0.24 mmol $SbCl_3$ were added to the precursor solution, respectively, while keeping the other conditions constant.

Characterization. Powder X-ray diffraction (PXRD) data of Sb^{3+}-doped ACl (A = Na, K, and Rb) sing crystals were obtained by using a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) images and the energy dispersive spectroscopy (EDS) elemental mapping of samples were obtained by using a scanning electron microscope (Hitachi SU8230). Photoluminescence (PL) and time-resolved PL (TRPL) measurements were conducted by excitation wavelength of 320 nm using a fs Yb:KGW laser (Pharos, Light Conversion). PL spectra was captured by a Si EMCCD (Andor iXon Life 888), and time-resolved PL was collected by a streak camera (Hamamatsu C10910 with the Slow sweep unit; M10913). For the temperature-dependent PL and TRPL measurements, samples were mounted in a helium cryostat (DE-204SF, Advanced Research Systems) under vacuum. PL excitation (PLE) measurements of samples were performed by using Horiba Nanolog Fluorescence Spectrometer for UV-VIS-NIR (400-1750nm). The photoluminescence quantum yield (PLQY) of our samples was measured using an Edinburgh FLS1000 fluorimeter with an integrating sphere.

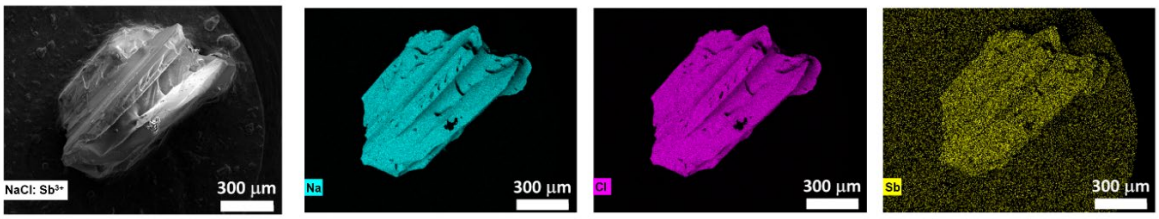

Figure S1. SEM image and EDS elemental mappings of NaCl:Sb^{3+} single crystal.

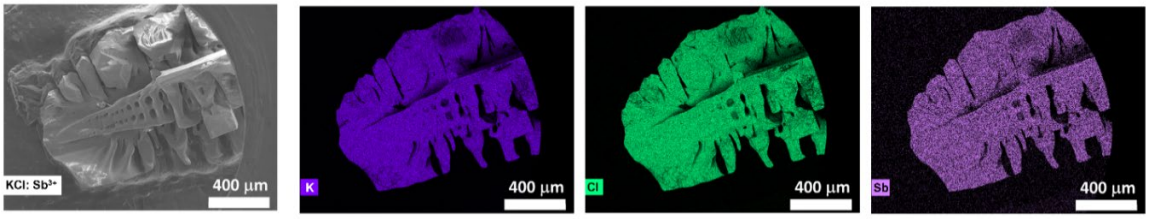

Figure S2. SEM image and EDS elemental mappings of KCl:Sb^{3+} single crystal.

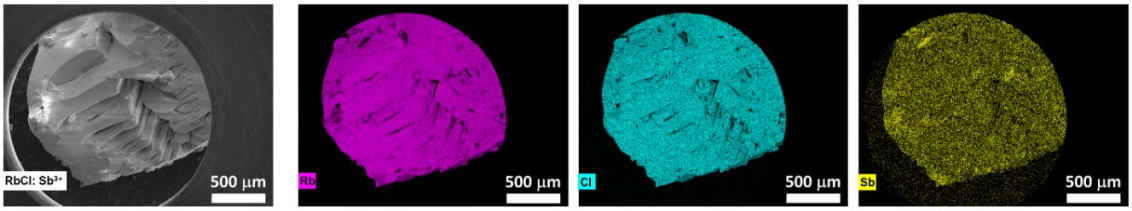

Figure S3. SEM image and EDS elemental mappings of RbCl:Sb^{3+} single crystal.

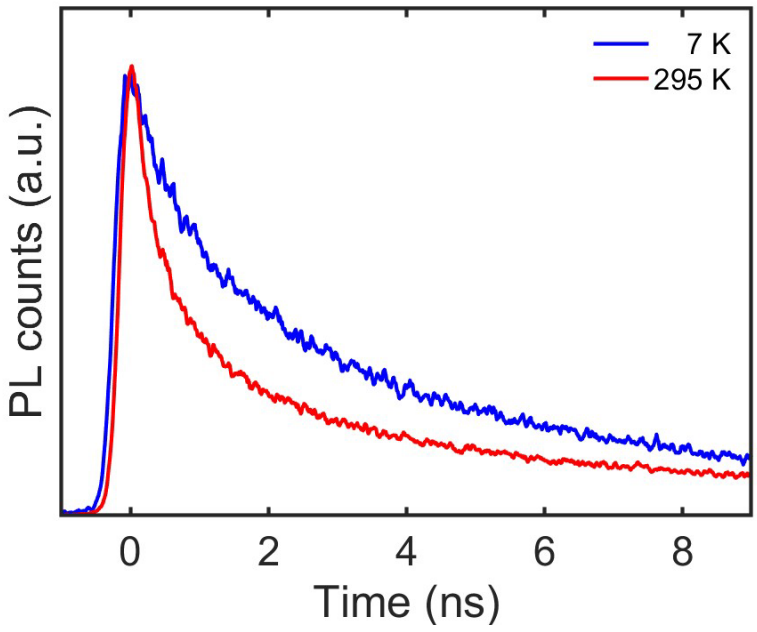

Figure S4. TRPL spectra of NaCl:Sb^{3+} measured on a 10 ns time scale at 295K and 7K.

