Dalton Transactions RSC Publishing

Electronic Supporting Information (ESI)

Cross-relaxation induced tunable emissions from the $Tm^{3+}/Er^{3+}/Eu^{3+}$ ions activated $BaGd_2O_4$ nanoneedles

*G. Seeta Rama Raju, E. Pavitra, and Jae Su Yu**

Department of Electronics and Radio Engineering, Institute for Laser Engineering, Kyung Hee University, 1 Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-701 Republic of Korea.

Characterizations:

XRD pattern of the BG nanoneedles were recorded on Mac Science (M18XHF-SRA) X-ray powder diffractometer with CuKα= 1.5406 Å. The morphology, selected area diffraction (SAED) pattern, and high resolution transmission electron microscope (HR-TEM) image measurements were performed using a field emission transmission electron microscope (FE-TEM JEOL JEM-2100F), fitted with the energy dispersive X-ray spectromenter (Oxford INCA). The powder contained solution was sprayed one time on the copper grid for measuring the TEM. The room-temperature photoluminescence (PL) and PL excitation (PLE) spectra were measured by using a Photon Technology International (PTI, USA) fluorimeter with a Xe-arc lamp of 60 W power. The digital photographs were captured at the time of PL measurement using Samsung Galaxy S2 smartphone camera. The CL properties were measured by a Gatan (UK) MonoCL3 system attached with the scanning electron microscope (Hitachi S-4300 SE).

