

Supplementary Information

Spectral Decoupling Between Radioluminescence and Persistent

Luminescence in Bi³⁺-Doped LiLu(WO₄)₂ for High-Security Information

Encryption

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Experimental section

Synthesis

Materials and methods: The phosphor materials were synthesized by the high-temperature solid-state reaction method. Firstly, raw materials of Li_2CO_3 (99.95%, Aladdin), Lu_2O_3 (99.99, Aladdin), WO_3 (99.95%, Aladdin) and Bi_2O_3 (99.95%, Aladdin) were weighed according to the stoichiometric composition of $\text{LiLu}_{1-x}(\text{WO}_4)_2:\text{xBi}^{3+}$ ($x = 0, 0.05, 0.1, 0.2, 0.5, 1$ mol%). After being ground thoroughly, the mixed powders were transferred into an alumina crucible, pre-fired at 600 °C for 4 h, subsequently sintered at 1000 °C for 5 h in a furnace. The used heating rate is 5 °C min^{-1} . Finally, after cooling to room temperature (RT), the synthesized compounds were ground again before further measurement.

Preparation of composite films

Polydimethylsiloxane (PDMS, SYLGARD[®] 184, Dow Corning) was chosen as the matrix for $\text{LiLu}(\text{WO}_4)_2$ (LLWO) and $\text{LLWO}:0.5\%\text{Bi}^{3+}$. First, 2.0 g of PDMS base resin and 0.2 g of curing agent were mixed in a beaker. After that, 2.0 g of $\text{LLWO}:0.5\%\text{Bi}^{3+}$ were dispersed in the PDMS precursor with stirring thoroughly. Then, the mixed well products were transferred into prepared mold. After curing at 70 °C for 12 h, the composite films with the target shape were obtained.

Characterization

X-ray diffraction (XRD) patterns were measured by a Rigaku D/MAX 2200 VPC diffractometer (40 kV and 26 mA) equipped with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The morphology of samples was studied by Gemi 500 scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Photoluminescence excitation (PLE), photoluminescence (PL), radioluminescence, and persistent luminescence were recorded using a spectrometer (Edinburgh, FLS1000) equipped with a 450 W Xe lamp, a visible PMT detector, and an external X-ray tube (AMPTEK, Mini-X). The spectral slit width used for the PersL decay tests was 10 nm. Prior to each test series, the phosphors were charged for 5 minutes using different light sources, and data recording commenced after a 5 s decay period. X-ray photoelectron spectra (XPS) were performed on a photoelectron

spectrometer (ESCALAB, Xi+) with Al K α as the X-ray source. The data of the reflection spectra were collected on an UV-vis-NIR spectrophotometer (Agilent, Cary 5000). Thermoluminescence (TL) glow curves were collected in an LTTL-3DS thermoluminescence spectrophotometer (Guangzhou Radiation Technology Co., Ltd.) in the temperature range for 300 to 650 K, heating at a linear rate of 5 K s⁻¹. The photographs were taken using a smartphone (Honor 90).

Trap depth calculation

The characteristic trap depth E (eV) was estimated using the Hoogenstraaten method:

$$\frac{\beta E}{k_B \cdot T_m^2} = s \exp\left(\frac{-E}{k_B \cdot T_m}\right) \quad (\text{Eq. S1})$$

Where β (K s⁻¹) is the heating rate, k_B is the Boltzmann constant, and s (s⁻¹) is the frequency factor. By rearranging the equation, the trap depth E (eV) is obtained from the slope of the linear fit of $\ln(T_m^2/\beta)$ versus $(k_B T_m)^{-1}$. Applying this method to the TL data presented in Fig. S12b,c yielded the corresponding E_1 and E_2 values.

Supplementary Tables (Table S1-2)

Table S1. The recent X-ray activated PersL materials.

