

## Supporting Information

# 1.2 $\mu\text{m}$ persistent luminescence of $\text{Ho}^{3+}$ in $\text{LaAlO}_3$ and $\text{LaGaO}_3$ perovskites

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# Experimental Section

## Materials and Synthesis

LAO:Ho, LAO:Ho-Cr-Sm, LGO:Ho and LGO:Ho-Cr ceramic phosphors with the compositions of  $\text{La}_{0.99}\text{Ho}_{0.01}\text{AlO}_3$ ,  $\text{La}_{0.9898}\text{Ho}_{0.01}\text{Sm}_{0.0002}\text{Al}_{0.995}\text{Cr}_{0.005}\text{O}_3$ ,  $\text{La}_{0.99}\text{Ho}_{0.01}\text{GaO}_3$  and  $\text{La}_{0.99}\text{Ho}_{0.01}\text{Ga}_{0.995}\text{Cr}_{0.005}\text{O}_3$ , respectively were fabricated by a conventional solid-state reaction method.  $\text{La}_2\text{O}_3$  (99.99%),  $\text{Al}_2\text{O}_3$  (99.99%),  $\text{Ga}_2\text{O}_3$  (99.99%),  $\text{Ho}_2\text{O}_3$  (99.99%),  $\text{Sm}_2\text{O}_3$  (99.99%) and  $\text{Cr}_2\text{O}_3$  (99.9%) were used as raw materials. The  $\text{La}_2\text{O}_3$  powder was used immediately after heat treatment at 800°C for 10 h due to its strong hygroscopic characteristic, then all the starting powders were mixed by a ball milling method (Premium Line P-7, Fritsch) with anhydrous ethanol for several hours. The mixed powder was dried at 80°C for 36 h, compacted to form a ceramic green body ( $\phi 20$  mm, 2 mm thickness) under uniaxial pressing of 50 MPa, and finally sintered at 1500°C for 10 h (LAO:Ho & LAO:Ho-Cr-Sm) and 1200°C for 10 h (LGO:Ho & LGO:Ho-Cr) in air, respectively. The LAO:Cr ( $\text{LaAl}_{0.995}\text{Cr}_{0.005}\text{O}_3$ ), LAO:Ho-Cr ( $\text{La}_{0.99}\text{Ho}_{0.01}\text{Al}_{0.995}\text{Cr}_{0.005}\text{O}_3$ ) and LGO:Cr ( $\text{LaGa}_{0.995}\text{Cr}_{0.005}\text{O}_3$ ) ceramic phosphors prepared by the same experimental procedure were used as references. All the prepared samples were double-face polished to be thickness of  $1.5 \pm 0.1$  mm using a copper plate and diamond slurry.

## Characterization

Phase crystallization of the LAO:Ho, LAO:Ho-Cr-Sm, LGO:Ho and LGO:Ho-Cr samples were identified by the X-ray diffraction (XRD) measurement (Ultima IV, Rigaku), utilizing nickel filtered  $\text{Cu K}\alpha_1$  radiation (1.5406 Å) at 40 kV and 40 mA. The diffuse reflectance spectra of the LAO:Ho and LGO:Ho samples were measured by a spectrophotometer (UV-3600, Shimadzu) equipped with an integrating sphere. Fluorescence decay curves of the LAO:Ho, LAO:Ho-Cr, LGO:Ho and LGO:Ho-Cr samples were measured with a fluorescence lifetime spectrometer (Quantaaurus-Tau-C11367, Hamamatsu Photonics) using a pulsed Xe lamp covered with a 450 nm or 590 nm band-pass filter as the excitation source for  $\text{Ho}^{3+}$  or  $\text{Cr}^{3+}$ , respectively. Photoluminescence (PL) spectra of the LAO:Ho and LGO:Ho samples by pumping with a 532 nm CW laser (Millennia pro 6sJS, Spectra-Physics)