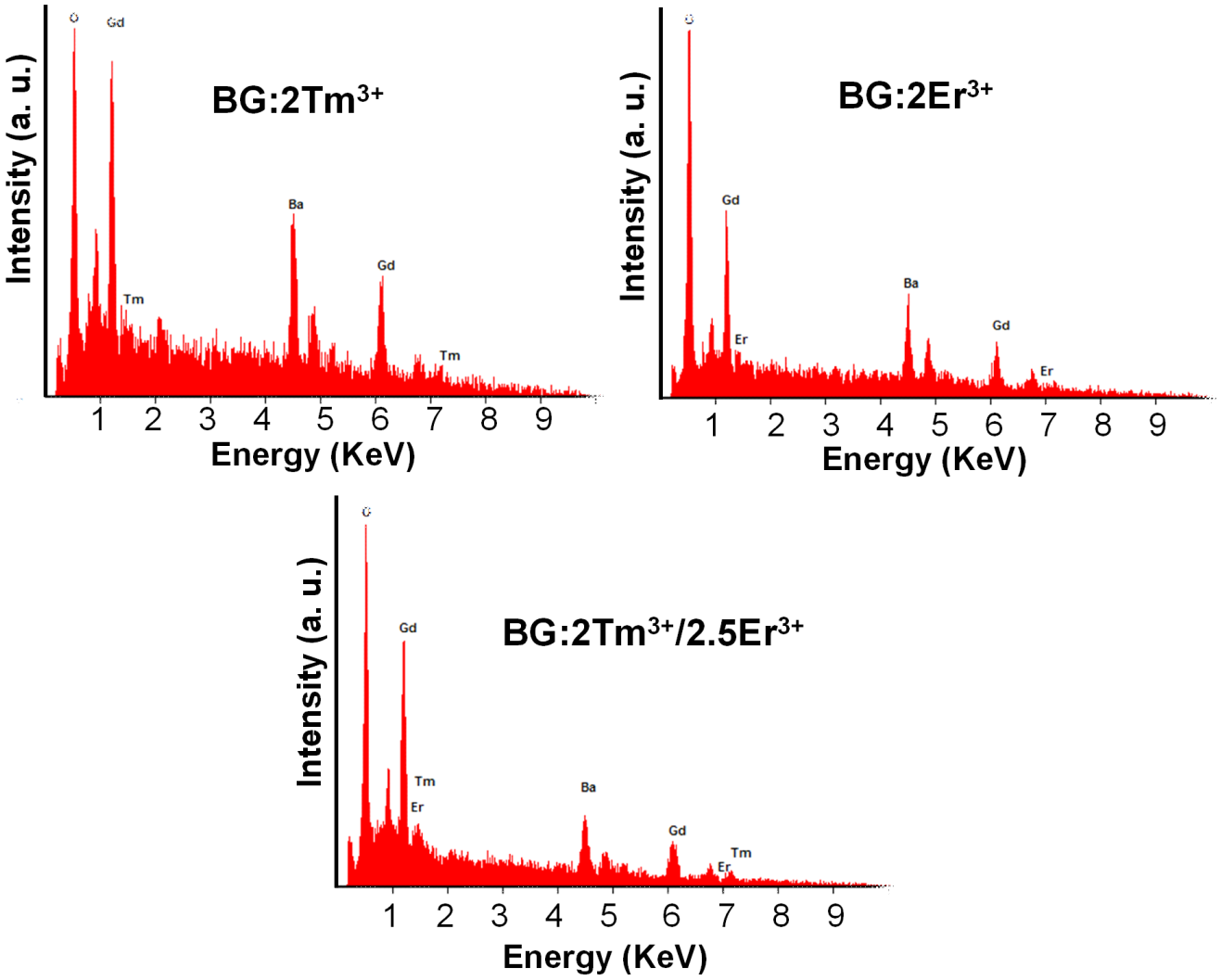

Fig. S1. EDS of the samples after annealing at 1300 °C