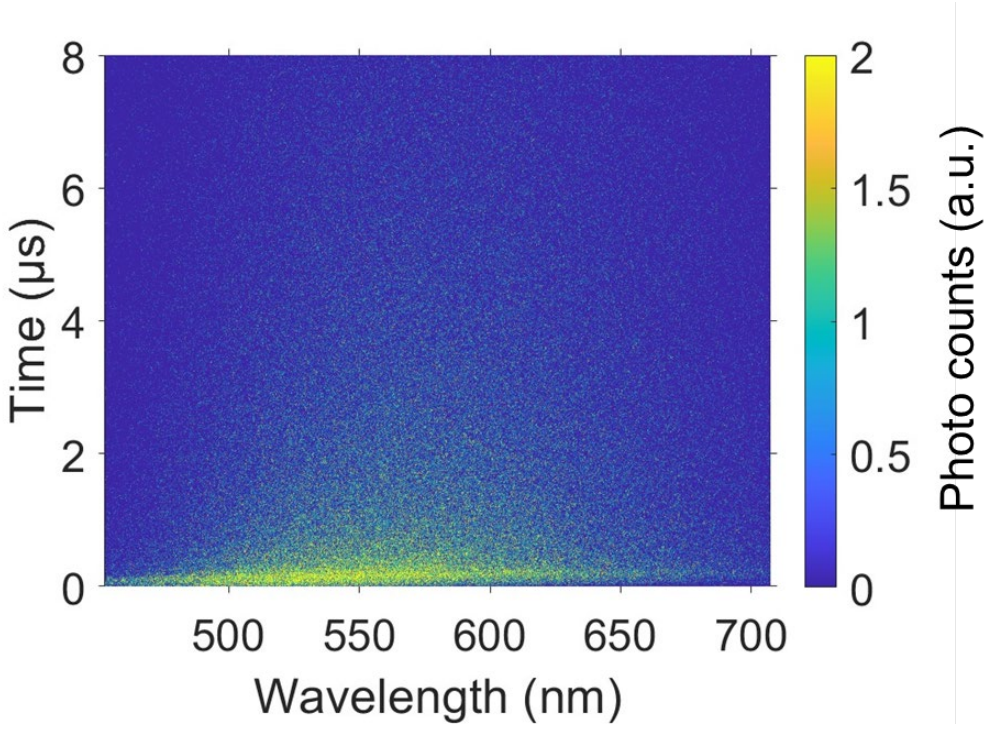

Figure S5. TRPL 2D mapping of KCl:Sb^{3+} measured at room temperature.

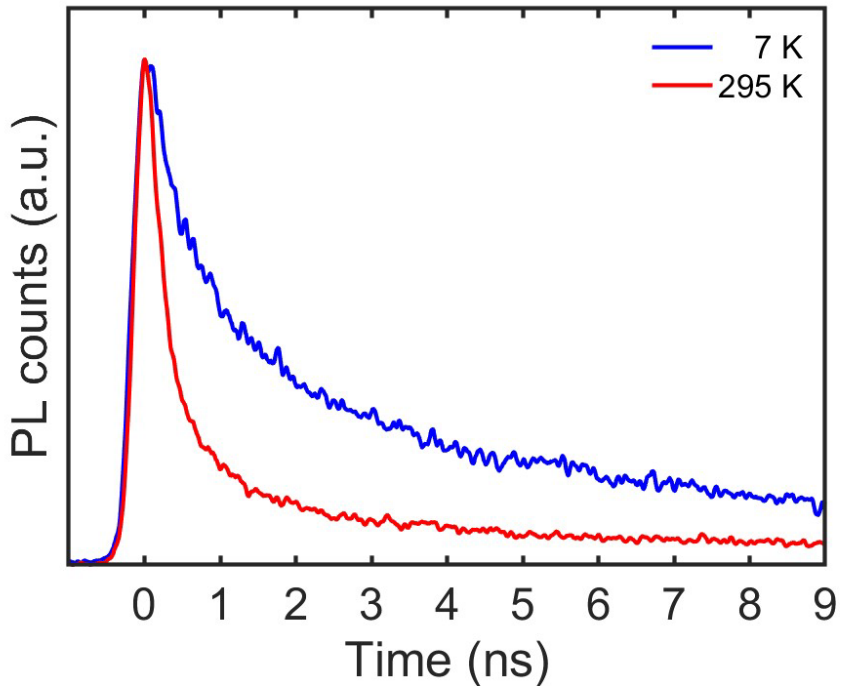

Figure S6. TRPL spectra of KCl:Sb^{3+} measured on a 10 ns time scale at 295K and 7K.

