Supporting Information

Multi-mode tunable luminescence in Bi^{3+}-activated oxyfluoride phosphors for multi-level anti-counterfeiting application

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Table S1. Main parameters of the refinement of $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0-0.75) phosphors.

Phosphors	x = 0	x = 0.15	x = 0.3	x = 0.45	x = 0.6	x = 0.75
Space group			*I*4/*mcm*			
$a = b$ (Å)	6.7896	6.8210	6.8414	6.8799	6.9283	6.9965
c (Å)	11.3771	11.3551	11.3165	11.2685	11.2290	11.1810
V (Å^3)	524.4687	528.3053	529.6662	533.3684	539.0084	547.3180
R_p (%)	9.70	11.53	9.70	9.45	14.04	19.46
R_{wp} (%)	13.14	15.61	12.78	12.80	19.70	25.15
R_{exp} (%)	4.86	5.06	4.91	5.17	4.88	5.08
χ^2	2.70	3.08	2.60	2.47	4.03	4.94

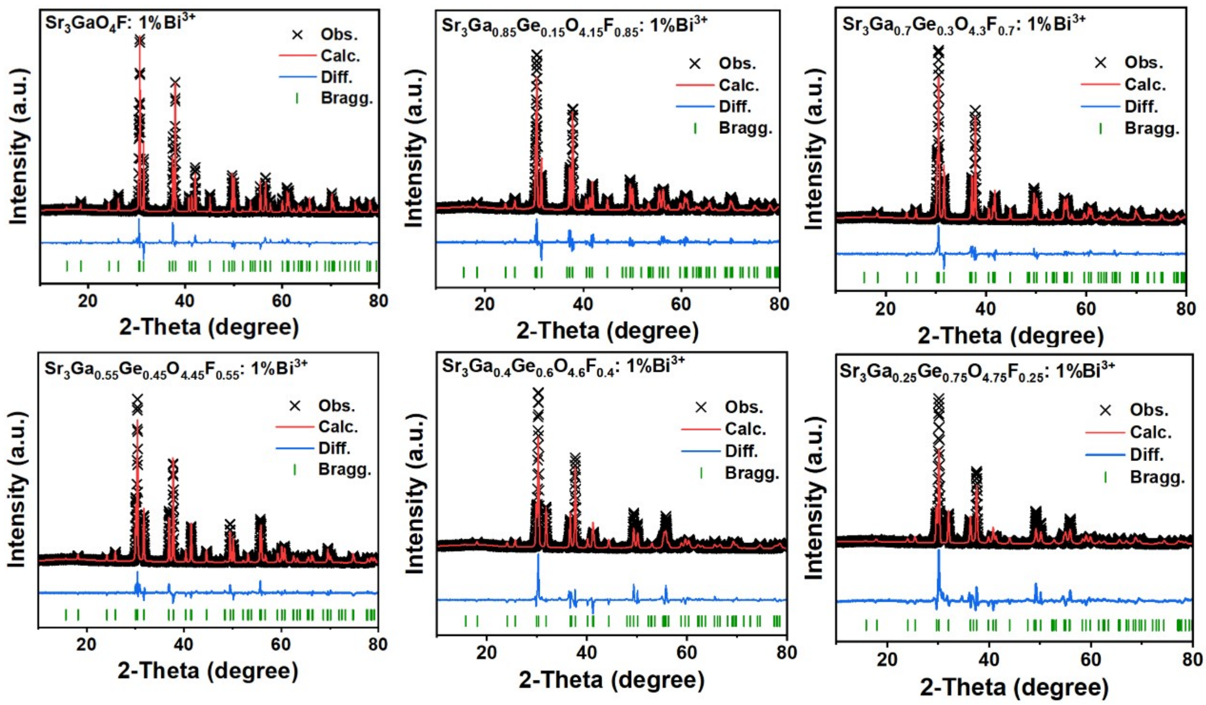

Fig. S1 Rietveld refinement of $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0-0.75) phosphors.