Material	RL (nm)	PersL (nm)	Spectral overlap type	Duration (h)	Ref.
LiLu(WO ₄) ₂ :Bi ³⁺	500	550	Partial	8	This work
Cs ₂ NaYF ₆ :Pr ³⁺	250	250	Full	2	1
CaF ₂ :Gd ³⁺	313	313	Full	24	2
YBO ₃ :Bi ³⁺ ,Li ⁺	321	326	Full	2	3
LaGaO ₃ :Bi ³⁺ ,Sb ³⁺	372	372	Full	2000	4
Sr ₄ Al ₁₄ O ₂₅ :Eu ²⁺ ,Dy ³⁺ , B ³⁺	490	490	Full	1	5
SrAl ₂ O ₄ :Eu ²⁺ ,Dy ³⁺ ,B ³⁺	520	520	Full	1	5
LaF ₃ :Tb ³⁺	542	542	Full	-	6
Zn ₂ SiO ₄ :Mn ²⁺ ,Yb ³⁺ ,Li ⁺	520-550	520-550	Full	3	7
NaYF ₄ :Er ³⁺	540	540	Full	20	8
NaYF ₄ :Tb ³⁺	550	550	Full	-	9
NaLuF ₄ :Tb ³⁺	550	550	Full	720	10
CaF ₂ :Tb ³⁺ @CaLuF ₅	550	550	Full	-	11
CsY ₂ F ₇ :Tb ³⁺ @NaYF ₄	550	550	Full	0.7	12
CsCdCl ₃ :In ³⁺ ,Mn ²⁺	562	562	Full	10	13
SrZnP ₂ O ₇ :Sm ³⁺ ,Li ⁺	596	596	Full	0.1	14
Mg ₃ Y ₂ Ge ₃ O ₁₂ :Pr ³⁺ ,Ce ³⁺ , Er ³⁺	488, 610	488, 610	Full	0.1	15
Lu ₃ Ga ₅ O ₁₂ :Eu ³⁺	588	588	Full	1	16
CsCdCl ₃ :Mn ²⁺ ,R (R = Ti, Zr, Hf, Sn)	570-605	570-605	Full	1	17
LiYGeO ₄ :Mn ²⁺ , Bi ³⁺	350 620	620	Partial	-	18
Y ₃ Al ₂ Ga ₃ O ₁₂ :Cr ³⁺	710	710	Full	0.1	19
LiInSi ₂ O ₆ :Cr ³⁺ ,Pr ³⁺	750	750	Full	-	20
LaGaO ₃ :Sb ³⁺ ,Cr ³⁺	750	750	Full	500	21

$\text{ScBO}_3:\text{Cr}^{3+}$	771	771	Full	1.5	22
$\text{CaTiO}_3:\text{Cr}^{3+}, \text{Y}^{3+}$	772 nm	772 nm	Full	1	23
$\text{NaLuF}_4:\text{Gd}^{3+}, \text{Tm}^{3+}$	800	800	Full	0.3	24
$\text{Cs}_2\text{ZrCl}_6:\text{W}^{4+}$	445 900	900	Partial	10	25
$\text{NaYF}_4:\text{Ln}^{3+}@\text{NaYF}_4$ (Ln = Er, Nd, Ho, Tm)	1000- 1700	1000-1700	Full	72	26

Table S2. Crystallographic data of $\text{LiLu}(\text{WO}_4)_2:0.5\%\text{Bi}^{3+}$ as determined by the Rietveld refinement of powder XRD data at room temperature*.

	Atom	Category	x	y	z	Occ.
1	Li1	Li+1	0.000000	0.315000	0.250000	1
2	Bi1	Bi+3	0.500000	0.694236	0.250000	0.005
3	Lu1	Lu+3	0.500000	0.694236	0.250000	0.995
4	W1	W+6	0.265301	0.182932	0.015583	1
5	O1	O-2	0.160872	0.110788	0.603983	1
6	O2	O-2	0.231433	0.376439	0.136655	1
7	O3	O-2	0.277655	0.622643	0.386333	1
8	O4	O-2	0.342225	0.095580	0.378279	1

* monoclinic crystal structure, space group: P12/c1, a = 4.9852 Å, b = 5.79404 Å, c = 10.79881 Å, alpha = 90°, beta = 114.3598°, gamma = 90°, V = 284.1485 Å³, R_{wp} = 4.18084%, R_p = 5.34462%, and $\chi^2 = 1.87171$.