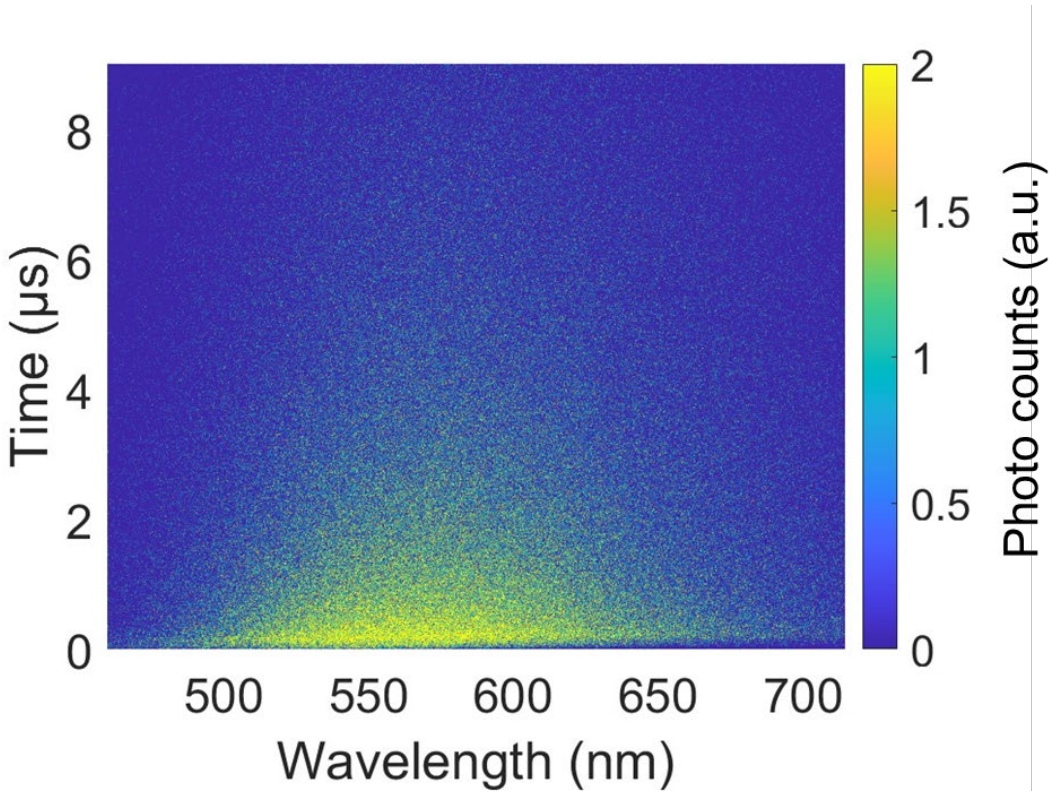

Figure S7. TRPL 2D mapping of RbCl:Sb^{3+} measured at room temperature.

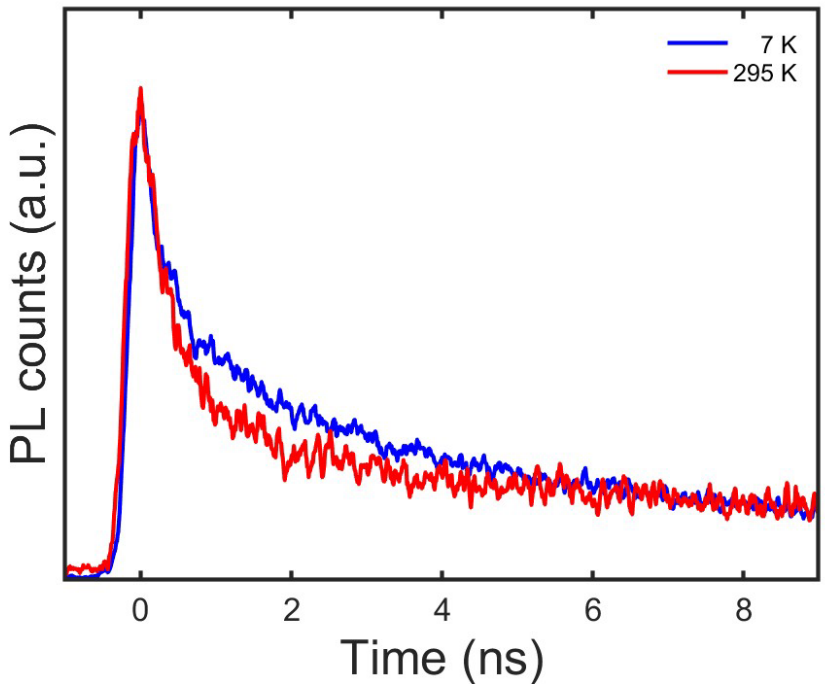

Figure S8. TRPL spectra of RbCl:Sb^{3+} measured on a 10 ns time scale at 295K and 7K.