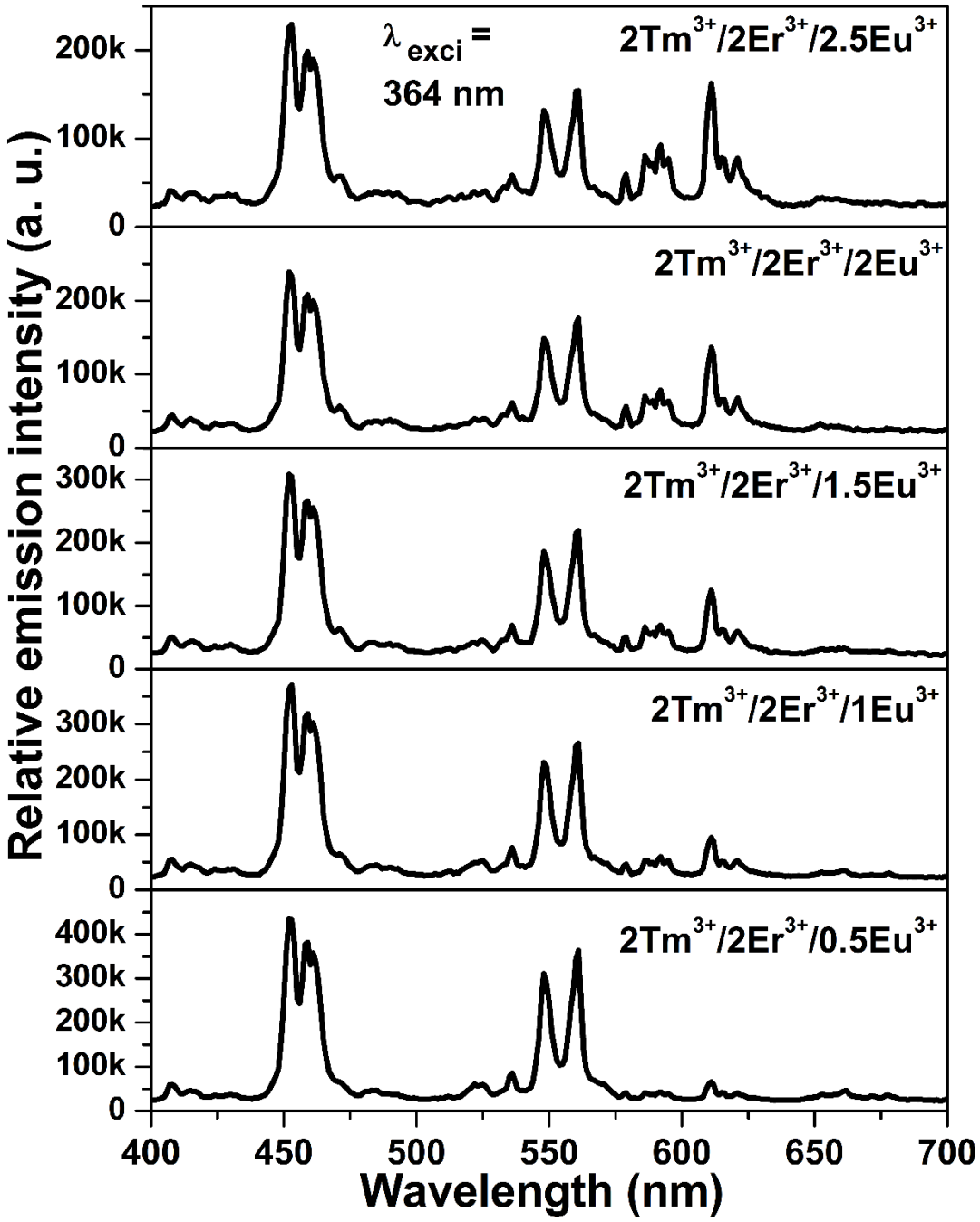

Fig. S2. PL spectra of BG:$2Tm^{3+}/2Er^{3+}$ as a function of Eu^{3+} ion concentration