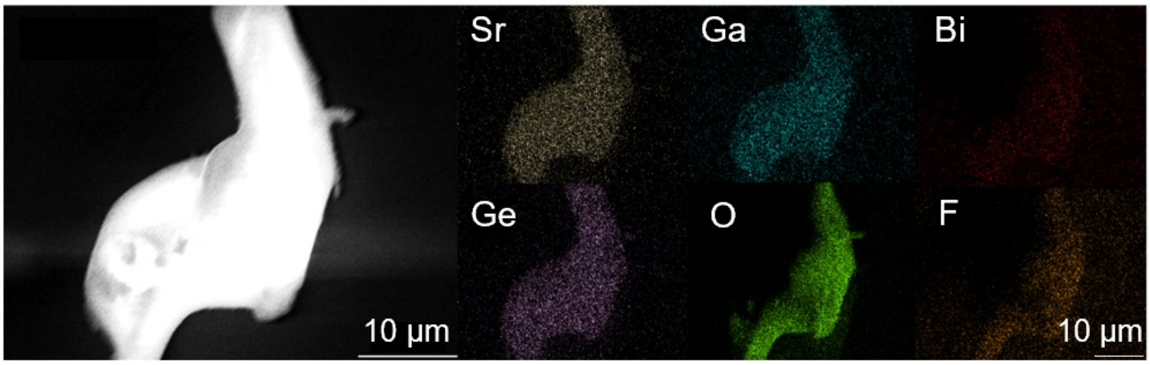

Fig. S2 SEM images and the corresponding elemental mapping images of $Sr_3Ga_{0.25}Ge_{0.75}O_{4.75}F_{0.25}$:1%$Bi^{3+}$ phosphor.

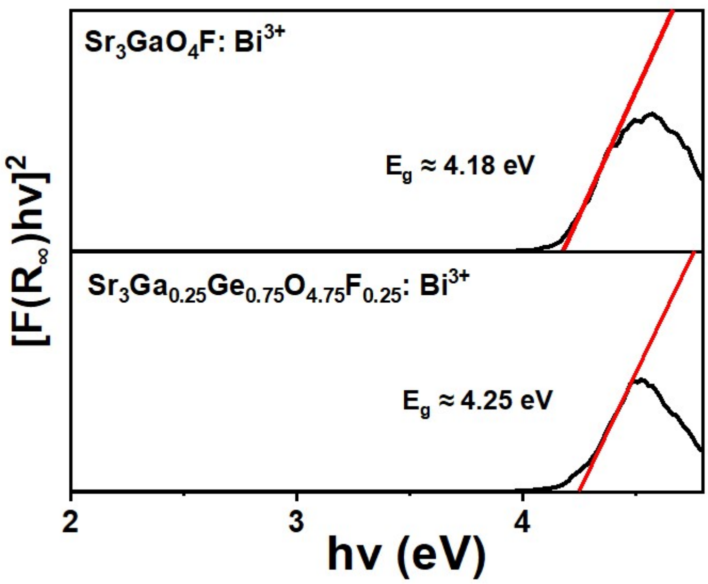

Fig. S3 DR spectrum of Sr_3GaO_4F:1%Bi^{3+} and $Sr_3Ga_{0.25}Ge_{0.75}O_{4.75}F_{0.25}$:1%$Bi^{3+}$ with $[F(R_\infty)*hv]^2$ as a function of photon energy *hv*.