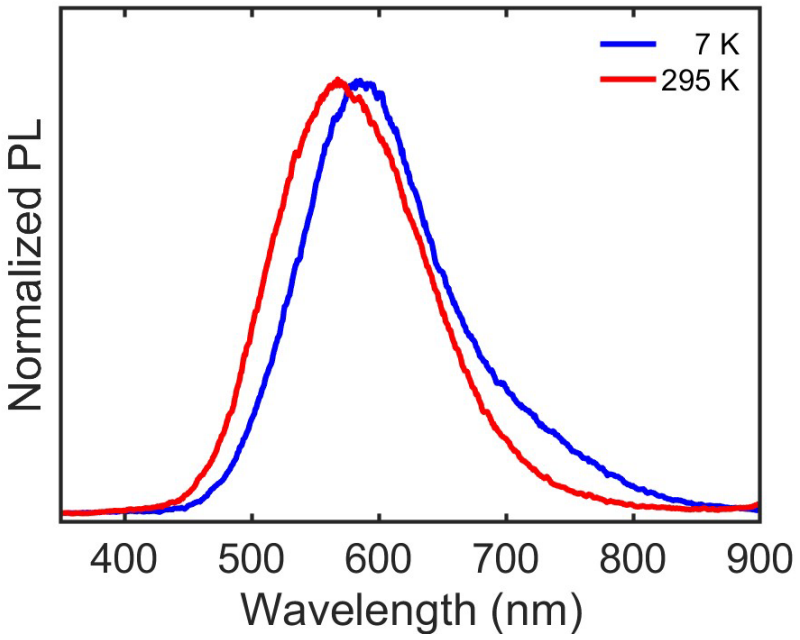

Figure S9. Comparison of PL spectra of KCl:Sb^{3+} measured at 295K and 7K.

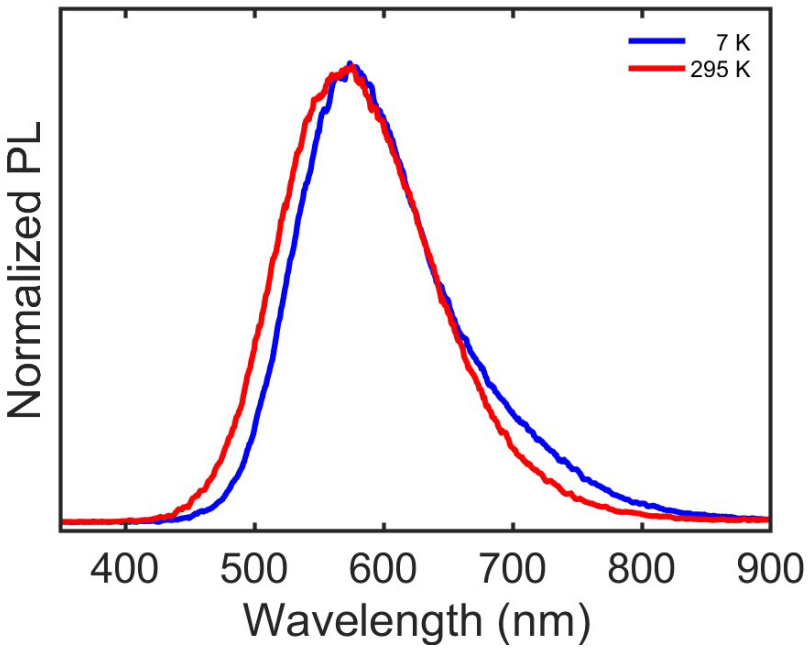

Figure S10. Comparison of PL spectra of RbCl:Sb^{3+} measured at 295K and 7K.