were recorded in the range of 900-2300 nm by a combination of optical chopper, monochromator, InSb NIR detector (J10D-M204-R01M-60-SP28, Teledyne Judson Technologies), and lock-in amplifier. PL spectra of the LAO:Ho and LGO:Ho samples by pumping with a 450 nm laser diode (LD) (PL-TB450, OSRAM) and persistent luminescence (PersL) spectra of the LAO:Ho-Cr-Sm and LGO:Ho-Cr samples after ceasing the UV illumination were measured by a Si CCD spectrometer (QE65-Pro, Ocean Optics) from 500 to 950 nm and an InGaAs spectrometer (NIR-Quest512, Ocean Optics) from 950 to 1600 nm connected with UV-Vis or NIR optical fibers. All the PL and PersL spectra monitored by CCD spectrometers were calibrated by using a standard halogen lamp (DH-2000, Ocean Optics). The photoluminescence excitation (PLE) spectra of the LAO:Ho, LAO:Ho-Cr, LGO:Ho and LGO:Ho-Cr samples monitoring  $\text{Ho}^{3+}$  emission (1200 nm) were measured by an InGaAs photodiode (PD) (IGA-030-H, Electro-Optical System Inc.) with a monochromator (Acton SP308, Princeton Instruments), and a 300 W Xe lamp (R300-3J, Lamp House) was used as the excitation source. The Xe lamp with a UV mirror module (250-380 nm) was used as the charging source for thermoluminescence (TL)-2D contour plot measurements. The ceramic sample was placed on a thermal stage (FTIR-600, Linkam Scientific) to control its temperature and firstly illuminated by UV light at 100 K for 10 min, then heated at 10 min after ceasing the illumination up to 600 K at a rate of 10 K/min. The Si and InGaAs spectrometers were operated simultaneously with the TL measurement to monitor the TL spectra at different temperatures. Persistent luminescent decay curves of the LAO:Ho-Cr-Sm and LGO:Ho-Cr samples after being excited for 5 min by the Xe lamp with the same UV mirror module were measured at 25°C using a PMT (R928, Hamamatsu Photonics) or the InGaAs PD detectors. In order to monitor the  $\text{Cr}^{3+}$  luminescence, the PMT detector was covered with 680 nm short-cut and 775 nm long-cut filters to filter out all but the  $\text{Cr}^{3+}$  luminescence. In order to monitor the  $\text{Ho}^{3+}$  luminescence, the InGaAs PD was covered with a 1000 nm short-cut filter to filter out all but the  $\text{Ho}^{3+}$  luminescence, then the decay curves were calibrated into the absolute radiance (in unit of  $\text{mW}\cdot\text{sr}^{-1}\cdot\text{m}^{-2}$ ) using a radiance measurement setup (BW-L1, Konica-Minolta) comprising a CCD spectrometer (Glacier X, B&W Tek Inc), an optical fiber and a collimator lens.