Supplementary Figure (Figure S1-S11)

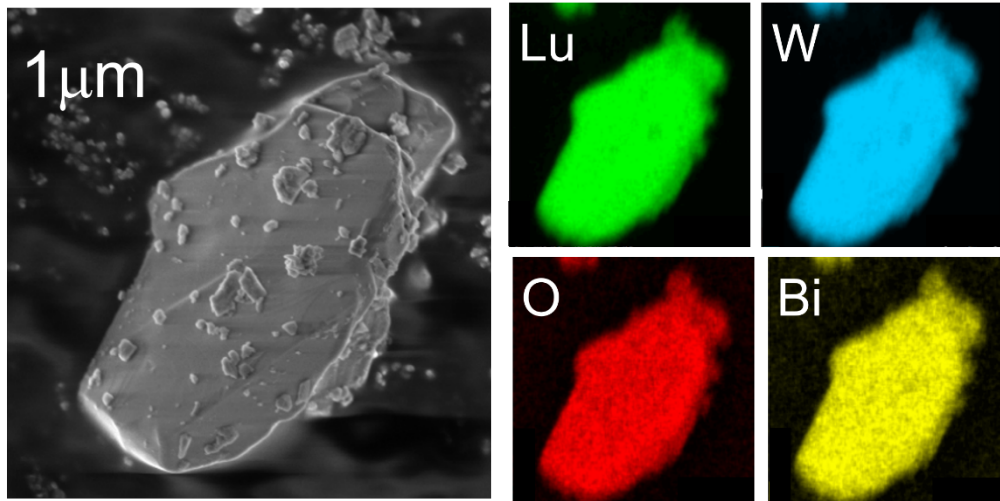


Fig. S1 SEM image of LLWO:0.5%Bi³⁺ phosphor and corresponding elemental mapping.

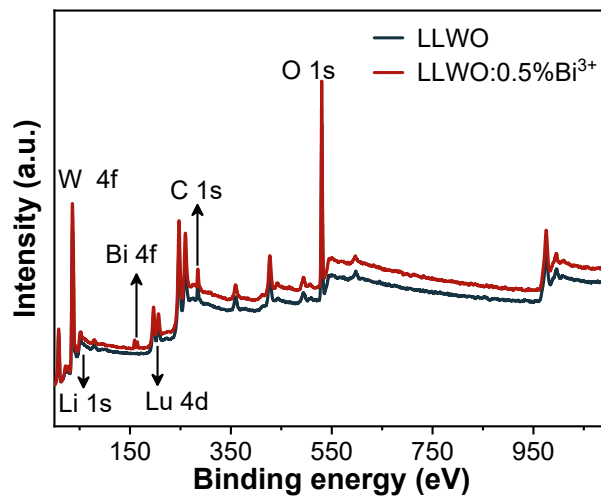


Fig. S2

Fig. S2. XPS survey scan spectra of LLWO and LLWO:0.5%Bi³⁺ samples.

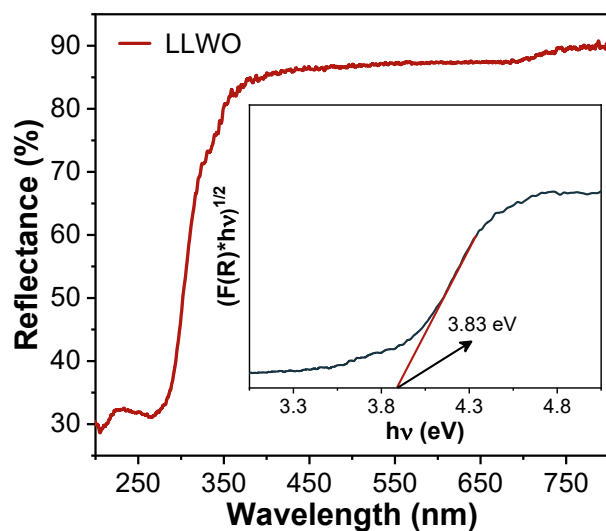


Fig. S3 DRS of LLWO host. The inset shows the relationship of $[F(R) \cdot hv]^{1/2}$ versus photon energy $h\nu$ for LLWO.