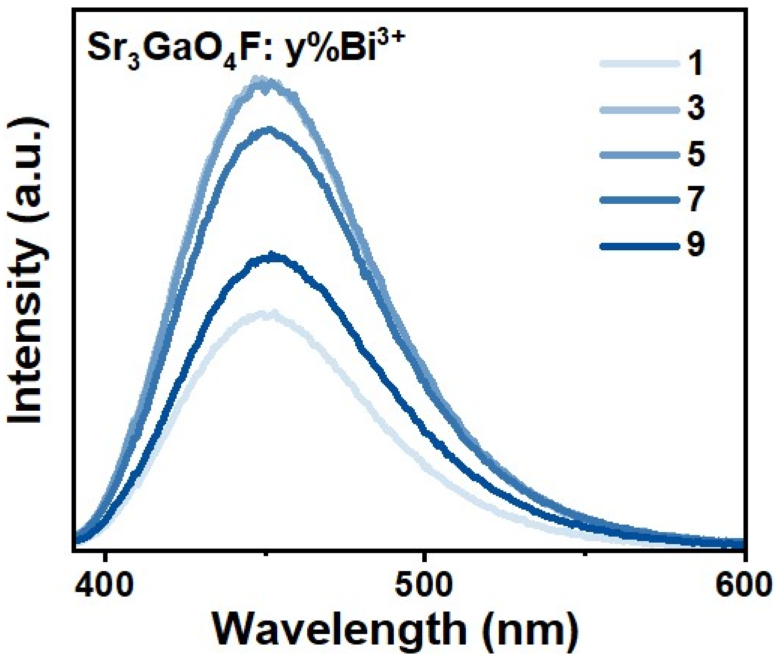

Fig. S4 PL spectra of Sr_3GaO_4F:*y*%Bi^{3+} (*y* = 0.01-0.09) phosphors.

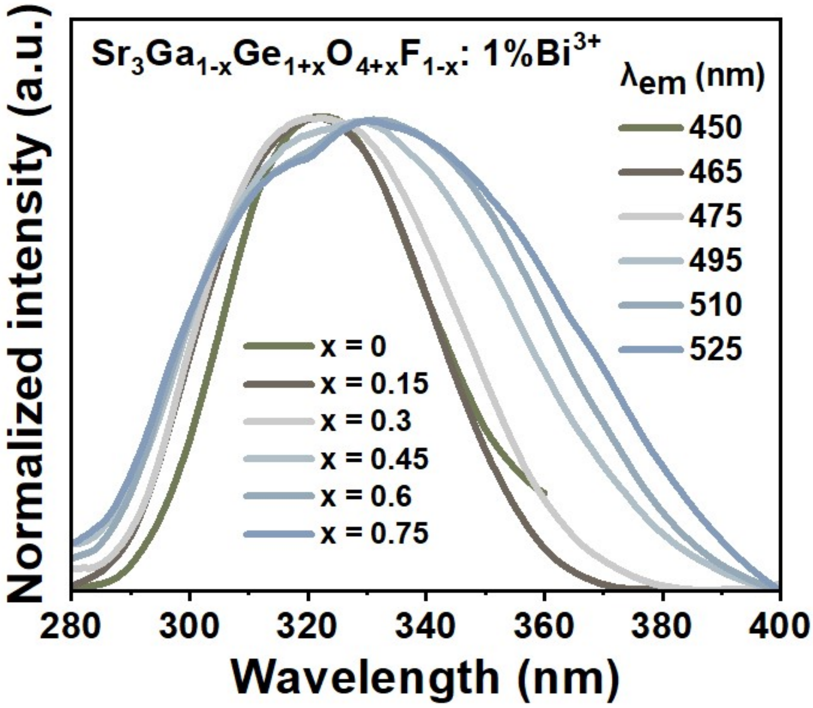

Fig. S5 Normalized PLE spectra of $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0-0.75) phosphors.

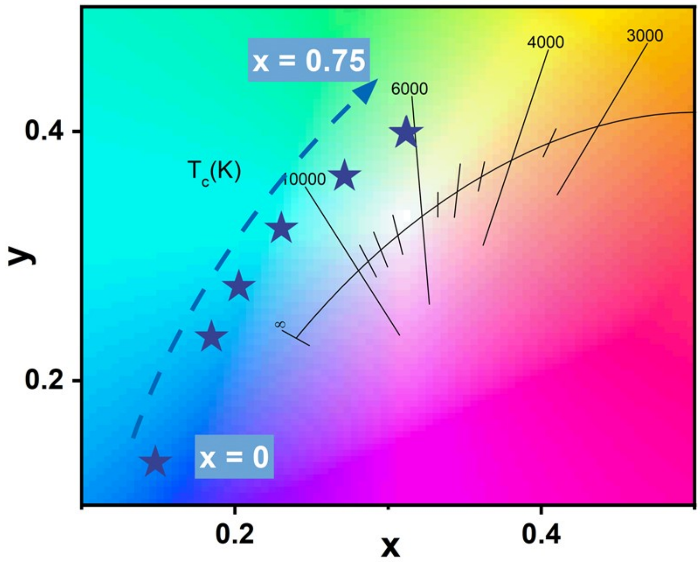

Fig. S6 CIE chromaticity coordinates of $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0-0.75) phosphors under 365 nm excitation.

