Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Site Occupation and Upconversion Process Enabled Multicolor Emission in $Gd_3GaO_6:Bi^{3+},Er^{3+}$ Phosphor for Quad-modes Anti-Counterfeiting

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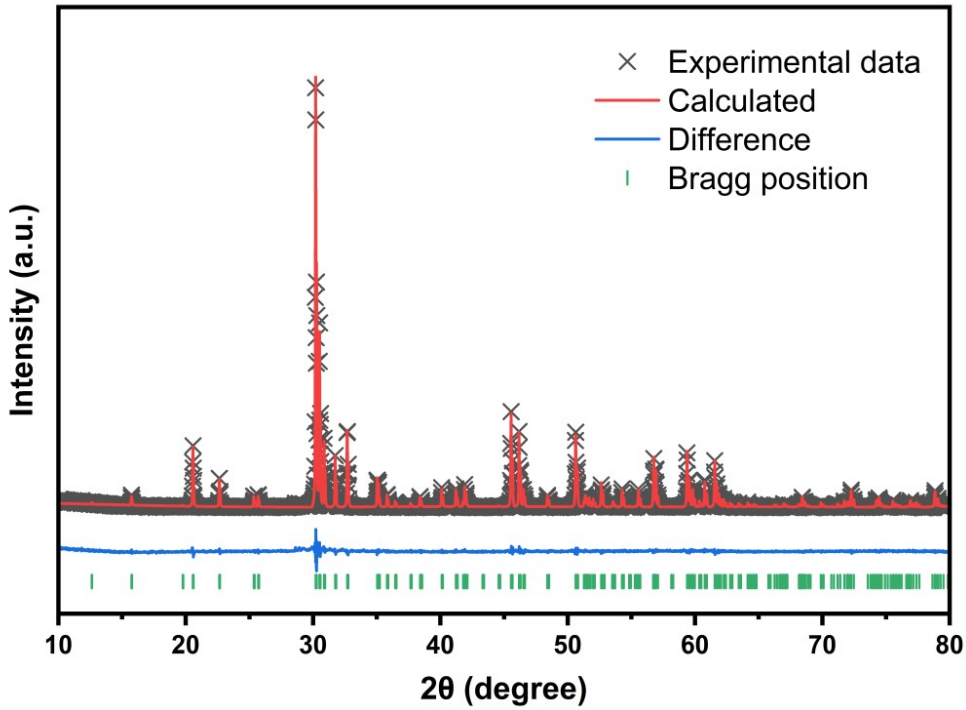

Figure S1. Rietveld refinement of the XRD pattern of GGO:0.05Bi^{3+},0.04Er^{3+}.

Table S1. Lattice parameters of GGO:xBi^{3+} phosphors obtained from the Rietveld XRD refinement.

Sample	GGO:0.03Bi^{3+}	GGO:0.05Bi^{3+}	GGO:0.07Bi^{3+}	GGO:0.09Bi^{3+}	GGO:0.12Bi^{3+}
Space group	Cmc21	Cmc21	Cmc21	Cmc21	Cmc21
Symmetry	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a, Å	8.994740	8.995690	8.996921	8.998005	8.998291
b, Å	11.281330	11.281572	11.282493	11.282776	11.283068

c, Å	5.481872	5.482107	5.482294	5.482681	5.482857
α = β = γ	90°	90°	90°	90°	90°
V	556.260	556.354	556.495	556.615	556.665
Rwp, %	7.68	8.23	10.55	8.17	8.53
Rp, %	6.57	7.08	8.83	6.99	7.14
χ^2	2.140	2.495	2.170	2.414	2.261