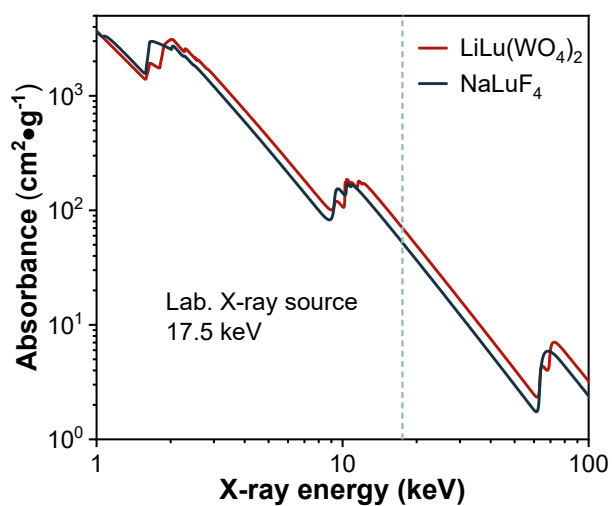


Fig. S4 Absorption spectra of LLWO and NaLuF₄ as a function of X-ray energy.

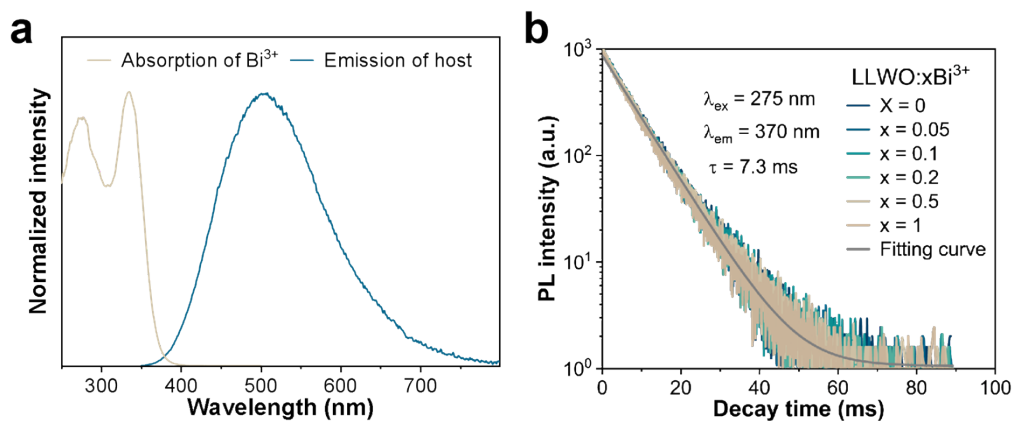


Fig. S5 a) PL and PLE spectra of LLWO:0.5%Bi³⁺. The PL spectrum was recorded with 275 nm excitation, while the PLE spectrum was monitored at an emission wavelength of 550 nm. The former reflects the intrinsic emission of the host, and the latter reflects the absorption of Bi³⁺. b) Fluorescence decay and lifetimes of LLWO:x%Bi³⁺ phosphors.

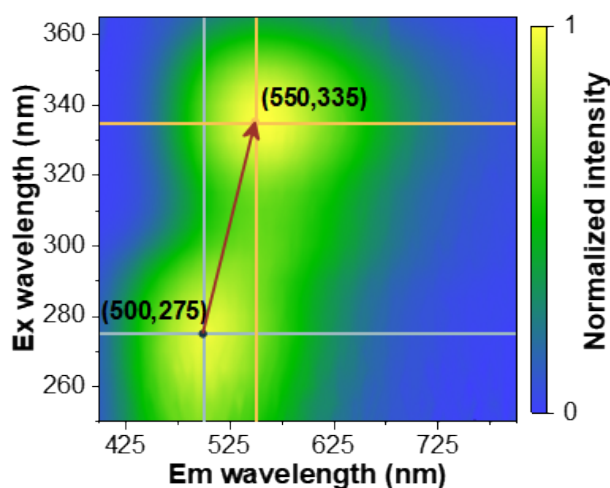


Fig. S6 Contour plot of the excitation-dependent PL spectrum of the LLWO:0.5%Bi³⁺.