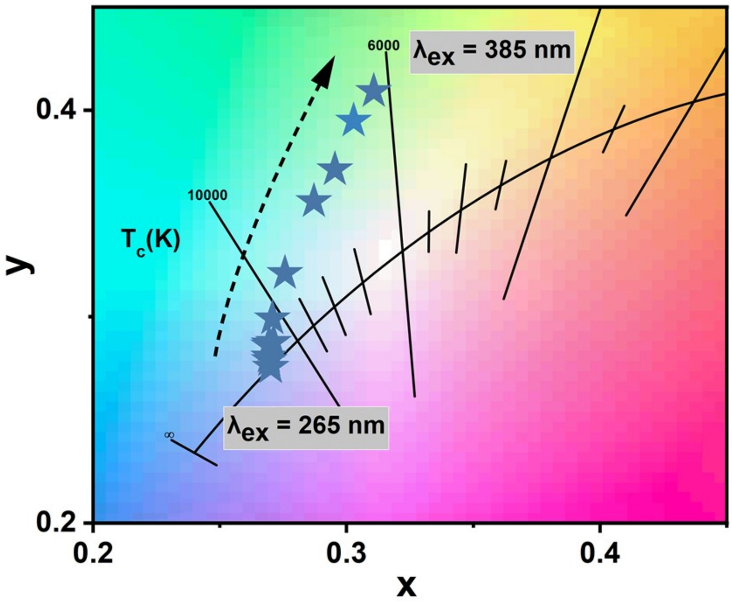

Fig. S7 CIE chromaticity coordinates of $Sr_3Ga_{0.25}Ge_{0.75}O_{4.75}F_{0.25}$:1%$Bi^{3+}$ under various excitation wavelengths from 265 to 385 nm.

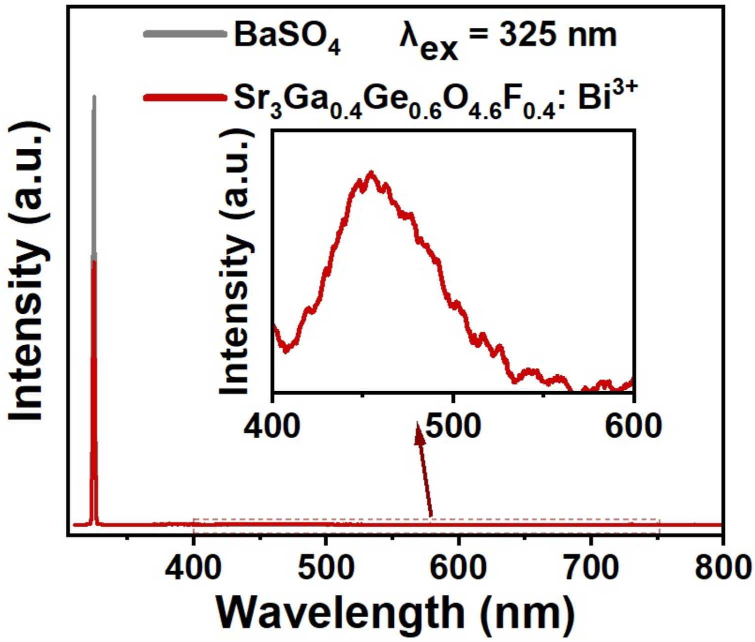

Fig. S8 Spectra of $Sr_3Ga_{0.4}Ge_{0.6}O_{4.6}F_{0.4}$:1%$Bi^{3+}$ and $BaSO_4$ to determine IQE value.

