Lead-free Antimony-based Light-Emitting Diodes through Vapor-Anion Exchange Method

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Experimental Section

Chemicals: PEDOT: PSS (Clevios P VP.AI 4083, Heraeus Germany), SbI_3 (99.9%, Alfa Aesar), $SbBr_3$ (99.9%, Alfa Aesar), $SbCl_3$ (99.9%, Alfa Aesar), CsI (99.9%, Alfa Aesar), dimethyl sulfoxide (Sigma–Aldrich), *N*,*N*-dimethylformamide (Sigma–Aldrich), TPBi (Luminescence Technology), and LiF (Luminescence Technology) were used as received, without further purification.

$Cs_3Sb_2X_9$ films through Vapor-Anion exchange: Steps for preparing films

1. Mix 0.25 M of SbI_3 and 1 M of CsI in DMSO and then continuous stir (150 rpm) the mixture for 6 h at 70 °C.
2. This solution was dropped onto the PEDOT:PSS-coated substrates and spin-coated for 40 s at 8000 rpm.
3. These films (two samples at a time) were moved directly to a glass bottle (diameter: 4 cm; height: 6 cm) preheated at 200 °C.
4. 10 µL (40 wt%) of SbI_3 in DMF is added in the corner of the bottle.
5. This bottle was then covered with a cap.
6. The films were maintained at 200 °C for 15 min; the temperature was decreased gradually to 150 °C before bringing the sample to room temperature, to avoid quenching.

   For the halide-exchanged films, 10 µL (80 wt%) of $SbBr_3$ or 10 µL (90 wt%) of $SbCl_3$ was placed in corners of the bottles, instead of SbI_3, to form films of $Cs_3Sb_2Br_9$ or $Cs_3Sb_2I_9$, respectively. Note that the precursor ($CsI:SbI_3$) for spin-coating was the same when preparing all of the films; the only thing changed was the solution used for the halide exchange in the second step.

Structural Characterization: XPS and UPS were performed at room temperature using a PHI 5000 Versa Probe apparatus equipped with an Al Kα X-ray source (1486.6 eV). UPS was used to measure the valence band using He I emission (21.2 eV, ca. 50 W) as the source of UV light; the take-off angle was 90°. Samples for UPS were prepared on ITO substrates only, using the same method as that for preparing the active layer of the device. SEM images and EDX spectra were recorded using an FEI Nova 200 scanning electron microscope (15 kV). Samples were prepared on ITO substrates. XRD patterns were recorded at room temperature using X'Pert3 Powder, PAN analytical equipped with a diffracted beam monochromator set for Cu Kα radiation (λ = 1.54056 Å). Samples were formed on glass substrates.

Optical Characterization: UV–Vis absorption spectra were recorded using a JASCI V-670 spectrophotometer. ITO and PEDOT:PSS-coated substrates were used to record the baseline; the absorption spectra of the active layers, deposited using the above-mentioned methods on given substrates, were then recorded. PL measurements were performed using a closed-cycle cryogenic system (Attodry 800, Attocube) equipped with a scanning confocal microscope and a spectrometer (Andor) consisting of a monochromator and a thermo-electric cooling CCD camera. PL spectra were recorded at both 4.7 K and room temperature. A 405-nm continuous wave (CW) laser diode excitation source was used and a 420-nm long-pass filter was placed before the spectrometer to filter out the laser signal. A 100x objective lens (0.82 NA; Attocube) was used to focus the pulsed laser to a small spot (diameter: 1 μm^2) with an average power density of 53 kW/cm^2.

Device Characterization: Radiance spectra were recorded using an Ocean Optics miniature spectrometer (bandwidth: 590–1235 nm).