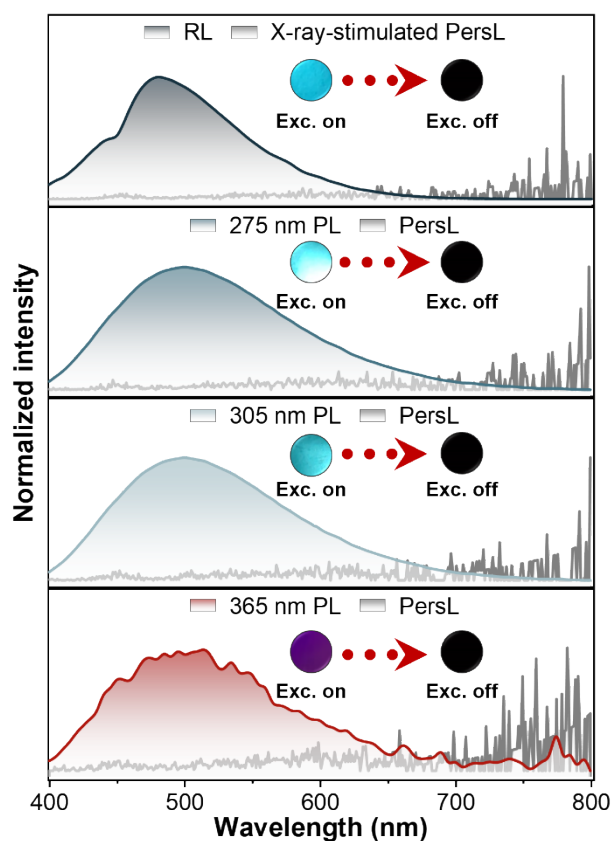


Fig.S7 Comparison of normalized RL, PL, and PersL spectra and photographs of LLWO under/after different excitation sources. Notably, the LLWO host exhibits weak emission upon 365 nm excitation, the purple luminescence is originated to the excitation source.

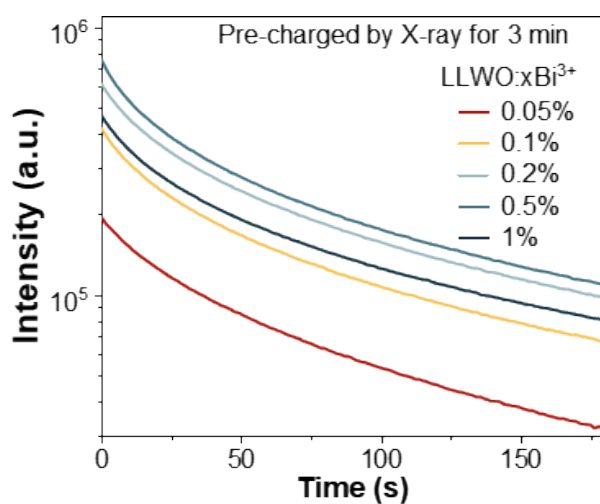


Fig. S8 PersL decay curves of LLWO: $x\text{Bi}^{3+}$ ($x = 0.05\text{--}1$ mol%) monitored at 550 nm after 3.5 W X-ray irradiation for 3 min.