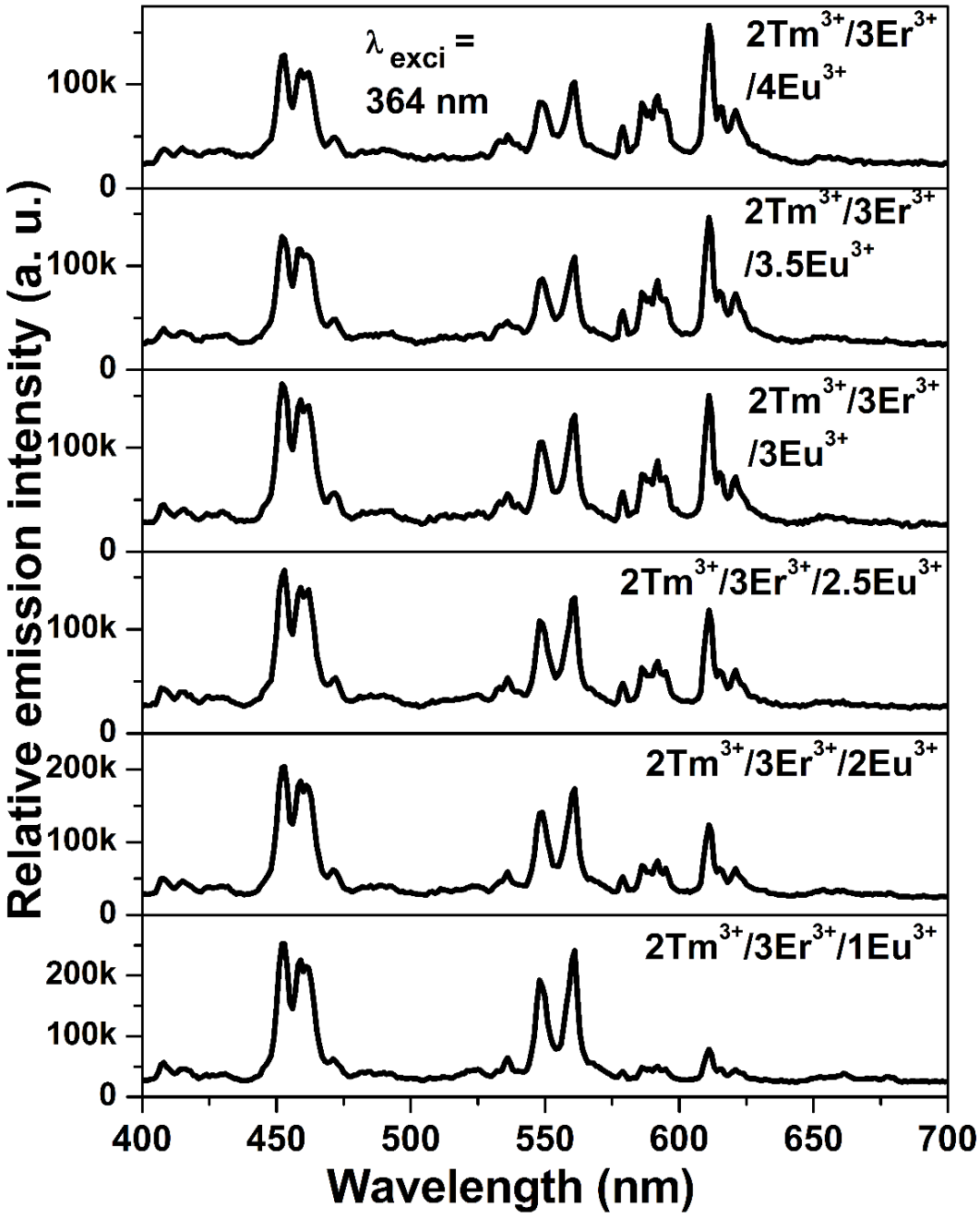

Fig. S3. PL spectra of BG:$2Tm^{3+}/3Er^{3+}$ as a function of Eu^{3+} ion concentration.

Fig. S2 and S3 showed the similar trend as BG:$2Tm^{3+}/2.5Er^{3+}/xEu^{3+}$ system.