Supporting Figures and tables

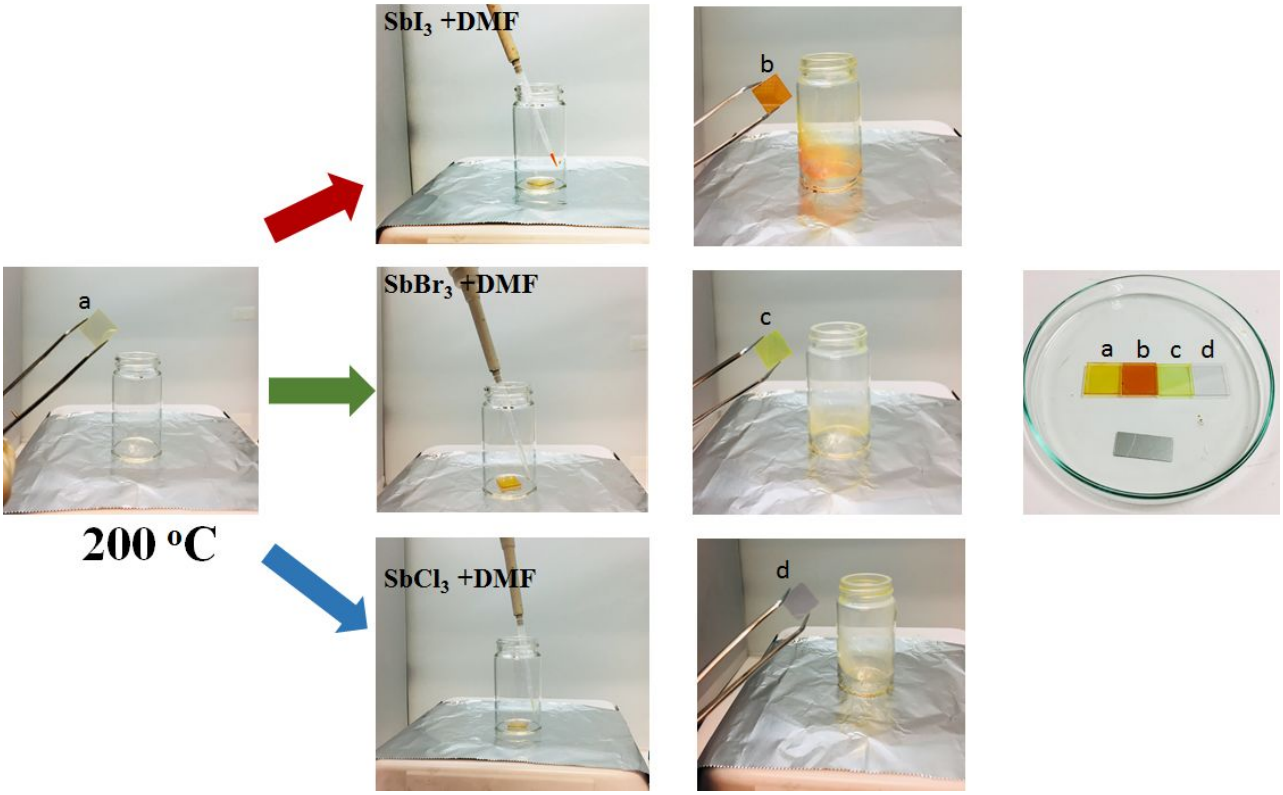

Figure S1. Real time photographs showing the experimental procedure: (a) spin coated film of CsI:SbI_3 films. (b) Layer $Cs_3Sb_2I_9$ film after SbI_3 + DMF vapor treatment. (c) Layer $Cs_3Sb_2Br_9$ film after $SbBr_3$ + DMF vapor treatment, i.e. after anion exchange from I→ Br. (d) Layer $Cs_3Sb_2Cl_9$ film after $SbCl_3$ + DMF vapor treatment, i.e. after anion exchange from I→ Cl.