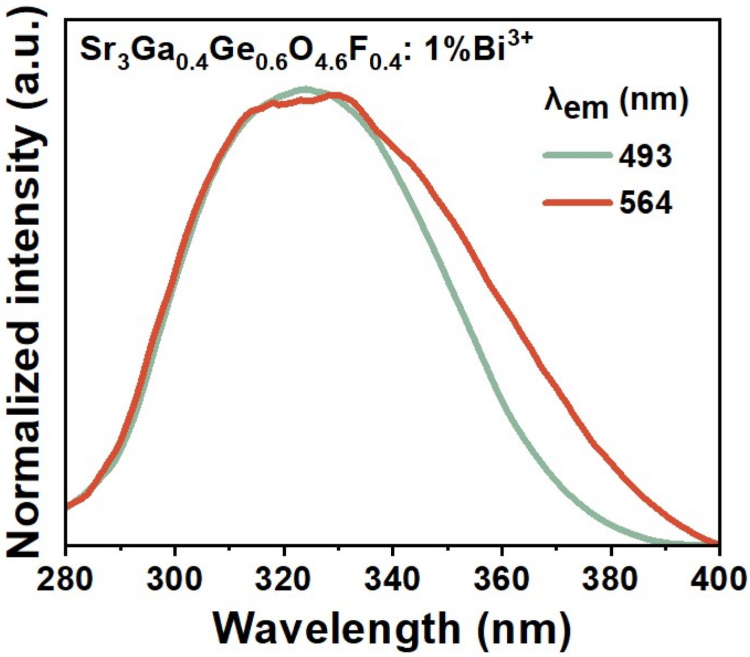

Fig. S9 PLE spectra of $Sr_3Ga_{0.4}Ge_{0.6}O_{4.6}F_{0.4}$:1%$Bi^{3+}$ monitoring at 493 and 564 nm.

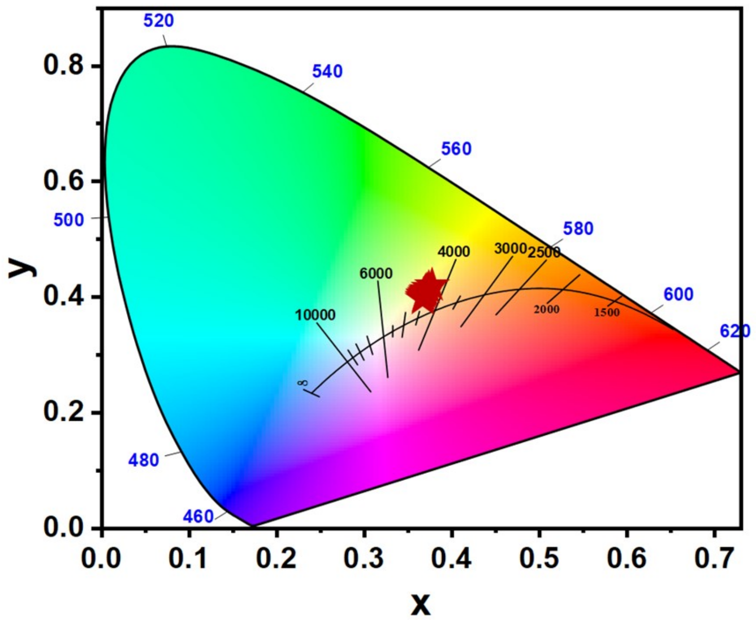

Fig. S10 CIE chromaticity coordinates of the fabricated pc-WLED device measured at different driving currents (20-200 mA).

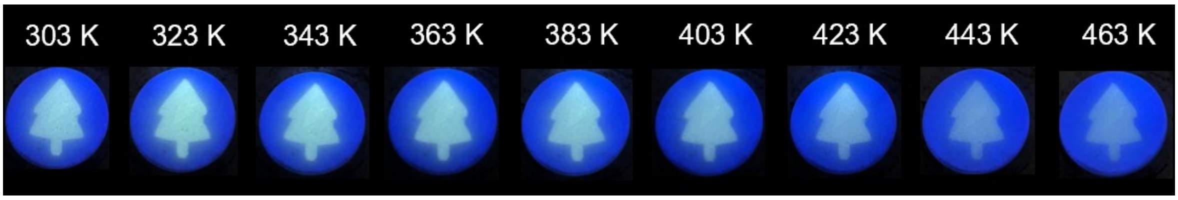

Fig. S11 Emitting colors at different temperatures of the composite PDMS film fabricated by $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0, 0.6) phosphors under the irradiation of 365 nm.