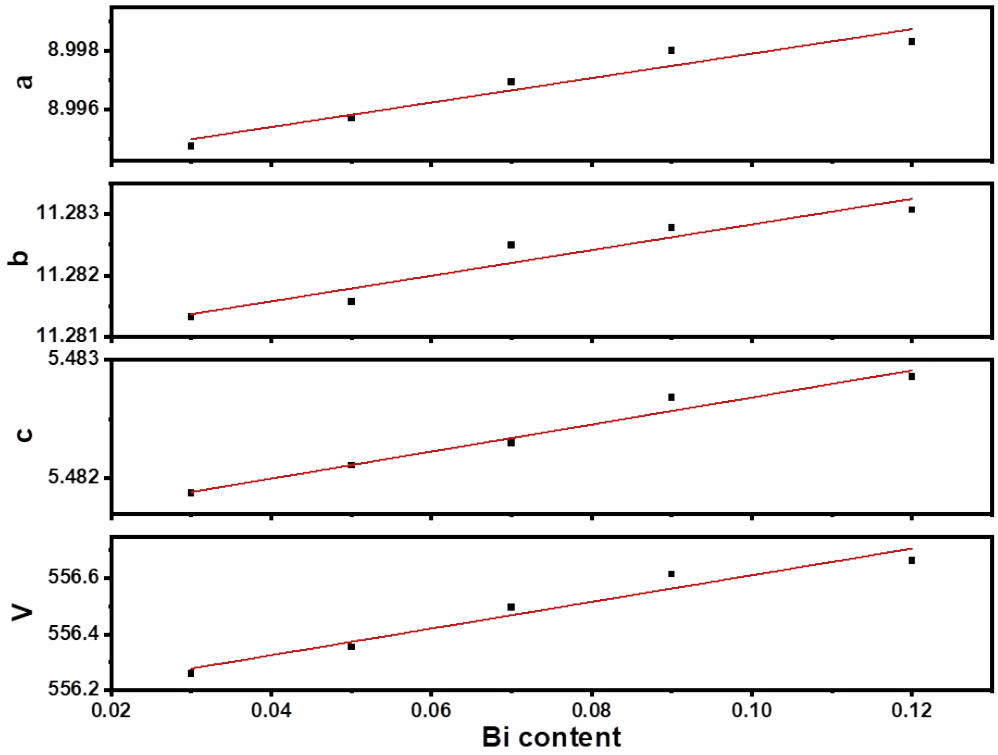

Figure S2. Unit cell parameters of the GGO:xBi^{3+} phosphors.

Table S2. Selected bond lengths of GGO:0.01Bi^{3+}.

	Bond Lengths (Å)		Bond Lengths (Å)
Gd1-O1	2.40711	Gd2-O1	2.4669
Gd1-O1	2.3018	Gd2-O1	2.4669
Gd1-O2	2.17711	Gd2-O2	2.3739
Gd1-O2	2.3559	Gd2-O2	2.3739
Gd1-O3	2.53911	Gd2-O3	2.28011
Gd1-O3	2.6396	Gd2-O3	2.28011
Gd1-O4	2.4118	Gd2-O4	2.45710
Average	2.405	Average	2.385

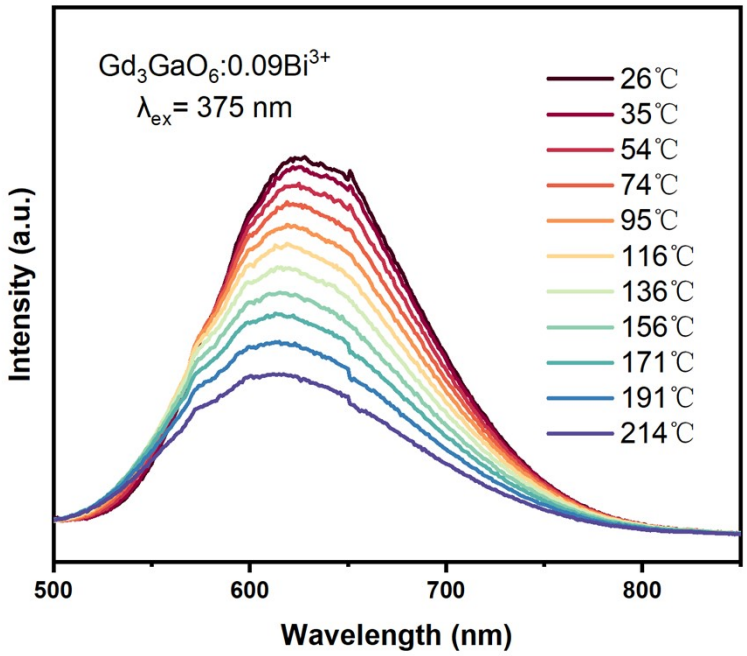

Figure S3. The temperature-dependent PL spectra of GGO:0.09Bi^{3+}.