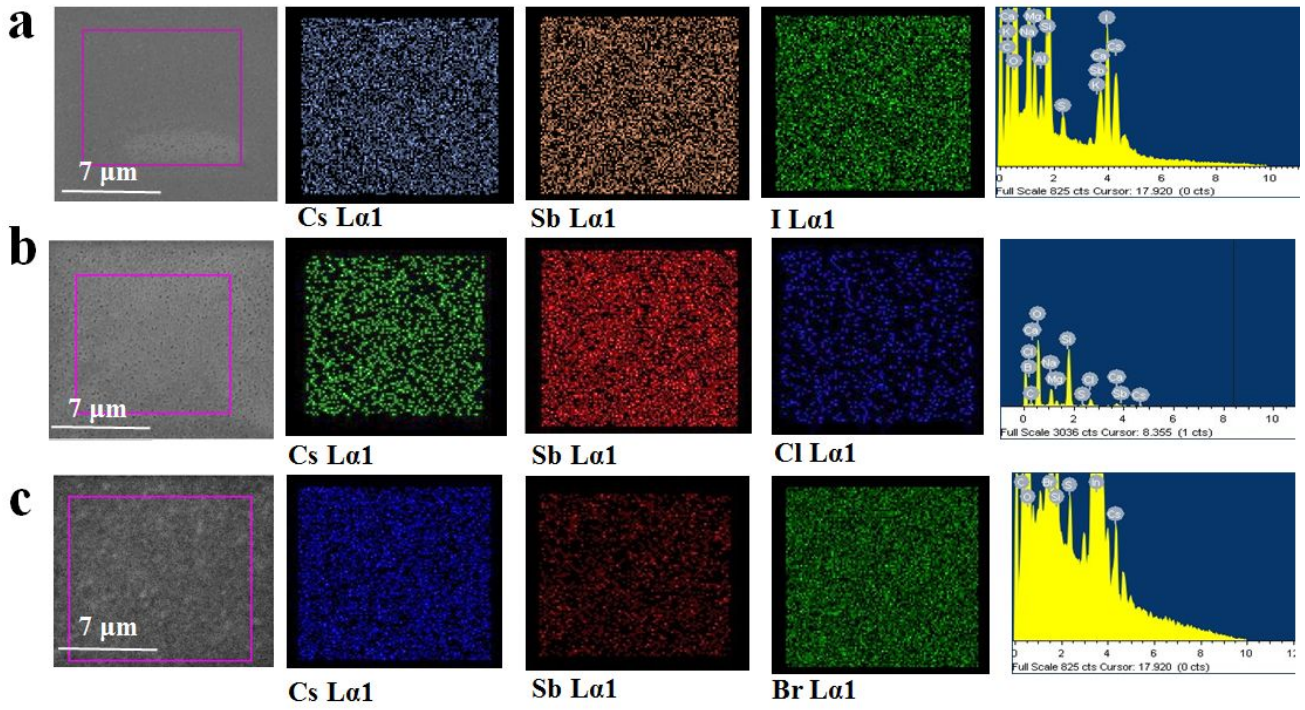

Figure S2. EDX elemental mapping of the surface morphologies after anion exchange: (a) $CsI:SbI_3$ film after SbI_3 vapor treatment, (b) $CsI:SbI_3$ film after $SbCl_3$ vapor treatment, and (c) $CsI:SbI_3$ film after $SbBr_3$ vapor treatment.