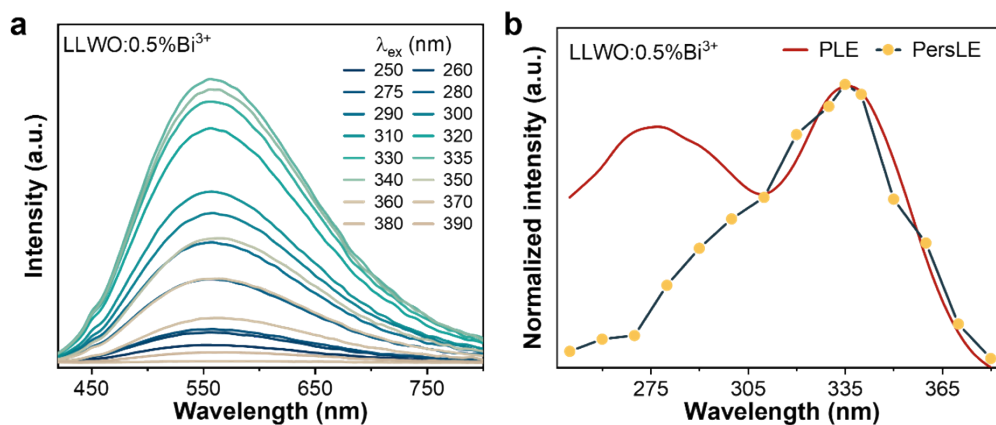


Fig. S9. a) PersL spectra of LLWO:0.5%Bi³⁺ under different excitation wavelength. The sample was pre-irradiated by UV lamp for 3 min and decayed for 10 s before each measurement. Heat treatment was conducted to clear traps after each measurement. b) PersL excitation spectrum obtained by plotting the integral intensity of PersL emission spectra.

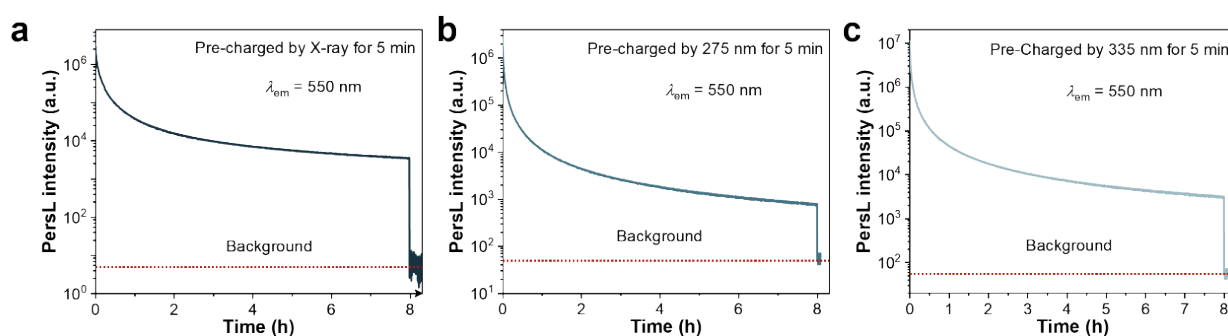


Fig. S10 a-c) After being charged with different excitation sources (3.5 W X-ray, 275 nm, and 335 nm) for 5 min, PersL decay curves of LLWO:0.5%Bi³⁺ recorded for 8 h.