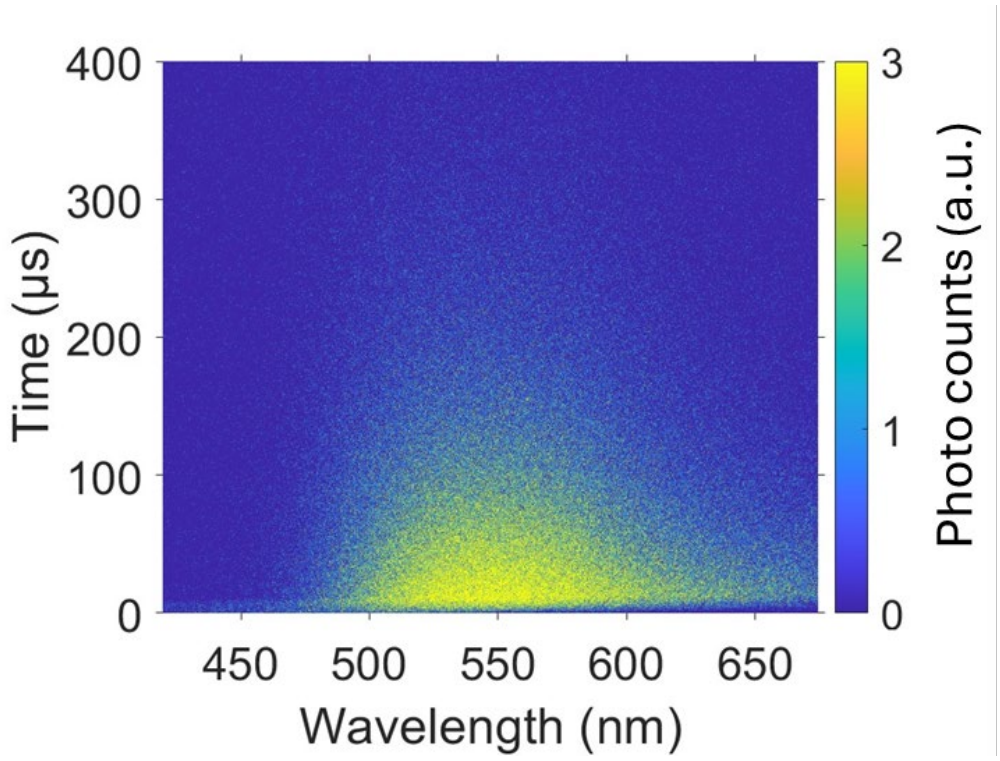

Figure S11. TRPL 2D mapping of NaCl:Sb^{3+} measured at 7K.

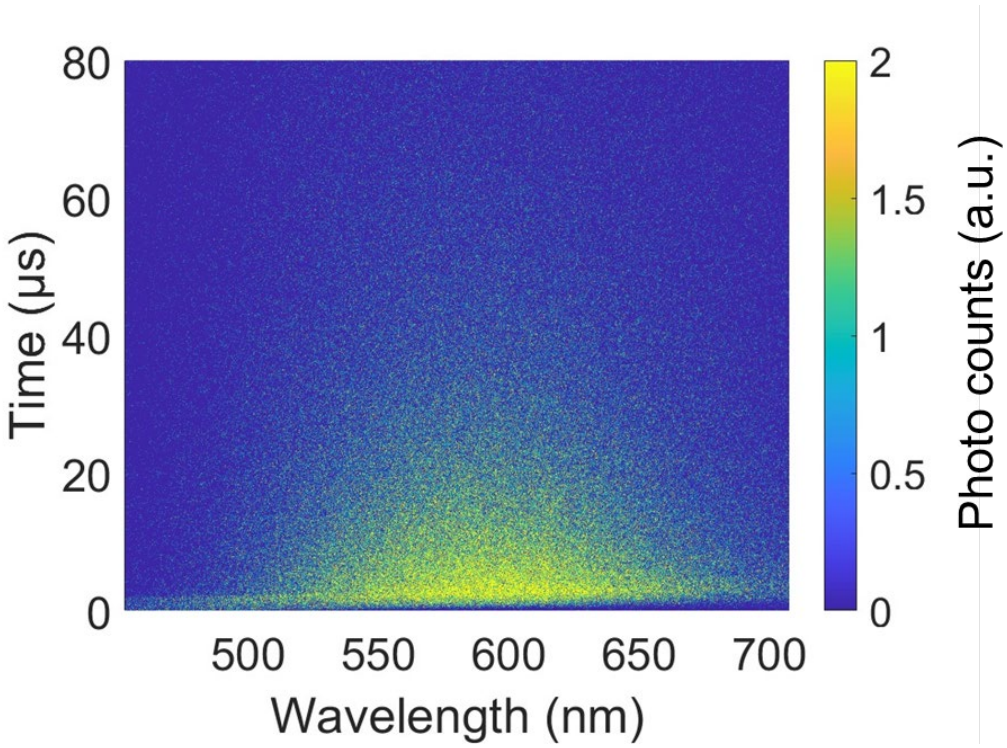

Figure S12. TRPL 2D mapping of KCl:Sb^{3+} measured at 7K.

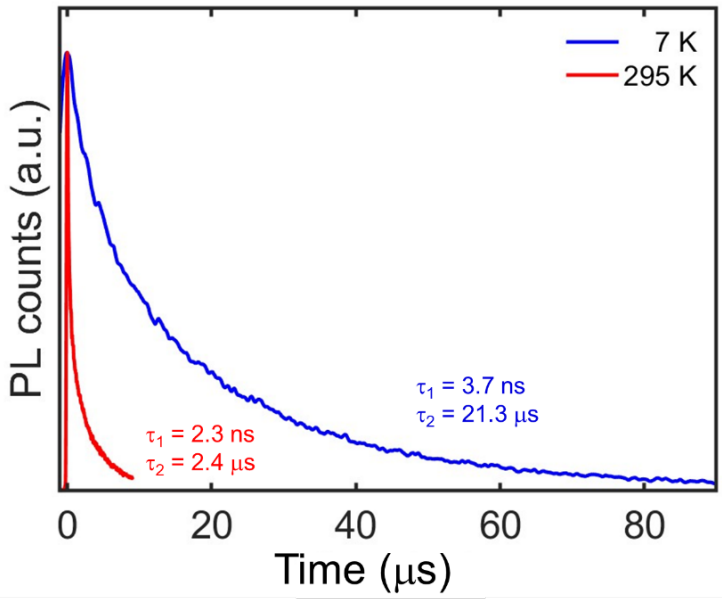

Figure S13. Comparison of TRPL spectra of KCl:Sb^{3+} measured on a 10 μs time scale at 295K and 7K.