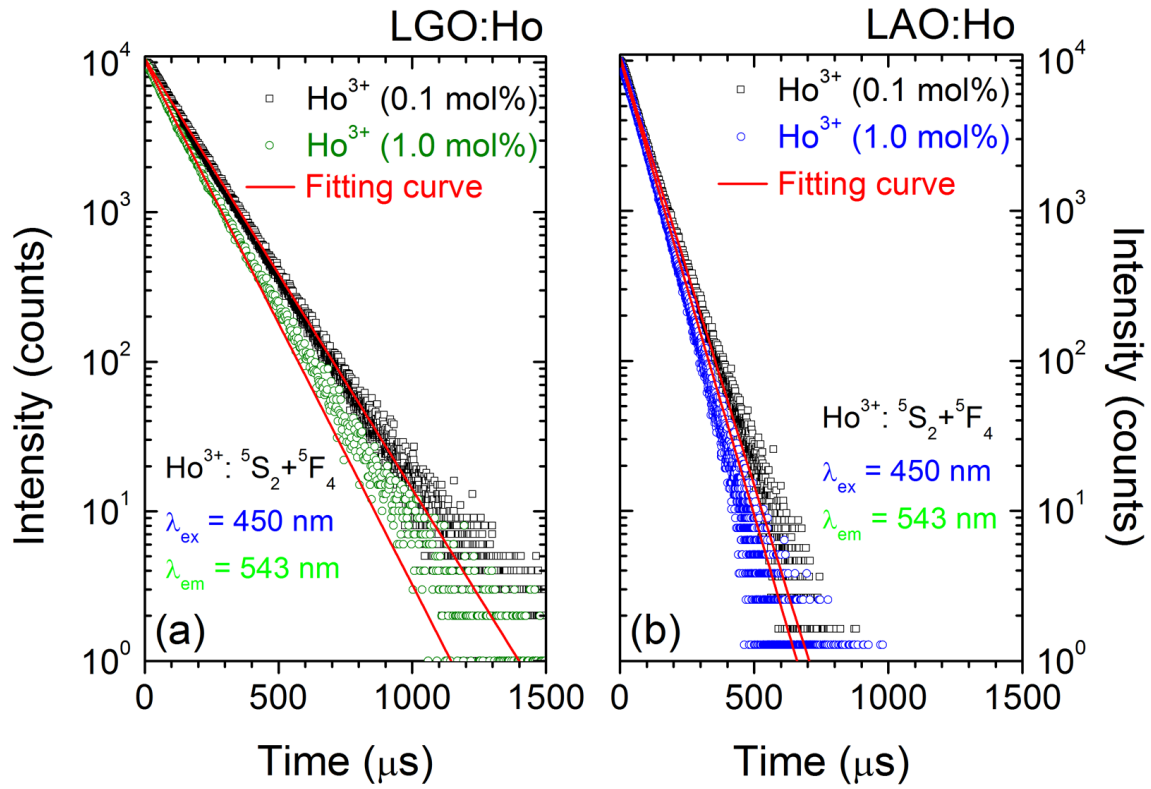


Fig. S1. Fluorescent decay curves of the (a) LGO:Ho and (b) LAO:Ho ceramic samples monitoring  $\text{Ho}^{3+}: {}^5\text{S}_2+{}^5\text{F}_4$  excited levels ( $\lambda_{\text{ex}}=450$  nm and  $\lambda_{\text{em}}=543$  nm) with two different  $\text{Ho}^{3+}$  doping concentrations (red lines: single-exponential fitting). Estimated lifetimes of the  $\text{Ho}^{3+}: {}^5\text{S}_2+{}^5\text{F}_4$  level from the single-exponential fitting are 76.0  $\mu\text{s}$  and 71.5  $\mu\text{s}$  for 0.1 mol% and 1.0 mol%  $\text{Ho}^{3+}$  doped LAO, as well as 140.9  $\mu\text{s}$  and 124.1  $\mu\text{s}$  for 0.1 mol% and 1.0 mol%  $\text{Ho}^{3+}$  doped LGO, respectively.

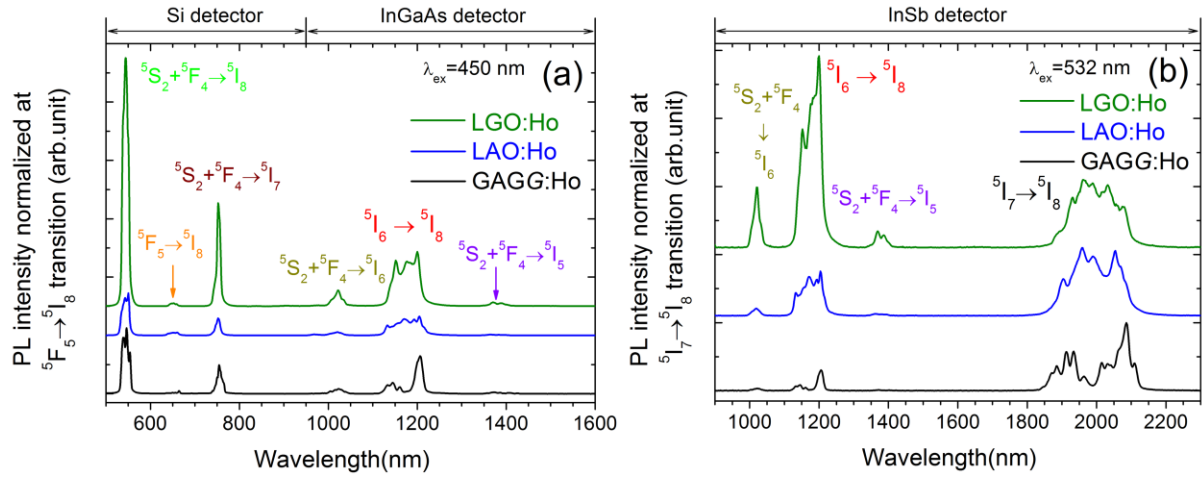


Fig. S2. PL spectra of the LAO:Ho, LGO:Ho and GAGG:Ho samples pumped by (a) 450 nm laser in the range of 500-1600 nm (b) 532 nm laser in the range of 900-2300 nm, the concentration of  $\text{Ho}^{3+}$  (1.0 mol%) in three samples is identical.