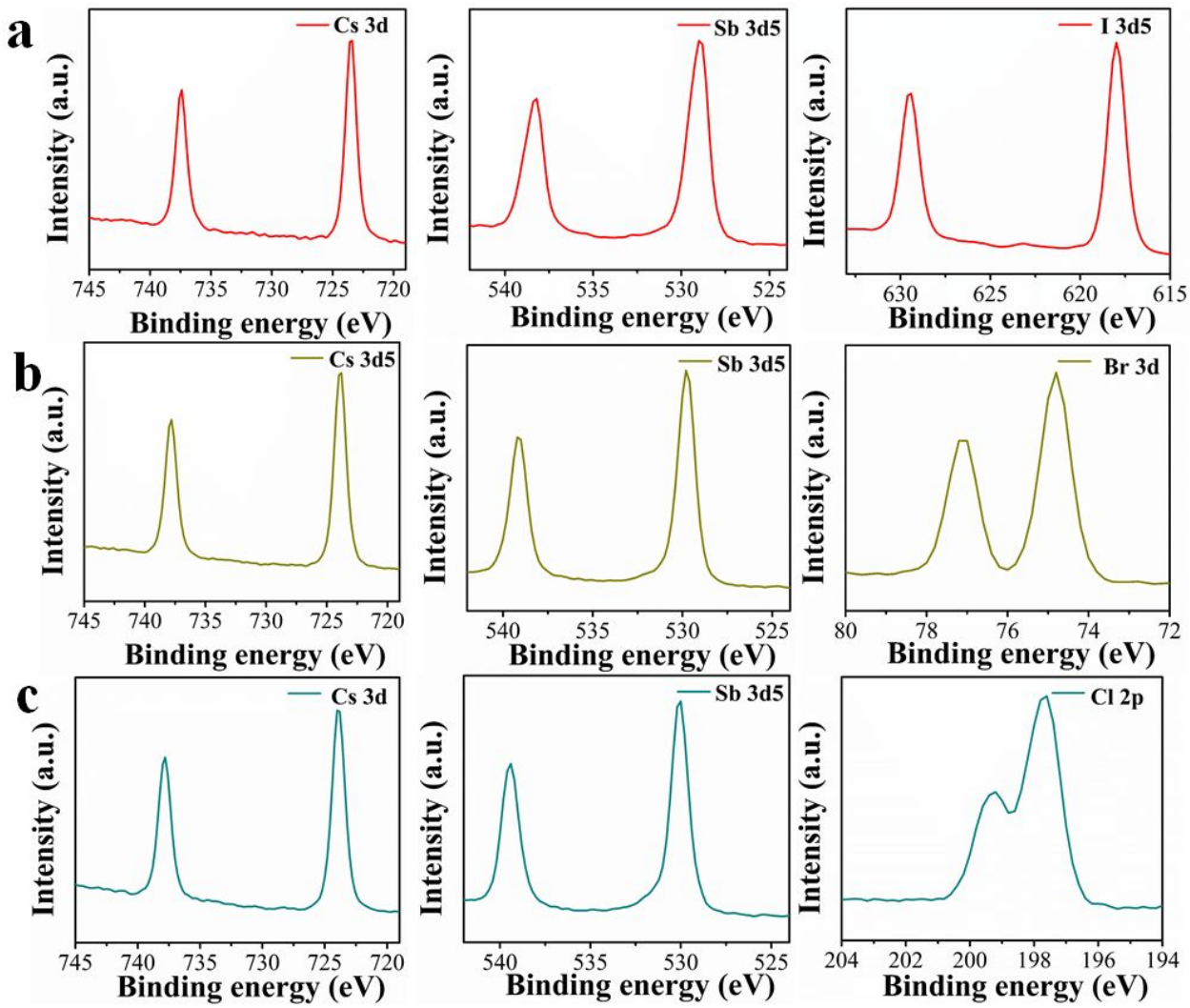

Figure S3. XPS elemental mapping after anion exchange: (a) CsI:SbI_3 film after SbI_3 vapor treatment, (b) CsI:SbI_3 film after $SbBr_3$ vapor treatment, and (c) CsI:SbI_3 film after $SbCl_3$ vapor treatment.

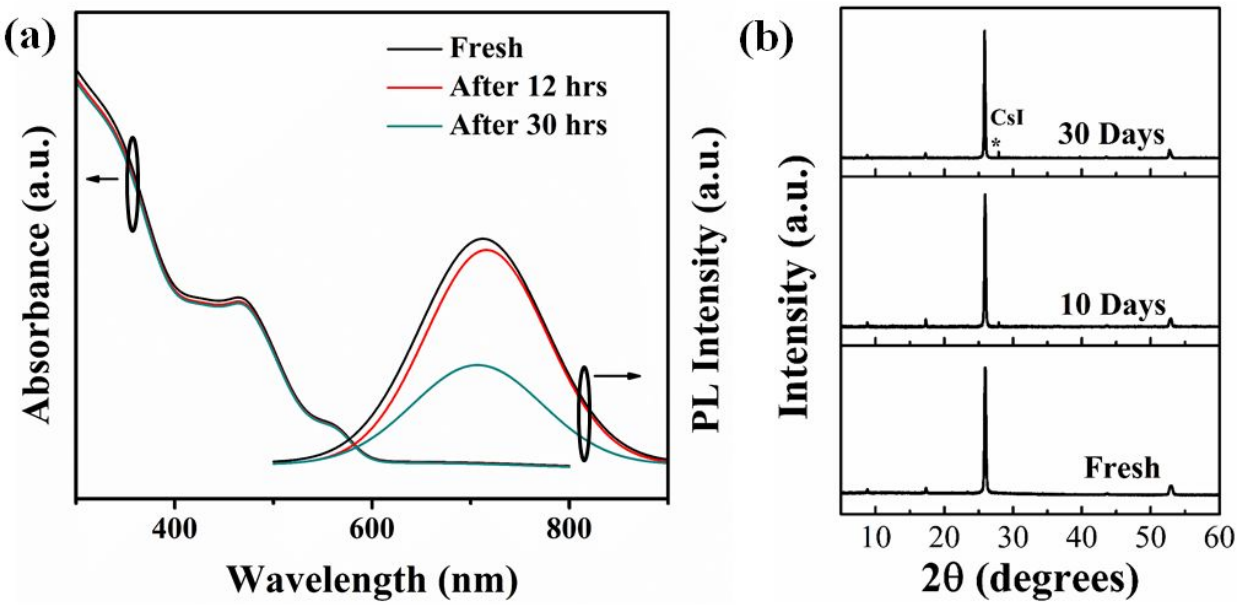

Figure S4. (a) Absorption and PL variation after keeping films in air (b) XRD peak revealing the slow evolution of CsI peak after 30 days.