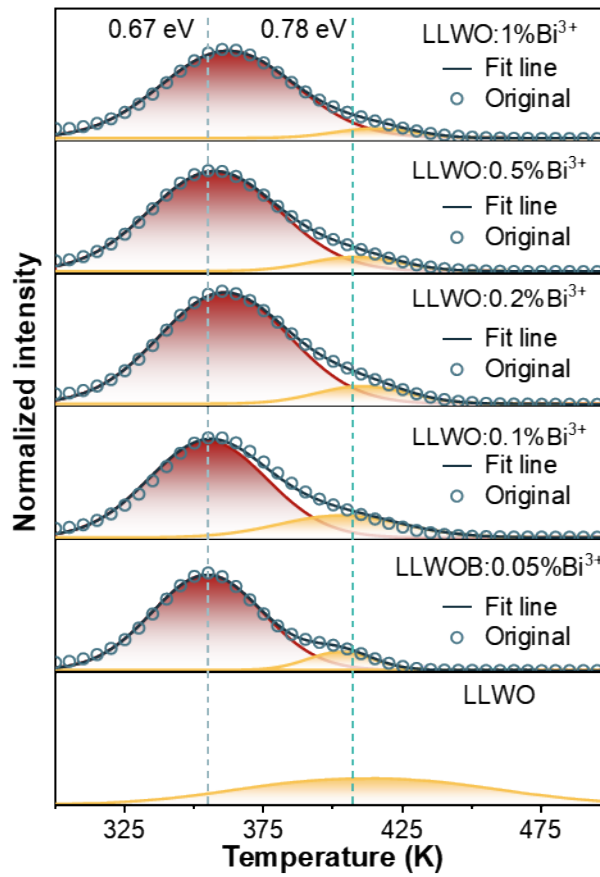


Fig. S11 Deconvolution TL glow curves of LLWO: $x\text{Bi}^{3+}$ ($x = 0\text{--}1\%$).

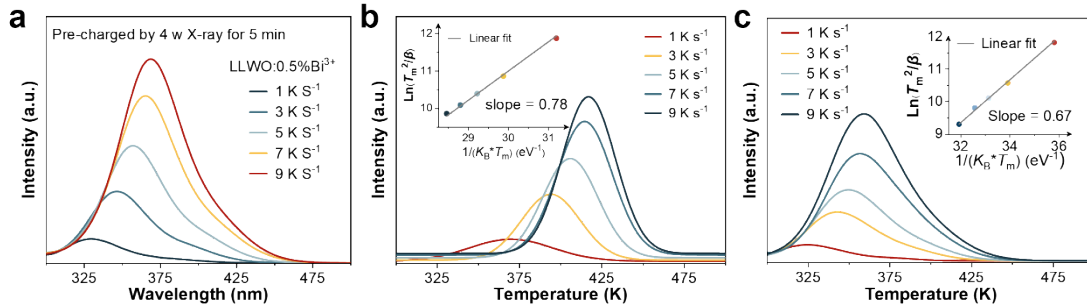


Fig. S12. a) TL glow curves of LLWO:0.5% Bi^{3+} at different heating rates β from 1 to 9 $\text{K}\cdot\text{S}^{-1}$. b, c) Deconvolution TL glow curves of LLWO:0.5% Bi^{3+} . Inset shows the fitting for the determination of the trap depth using the Hoogenstraaten method.

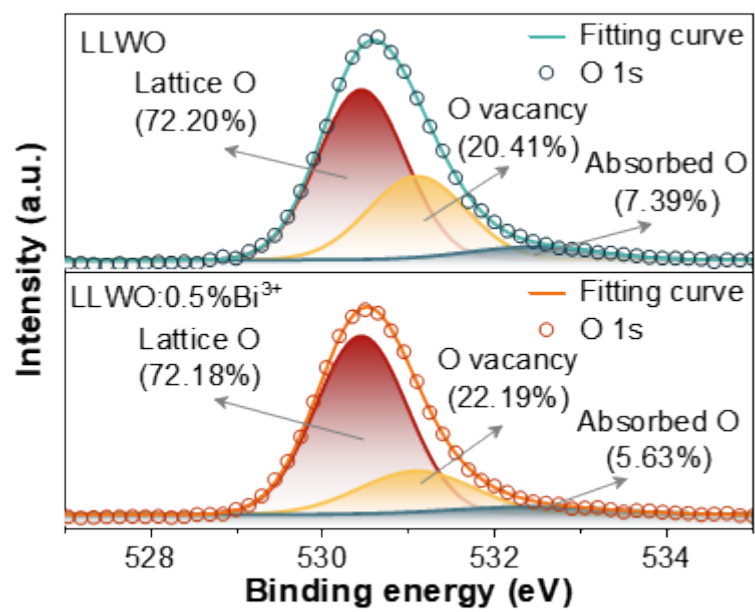


Fig. S13 XPS spectra of O 1s from the undoped LLWO and LLWO:0.5%Bi³⁺.

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