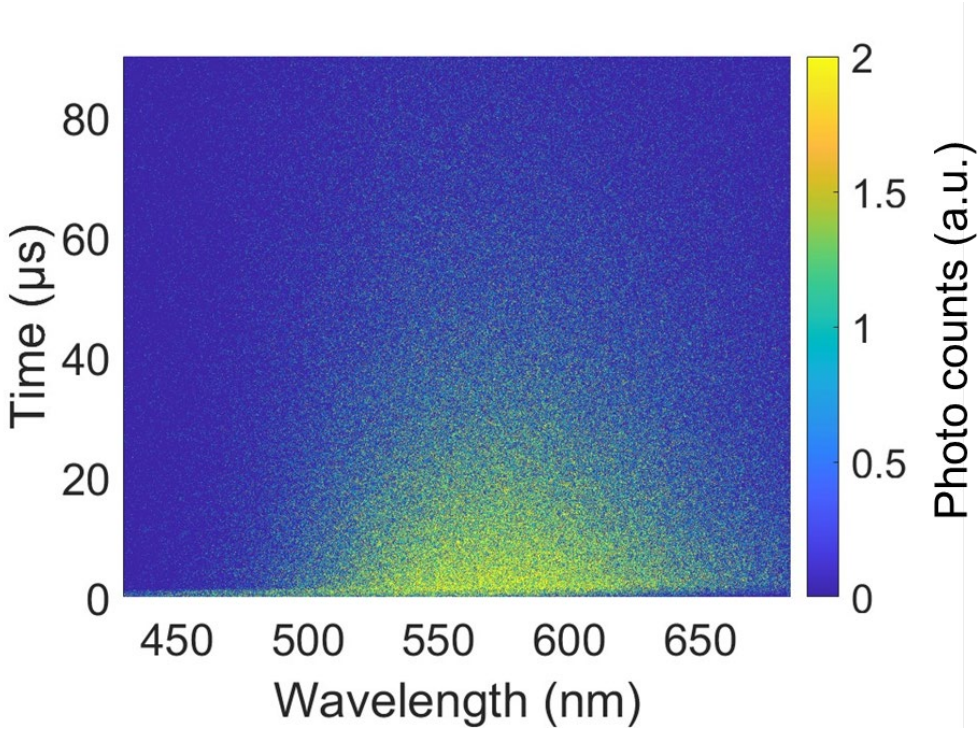

Figure S14. TRPL 2D mapping of RbCl:Sb^{3+} measured at 7K.

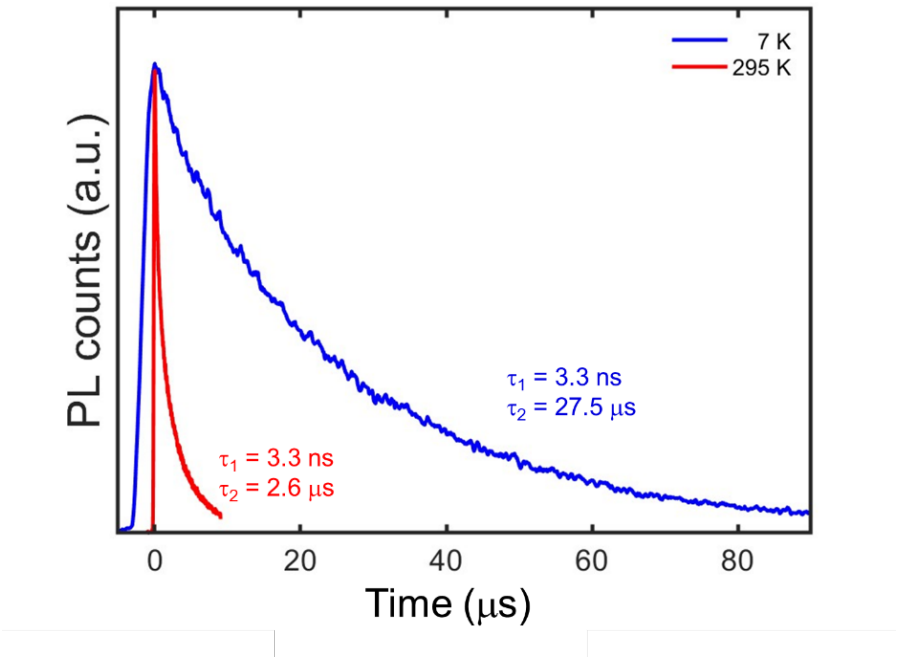

Figure S15. Comparison of TRPL spectra of RbCl:Sb^{3+} measured on a 10 μs time scale at 295K and 7K.