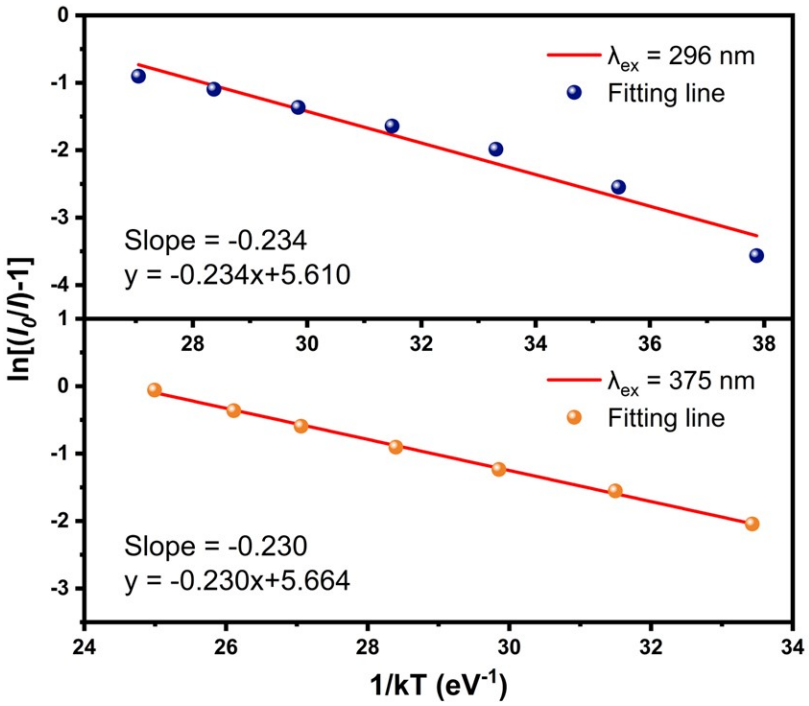

Figure S4. Activation energy of Bi(I) in GGO:0.01Bi^{3+} and Bi(II) in GGO:0.09Bi^{3+}.

As the temperature increases, the excited electrons diffuse to higher vibrational levels, and the energy barrier between the cross points and the excited state $^3P_1$ is called the activation energy. This activation energy (ΔE_a) can be calculated by the Arrhenius equation:[1, 2]

$$I_T = \frac{I_0}{1 + c\exp\left(-\frac{\Delta E_a}{kT}\right)}$$

Wherein I_T and I_0 represent the PL intensity at the experimental temperature and room temperature, respectively, k is the Boltzmann constant and c is a constant. **Figure S4** shows the linear curve of $\ln\left[(I_0/I_T) - 1\right]$ versus $1/kT$ with a slope of $-\Delta E_a$. Consequently, the activation energies ΔE_a for Bi(I) and Bi(II) are calculated to be 0.234 eV and 0.230 eV, respectively. From the above study, it can be seen that the thermal stability of Bi(I) and Bi(II) is similar, which is coherent with the calculations. The thermal quenching of the Bi^{3+} ions can be illustrated by the coordinate diagram, as shown in **Figure S5**. When a luminescent material is excited by UV light, the ground state electrons absorb energy and transition to the excited state. The excited electrons are then stabilized at the lower energy levels of the excited state by a lattice relaxation process and subsequently release photons by a direct transition back to the ground state. As the temperature increases, the excited electron overcomes the energy barrier (ΔE_a) with the help of phonons and achieves a transfer from the lower energy level of the excited state to the intersection of the ground and excited states, and then returns to the ground state through this intersection in a non-radiative transition.

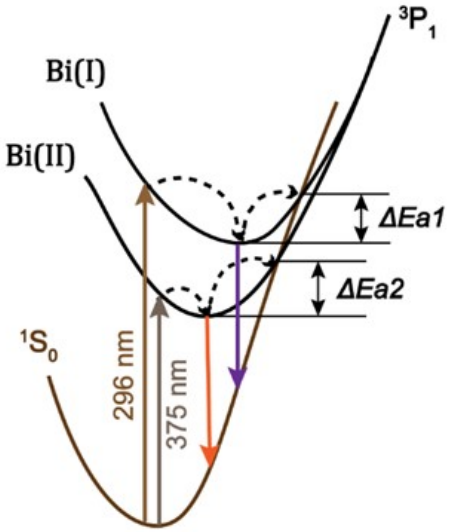

Figure S5. Coordinates of the configuration of the Bi^{3+}.

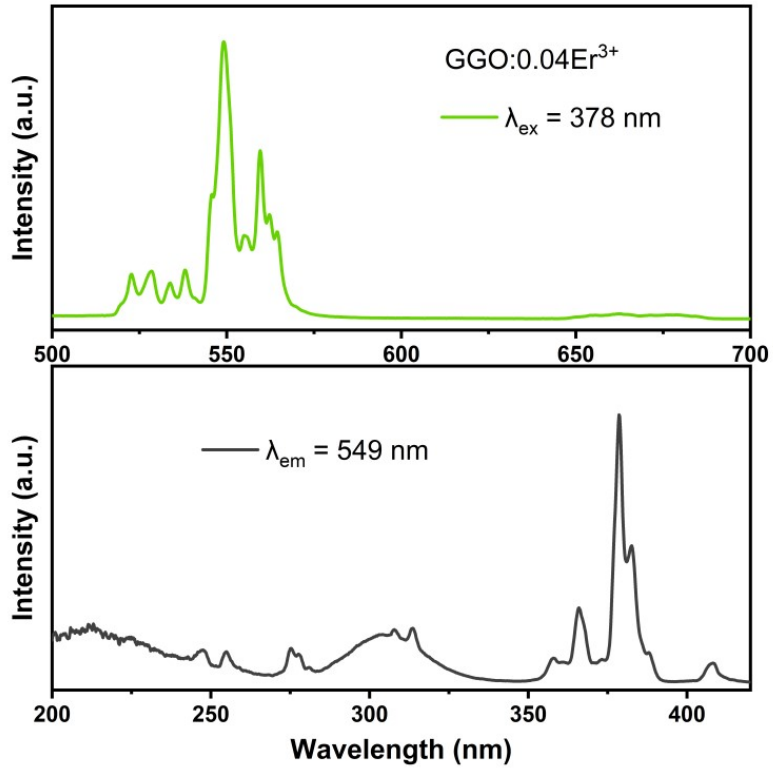

Figure S6. Downshifting PL and PLE spectra of GGO:Er^{3+}.