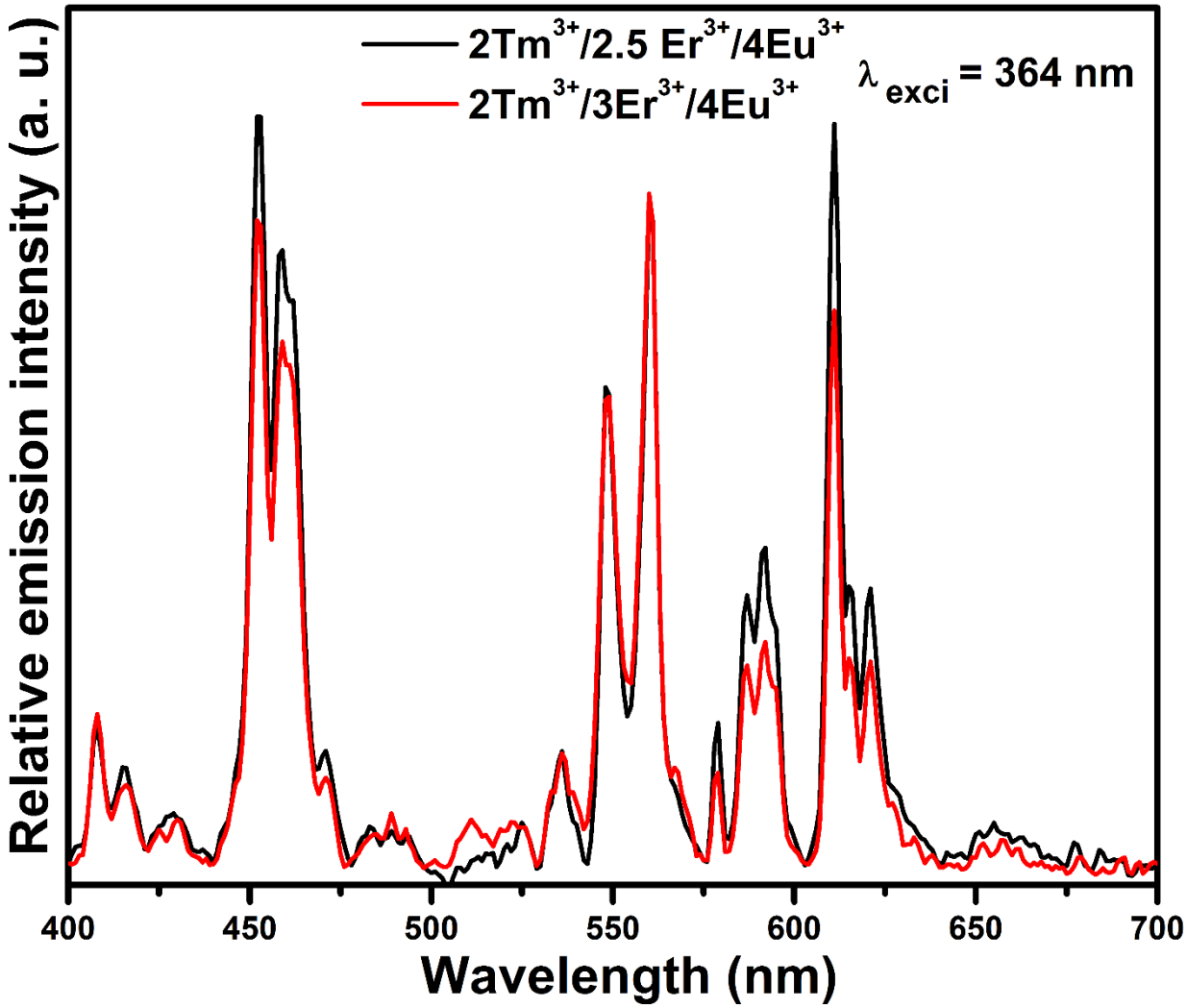

Fig. S4. PL spectra of BG:2Tm^{3+}/xEr^{3+}/4Eu^{3+} as a function of Er^{3+} ion concentration. The spectra shows the decreased emission intensities of Tm^{3+} and Eu^{3+} transitions with increased Er^{3+} ion concentration.