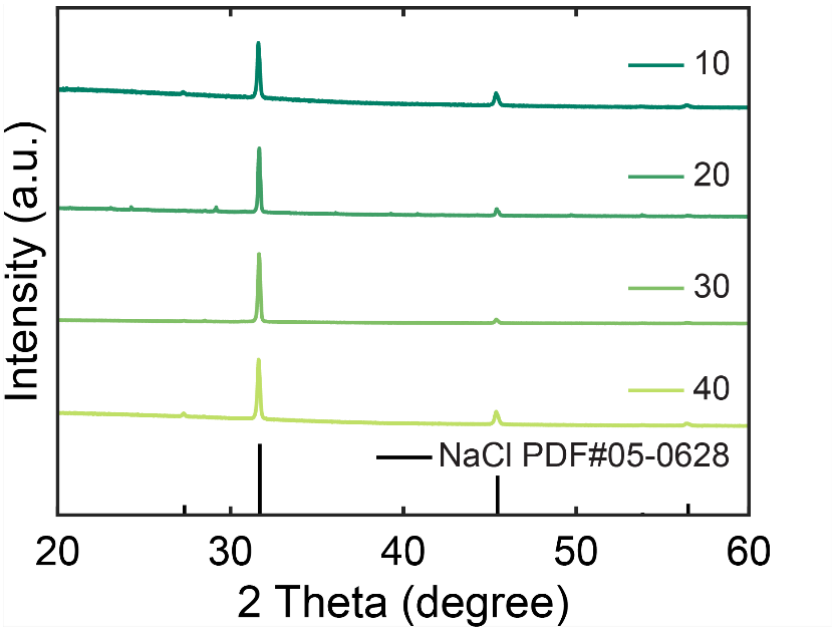

Figure S16. Comparison of PXRD patterns of NaCl:Sb^{3+} doped with different contents of Sb^{3+}.

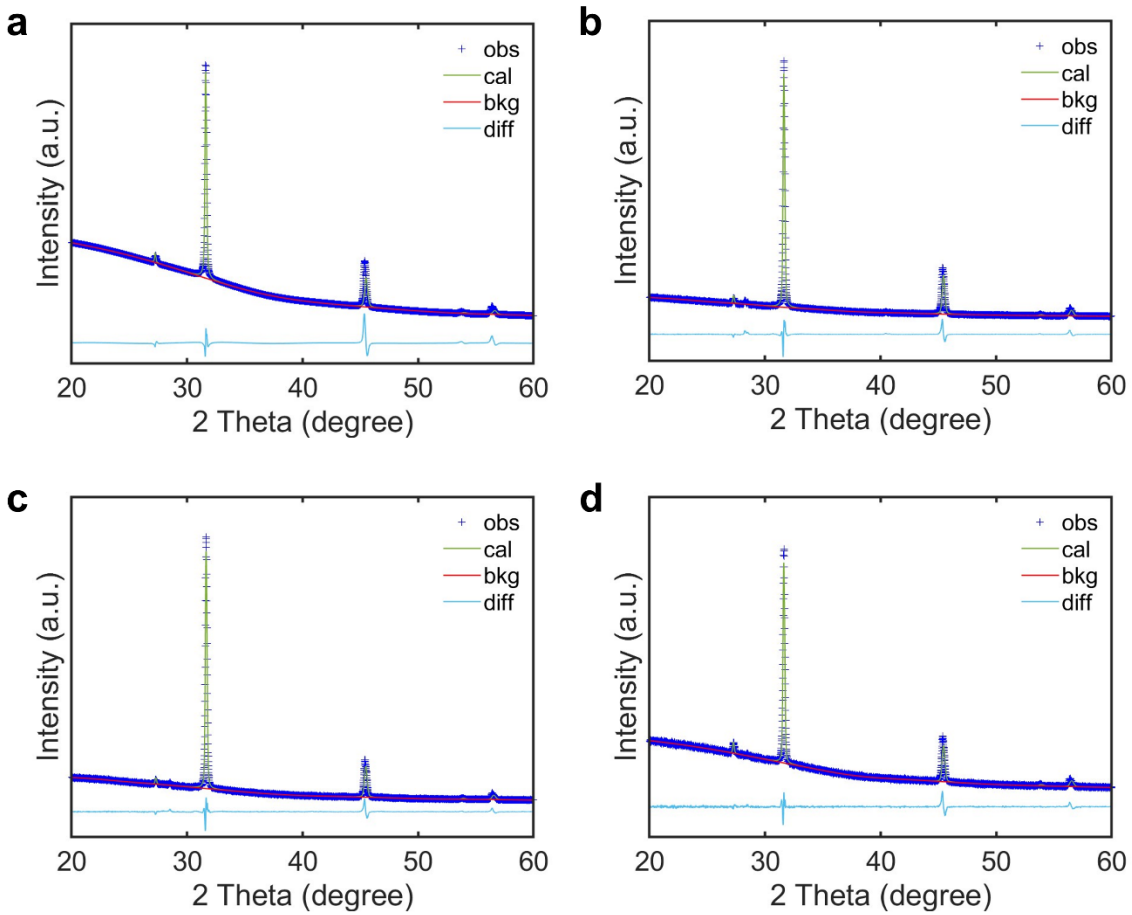

Figure S17. Powder XRD pattern (blue "+") of (a)10% Sb^{3+}-doped NaCl, (b) 20% Sb^{3+}-doped NaCl, (c) 30% Sb^{3}+-doped NaCl, and (d) 40% Sb^{3+}-doped NaCl single crystal with Rietveld refinement fits (green lines) using GSAS-II and their difference map (cyan lines).