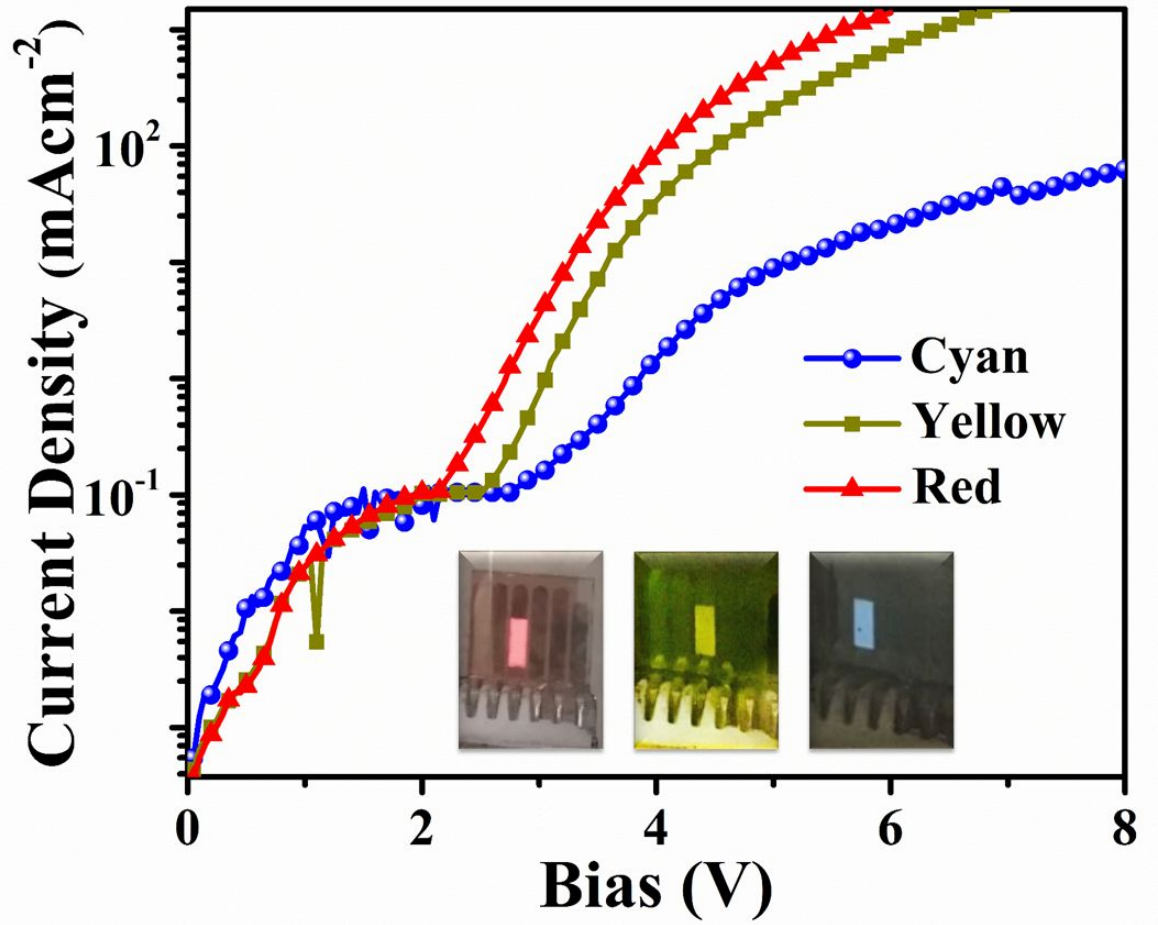

Figure S5. Averaged *J–V* curves of a series of devices prepared using the $Cs_3Sb_2X_9$ film. (inset is photographs of working LEDs)

Table S1. Stoichiometric ratios revealed through EDX elemental mapping.

	Cs/Sb	X/Sb	X/Cs
$Cs_3Sb_2I_9$	1.57	3.86	2.45
$Cs_3Sb_2Br_9$	1.45	3.62	2.36
$Cs_3Sb_2Cl_9$	1.68	3.40	2.02
Required	1.50	4.50	3

Table S2. Crystallite size from XRD

Perovskite	**$Cs_3Sb_2I_9$**	**$Cs_3Sb_2Br_9$**	**$Cs_3Sb_2Cl_9$**
2theta (degrees)	25.8528	27.6928	28.9194
FWHM (degrees)	0.25723	0.29898	0.26776
Crystallite size (nm)	316.8917	273.6585	306.3921

The average crystallite sizes were estimated using the Scherrer equation :

$$D = 0.89\lambda/\beta \cos$$

where D is the crystallite size, λ is the wavelength of the X-rays, β is the fwhm of the diffraction peak, θ is the diffraction angle, and the constant 0.89 is the shape factor.

Table S3. Literature reports on light emitting properties of lead free A3B2X9 rports.

Perovskite	**Material type**	**Tunability**	**Air Stability**	**Light emitting device**
$Cs_3Bi_2X_9$	Nanocrystals	Yes	10 days	Based on photoluminescence
$Cs_3Sb_2X_9$	Nanocrystals	Yes	30 days	No device display
$Cs_3Sb_2X_9$ (Current work)	Thin film (Solution processable)	Yes	30 days	Based on electroluminescence