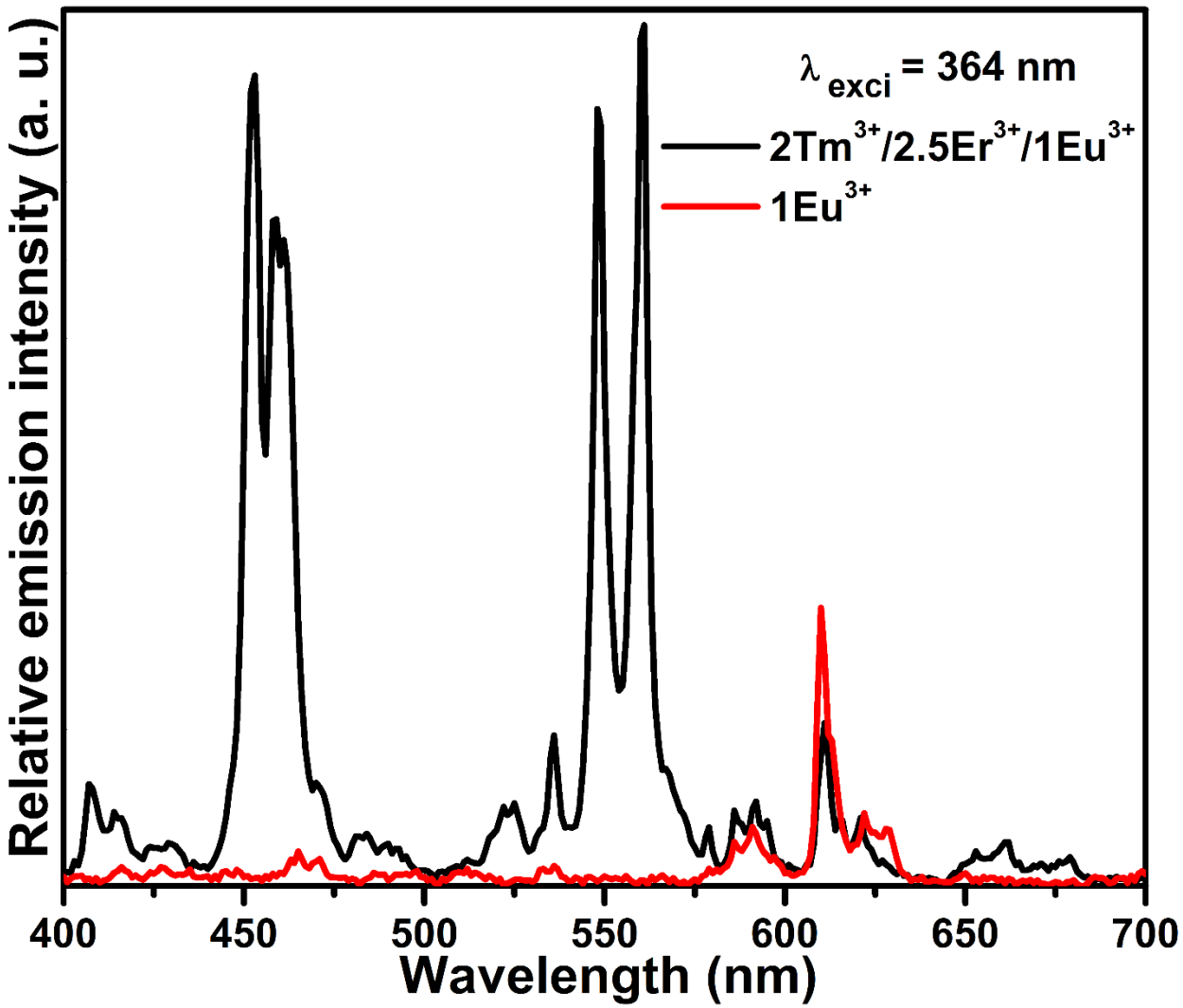

Fig. S5. PL spectra for the ($^5D_0 \rightarrow {}^7F_2$) emission intensity comparison in BG:2Tm^{3+}/2Er^{3+}/1Eu^{3+} and BG:1Eu^{3+}. The spectra show the difference in emission intensity between Eu^{3+} ions co-doped BG:2Tm^{3+}/2Er^{3+} and single-doped BG host lattice, which confirmed the cross-relaxation in this system.