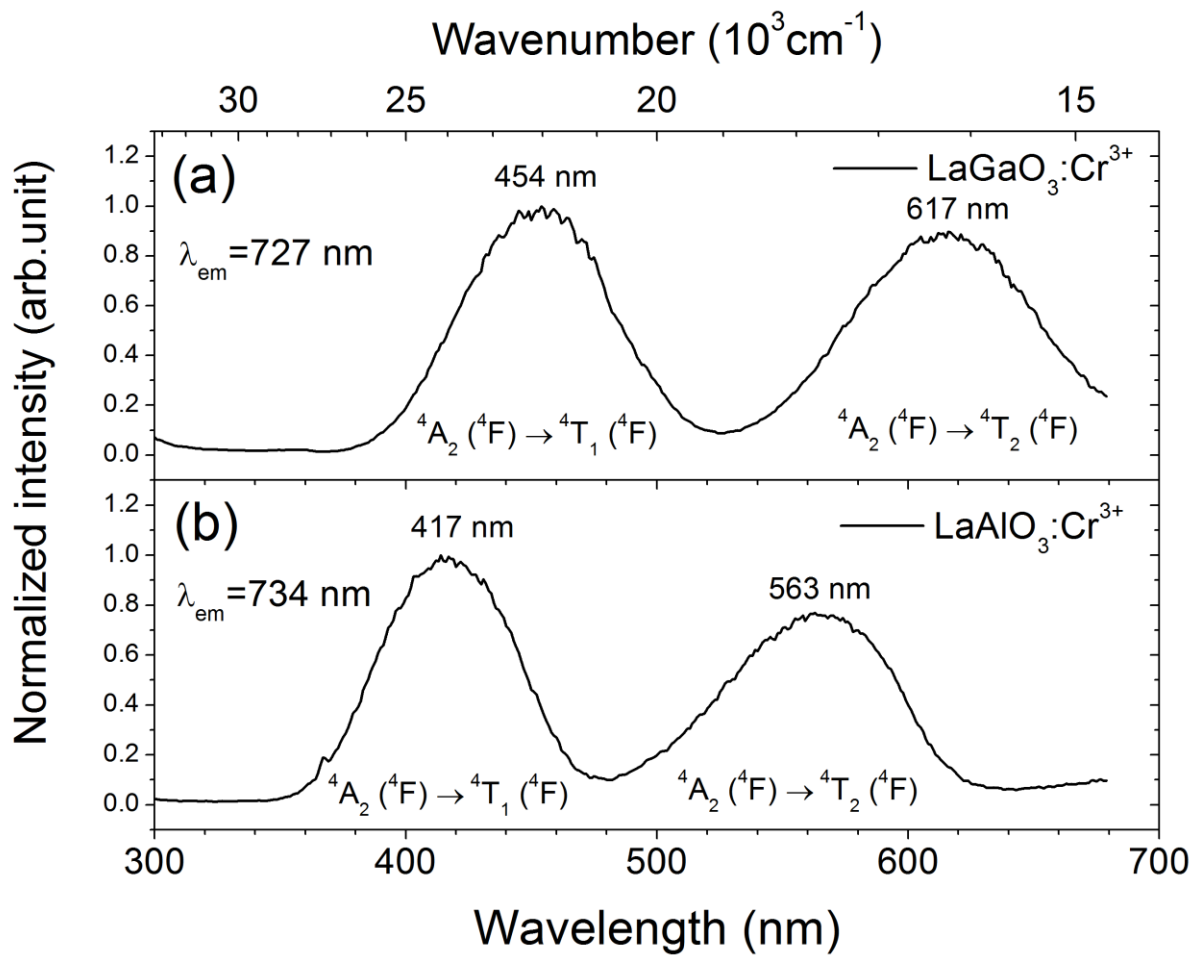


Fig. S3. Photoluminescence excitation (PLE) spectra of the (a)  $\text{LaGaO}_3:\text{Cr}^{3+}$  ( $\lambda_{\text{em}}=727$  nm) and (b)  $\text{LaAlO}_3:\text{Cr}^{3+}$  ( $\lambda_{\text{em}}=734$  nm) ceramic samples monitoring the *R*-line emission.