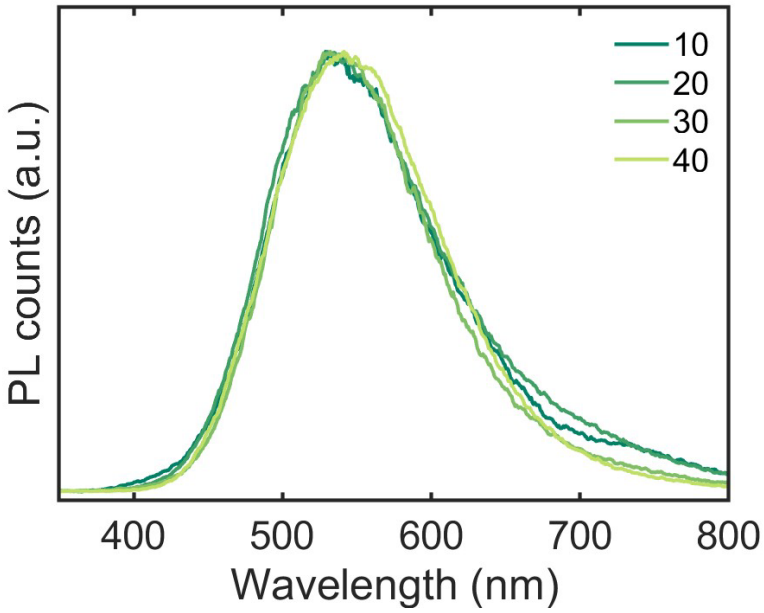

Figure S18. Comparison of PL spectra of NaCl:Sb^{3+} doped with different contents of Sb^{3+}.

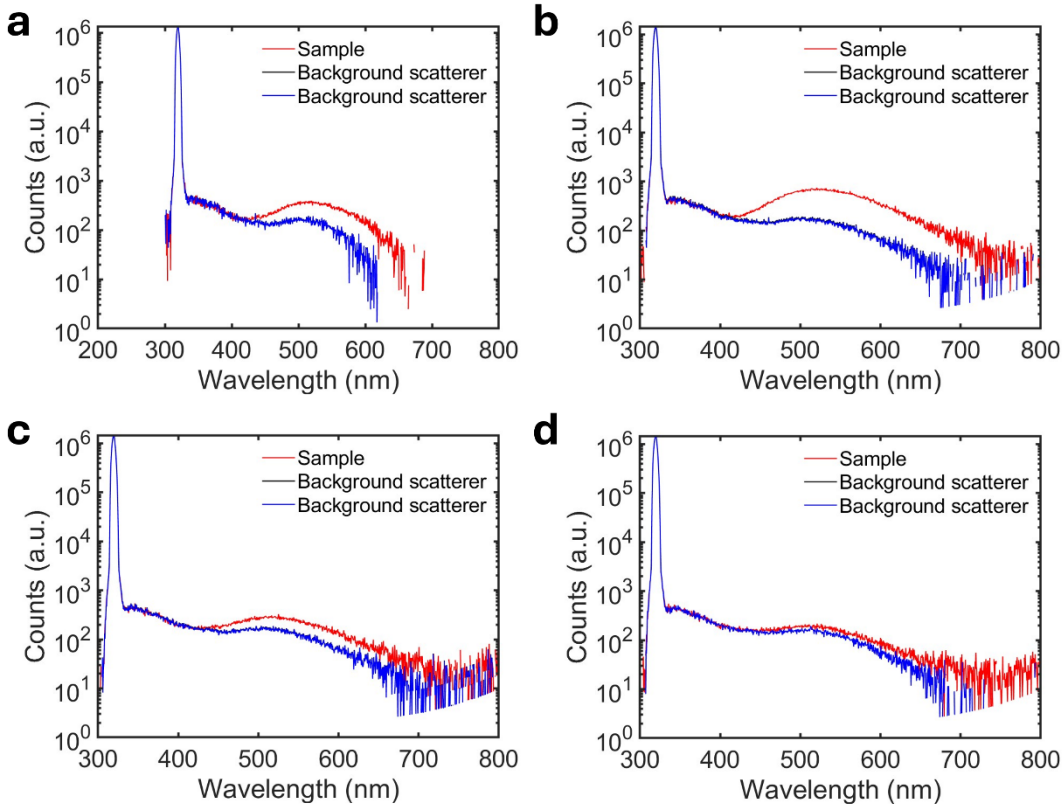

Figure S19. Photoluminescence quantum yield (PLQY) measurement of a) NaCl: 10% Sb^{3+}, b) NaCl: 20% Sb^{3+}, c) NaCl: 30% Sb^{3+}, and d) NaCl: 40% Sb^{3+}.

Samples	Unit cell *a* (Å)	Unit cell volume (Å^3)
10% Sb^{3+}: NaCl	5.59821	175.448
20% Sb^{3+}: NaCl	5.61914	177.423
30% Sb^{3+}: NaCl	5.61839	177.352
40% Sb^{3+}: NaCl	5.61794	177.309

Table S1. Unit cell parameters of refinement of the Sb^{3+}: NaCl with different Sb3+ concentrations.

Samples	Atomic ratio of Sb (%)
20% Sb^{3+}: NaCl	0.29
30% Sb^{3+}: NaCl	0.43
40% Sb^{3+}: NaCl	1.24
30% Sb^{3+}: KCl	0.54
30% Sb^{3+}: RbCl	0.74

Table S2. EDS results of Sb^{3+}-doped ACl (A = Na, K, and Rb) single crystals.