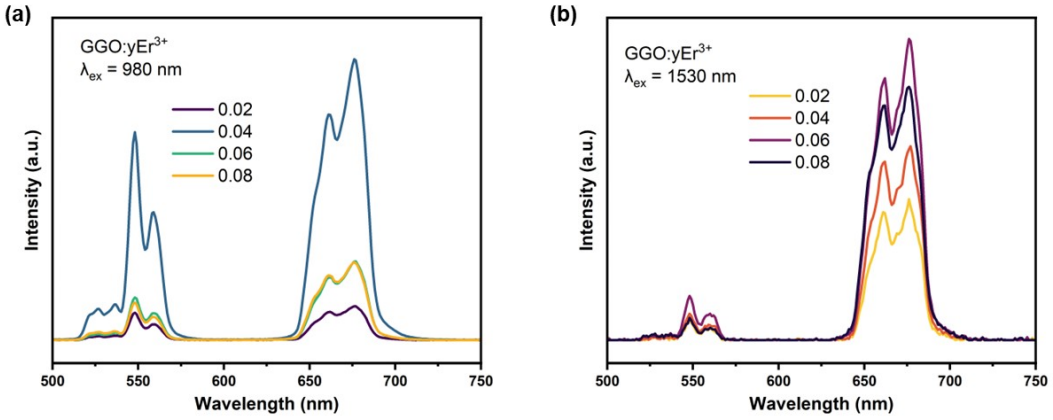

Figure S7. PL spectra of GGO:yEr^{3+} under (a) 980 nm excitation and (b) 1530 nm excitation.

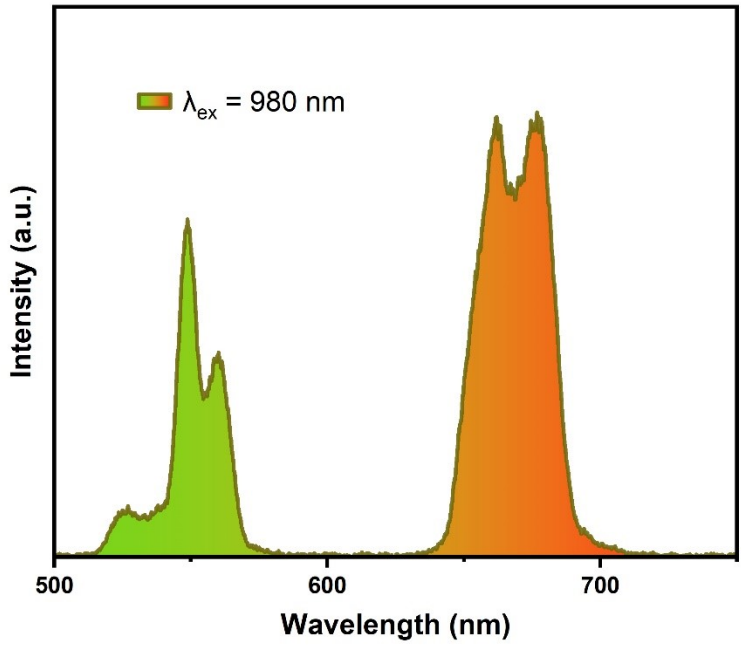

Figure S8. PL spectra of GGO:0.05Bi^{3+},0.04Er^{3+} under the excitation of 980 nm.

Reference:

1. Y. Guo, S. H. Park, B. C. Choi, J. H. Jeong and J. H. Kim, Dual-Mode Manipulating Multicenter Photoluminescence in a Single-Phased $Ba_9Lu_2Si_6O_{24}$:Bi^{3+},Eu^{3+} Phosphor to Realize White Light/Tunable Emissions, *Scientific Reports*, 2017, **7**, 15884.
2. G. Xing, Y. Feng, M. Pan, Y. Wei, G. Li, P. Dang, S. Liang, M. S. Molokeev, Z. Cheng and J. Lin, Photoluminescence Tuning in a Novel Bi^{3+}/Mn^{4+} Co-Doped La_2ATiO_6:(A = Mg, Zn) Double Perovskite Structure: Phase Transition and Energy Transfer, *Journal of Materials Chemistry C*, 2018, **6**, 13136-13147.