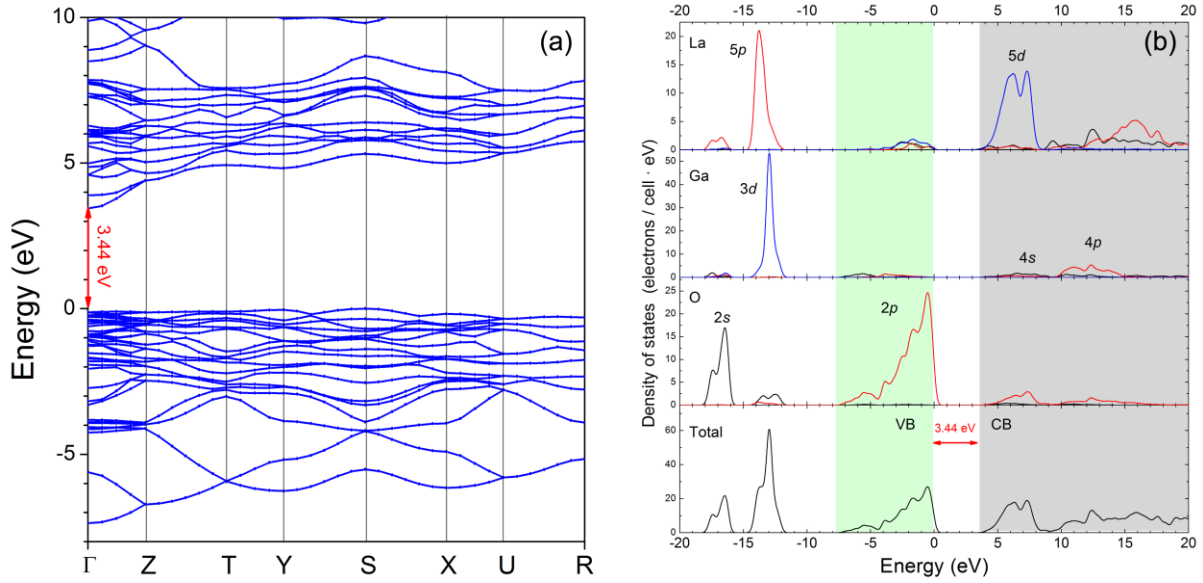


Fig. S4. (a) Calculated band structure of LaGaO<sub>3</sub>, (b) total and partial DOS of La, Ga, O atoms in LaGaO<sub>3</sub>.

The DFT simulation was performed based on the GGA-PBE [1] functional in order to obtain the density of states (DOSs) for LaGaO<sub>3</sub> using the CASTEP module of Materials Studio 2017 package [2]. The ionic core electrons were replaced by on-the-fly ultra-soft pseudopotentials [3] implemented in the CASTEP: [Ar] 5d<sup>1</sup>6s<sup>2</sup> for La, [Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>1</sup> for Ga, and [He] 2s<sup>2</sup> 2p<sup>4</sup> for O. Relativistic effects were included at the level of the Koelling-Harmon approximation of the Dirac equation [4]. The plane-wave basis energy cut-off was chosen as 630.0 eV. The convergence criteria were carefully chosen as follows: total energy tolerance 5.0×10<sup>-6</sup> eV/atom, maximum force tolerance 0.01 eV/Å, maximum stress component 0.02 GPa, maximum displacement 5.0×10<sup>-4</sup> Å, and the k-point grid (3×3×3) for LaGaO<sub>3</sub>. CIF file of orthorhombic LaGaO<sub>3</sub> was selected from Ref. [5].