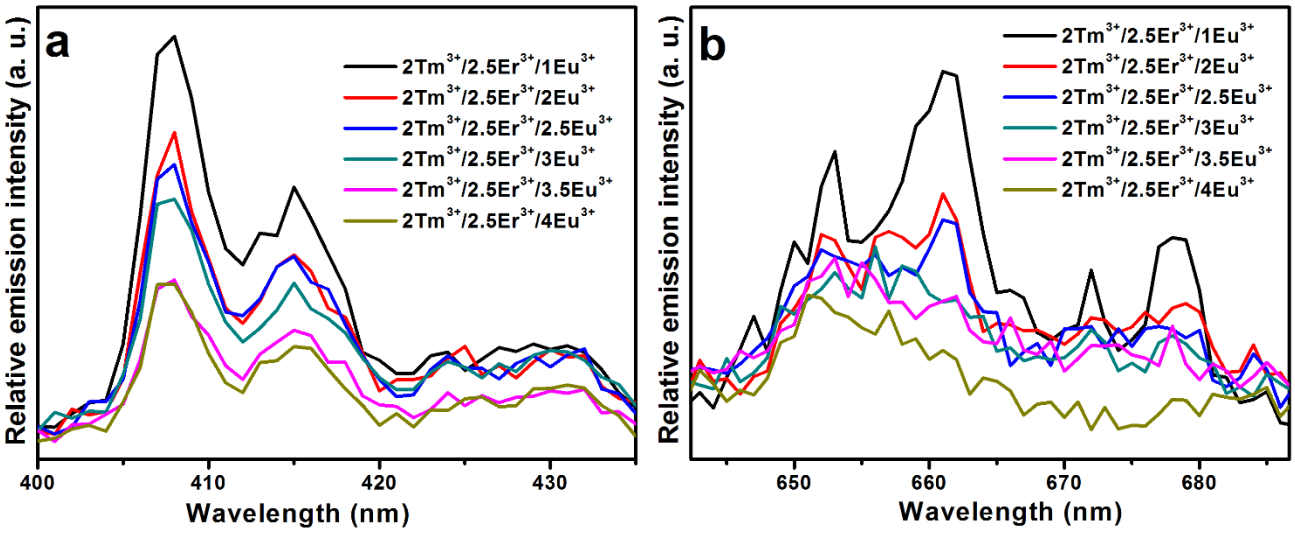

Fig. S6. PL spectra for the ($^2H_{9/2}\rightarrow{}^4I_{15/2}$) and ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) emission intensity comparison of BG:2Tm^{3+}/2Er^{3+} as a function of Eu^{3+} ion concentration. The spectra confirmed that the decreased intensity with increased concentration due to the cross-relaxation.