Experimental Section

1. Materials and synthesis procedures

A series of $Sr_3Ga_{1-x}Ge_xO_{4+x}F_{1-x}$:1%$Bi^{3+}$ (x = 0-0.75) phosphors were prepared by the high-temperature solid-phase method. High purity (99.99%) $SrCO_3$, SrF_2, Ga_2O_3, GeO_2 and Bi_2O_3 were used as raw materials, and they were weighed accurately based on the stoichiometric ratio and then ground in an agate mortar for 30 min to mix thoroughly. The mixtures were sintered at 900 °C for 5 h with a heating rate of 10 °C/min in a box furnace. After cooling down to room temperature, the products were ground to a fine powder for the subsequent characterization.

2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained utilizing a Rigaku Mini Flex 600 X-ray diffractometer with a Cu target Kα radiation source. The cell parameters were refined using the Maud 2.94. The scanning electron microscopy (SEM) images were recorded by an FEI ApreoHiVac equipped with an energy-dispersive X-ray analyzer. The photoluminescence (PL) spectra, photoluminescence excitation (PLE) spectra and temperature-dependent PL spectra were measured using a fluorescence spectrometer (FS5, Edinburgh) equipped with a compatible temperature-controlled test stage (HZ Instruments, RT600). The X-ray photoelectron spectroscopy (XPS) was measured by a Thermo Scientific K-Alpha electron spectrometer. The diffuse reflection (DR) spectra were measured using a UV-3600 spectrophotometer (Shimadzu Corporation, Tokyo, Japan) with $BaSO_4$ as the standard. The photoluminescence decay curves and internal quantum efficiency (IQE) value were measured using a fluorescence spectrometer (FLS1000, Edinburgh). The electroluminescence (EL) spectra of the fabricated phosphor-converted white light-emitting diode (pc-WLED) were measured using a HAAS2000 photoelectric measuring system (EVERFINE, China).

3. LED device fabrication

The $Sr_3Ga_{0.4}Ge_{0.6}O_{4.6}F_{0.4}$:1%$Bi^{3+}$ phosphor and transparent silicone were mixed in a mass ratio of 1:2 and stirred for a period of 15 minutes. The mixtures were coated on a 365 nm UV LED chip, and then they were solidified at 80 °C for 2 h to obtain the pc-WLED device.

4. Polydimethylsiloxane (PDMS) film fabrication

Bi^{3+}-doped oxyfluoride phosphor, PDMS and curing agent were weighted at a mass ratio of 2:10:1 and stirred for 30 min to mix evenly. The mixtures were then injected into a mold and solidified in an oven at 80 °C for 2 h, then the thin film can be obtained.

The calculation methods of lifetime value:

The lifetime values can be calculated based on the double exponential function as follows,[1]

$$I = I_0 + A_1 \exp\left(-\frac{t - t_o}{\tau_1}\right) + A_2 \exp\left(-\frac{t - t_0}{\tau_2}\right) \tag{S1}$$

$$\tau = \frac{A_1 \tau_1{}^2 + A_2 \tau_2{}^2}{A_1 \tau_1 + A_2 \tau_2} \tag{S2}$$

where I_0 is the initial intensity, I is the intensity at a given time, A_1 and A_2 are the pre-exponential factors, $(t-t_0)$ is the difference between the initial time of measurement after excitation pulse t_0 and time t, τ_1 and τ_2 are the lifetime values of the fast and slow components, τ is the average lifetime.

References:

1. K. Elzbieciak-Piecka, J. Drabik, D. Jaque and L. Marciniak, Cr^{3+} based nanocrystalline luminescent thermometers operating in a temporal domain. *Phys. Chem. Chem. Phys.*, 2020, **22**, 25949.