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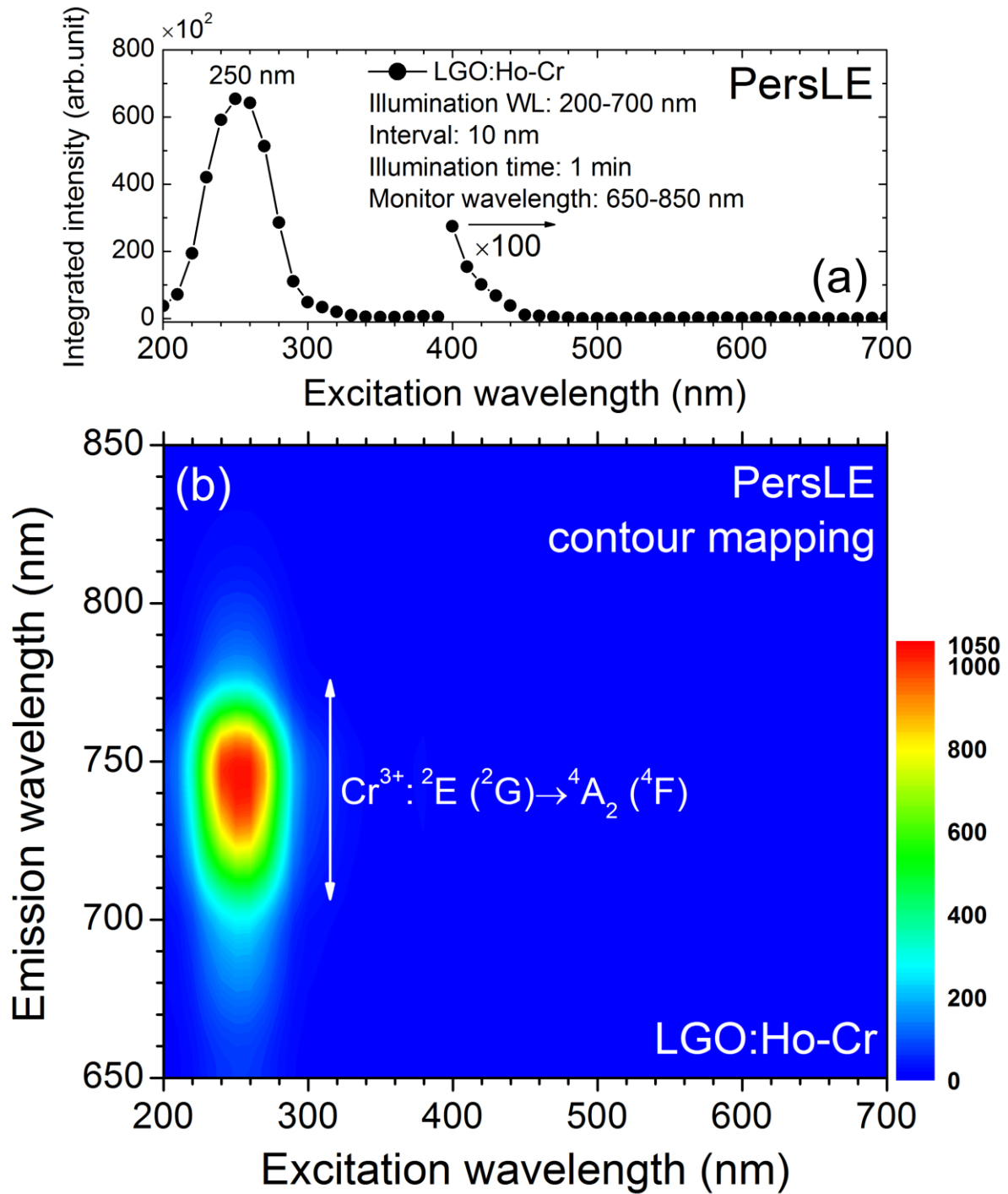


Fig. S5. (a) Persistent luminescence excitation (PersLE) spectrum of the  $\text{LaGaO}_3:\text{Ho}^{3+}\text{-Cr}^{3+}$  ceramic sample at 1 min after ceasing illumination by monochromatic light for 1 min (b) excitation ( $\lambda$ )-emission ( $\lambda$ ) 2D contour plot of the PersL spectra with different excitation wavelengths, the broadening of  $\text{Cr}^{3+}$  R-line emission is due to large width of the optical slit (wavelength resolution:  $\sim 20$  nm).



The persistent luminescence excitation (PersLE) spectrum and related two-dimensional (2D) contour plot of excitation and emission wavelengths of the  $\text{LaGaO}_3\text{:Ho}^{3+}\text{-Cr}^{3+}$  (LGO:Ho-Cr) sample after ceasing the illumination by monochromatic light for 1 min was measured by a fluorescence spectrophotometer (RF-5000, Shimadzu) using a home-made automatic operation program. Every persistent luminescence (PersL) spectrum was recorded at 1 min after ceasing the corresponding monochromatic light, the excitation wavelength was changed between 200 and 700 nm at 10 nm intervals, and the emission wavelength was monitored in the range from 650 to 850 nm.

The efficient charging wavelength region shown in the PersLE spectrum of LGO:Ho-Cr is mainly located at around 210-290 nm (peaking at ~250 nm), indicating that as for PersL, the high energy charging in the UV region mainly pumping the  $\text{Cr}^{3+}$ :  $^4\text{T}_1$  ( $^4\text{P}$ ) level and/or the mixed levels with the conduction band (*CB*) is more favorable than visible light for the delocalization of excited electrons. The energy gap between the  $^4\text{A}_2$  ( $^4\text{F}$ ) ground state of  $\text{Cr}^{3+}$  and the bottom of *CB* in LGO is roughly estimated by its photo-ionization threshold at 440 nm (~2.82 eV).