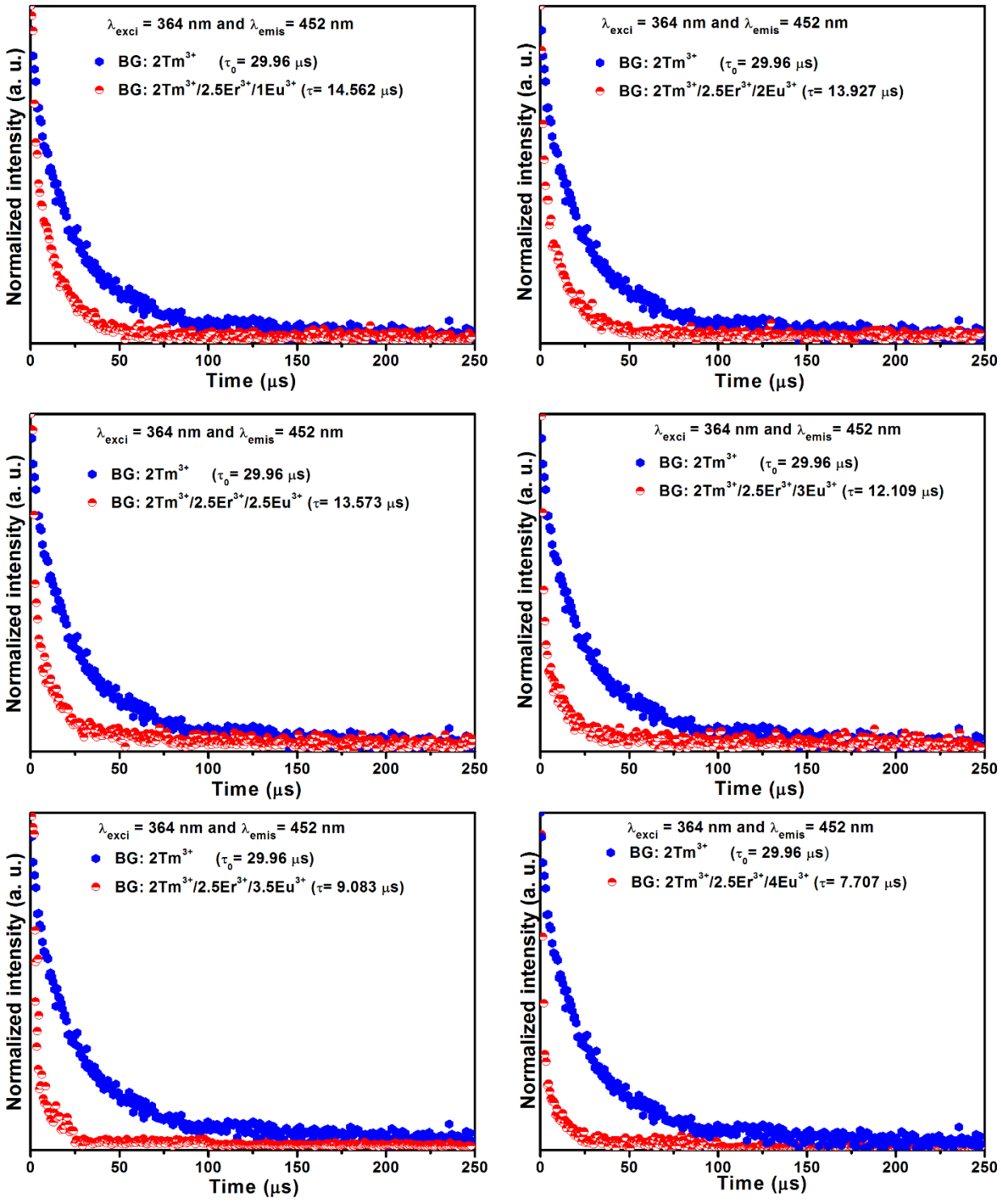

Fig. S7. Decay curves of the BG:$2Tm^{3+}$ and BG:$2Tm^{3+}$/$2.5Er^{3+}$/xEu^{3+} phosphors under the excitation at 364 nm and emission at 452 nm.

The decay curves for the BG;2Tm^{3+} and BG:2Tm^{3+}/Er^{3+}/xEu^{3+} (x=1, 2, 2.5, 3, 3.5, and 4 mol%) were measured using the 364 nm excitation and 452 nm emission wavelengths, as shown in Fig. S7. All the decay curves were well fitted to double exponential function and the obtained values were presented in the table S1. However, for comparison and calculation purpose, the average lifetime of these double exponential curves were calculated by the following equation:[1]

$$\tau_{expt} = \tau_{avg} = \frac{\int_0^\infty I(t)tdt}{\int_0^\infty I(t)dt}$$

where I(t) is the luminescence intensity at a time t. Using the decay profiles the energy transfer efficiency of Tm^{3+} was calculated and presented in the Table S1. It is worthy to mentioning that the upto 74% of energy was transferred from Tm^{3+} but from the emission spectra it was understood that the energy gained of Eu^{3+} was very low, indicates the presence of both energy transfer and cross-relaxation process.

Table S1: **Average lifetimes (τ_{avg}) and energy transfer efficiency (η) from Tm3+ to other rare-earth ions**

Phosphor	τ_1 (μs)	τ_2 (μs)	$\tau_{avg}=\frac{\int I(t)tdt}{\int I(t)dt}$ (μs)	$\eta= 1-\frac{\tau}{\tau_0}$
BG: 2Tm^{3+}	4.712	31.893	29.960	
BG: 2Tm3+/2.5Er3+/1 Eu^{3+}	3.091	16.087	14.562	0.52
BG: 2Tm3+/2.5Er3+/2 Eu^{3+}	2.904	15.541	13.927	0.54
BG: 2Tm3+/2.5Er3+/2.5 Eu^{3+}	2.513	14.291	13.573	0.55
BG: 2Tm3+/2.5Er3+/3 Eu^{3+}	2.446	13.804	12.109	0.60
BG: 2Tm3+/2.5Er3+/3.5 Eu^{3+}	1.801	11.473	9.083	0.70
BG: 2Tm3+/2.5Er3+/4 Eu^{3+}	1.208	9.115	7.707	0.74

1. F. Lahoz, I. R. Martin, J. Mendez-Ramos and P. Nunez, *J. Chem. Phys.*, 2004, **120**, 6180-6190.