Origin of visible and near IR upconversion in Yb³⁺-Tm³⁺-Er³⁺ doped BaMgF₄ phosphor through energy transfer and cross-relaxation processes

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ABSTRACT

Near infrared and green, red emission through upconversion and energy transfer processes in BaMgF₄ doped with Yb³⁺-Tm³⁺ and Yb³⁺-Tm³⁺-Er³⁺ excited at 980 nm were investigated. The BaMgF₄:Yb³⁺,Tm³⁺ phosphor showed a dominating UC emission at 800 nm. The origin of this 800 nm emission peak was explored through different possible cross-relaxation processes. The optimized composition of Yb³⁺ and Tm³⁺ was further co-doped with Er³⁺, these compositions also showed dominating 800 nm emission for lower concentrations of Er³⁺ which was gradually suppressed at higher Er³⁺ concentration. The enhancement of the visible emission of Er³⁺ in the BaMgF₄:Yb³⁺,Tm³⁺,xEr³⁺ doped phosphor suggests the efficient energy transfer from Yb³⁺ to Tm³⁺ and Tm³⁺ to Er³⁺. By tuning the concentrations of the dopants, a near white light emission under infrared excitation was also achieved.

1. Introduction

Rare-earth doped upconversion (UC) materials have drawn a great deal of attention due to their enhanced optical properties which open a way to their application in solar cells as solar spectral convertors [1], lasers [2], displays [3], bioimaging [4] and other applications [3]. Various oxide and fluoride-based host materials have been studied with different combination of rare-earth ions to explore their UC properties. Among the UC phosphors mostly fluoride-based phosphors have received much attention due to their low phonon energies, e.g. NaYF₄ [5–7] but, synthesis of phase pure NaYF₄ is not straight forward [8] and therefore other fluoride-based hosts (YF₃ [9], CaF₂ [10], Sr₂YbF₇ [11], BaYF₅ [12], BaMgF₄³) have been studied for their UC properties. Recently, we studied the UC properties of BaMgF₄ doped with Yb³⁺, Tb³⁺ and Yb³⁺, Er³⁺ [14]. In both these phosphors we obtained a characteristic emission of Tb³⁺ and Er³⁺. In the case of Tb³⁺ bright green emission was obtained at 544 nm. Based on the obtained results we proposed the use of this phosphor as a solar spectrum convertor in perovskite solar cells [13]. We also showed that the same host doped with Yb³⁺-Er³⁺ pair can be used in optical thermometry [14].

The rare-earth ion doped UC phosphors are remarkably efficient in transferring the excited state energy of the sensitizer (Yb³⁺) to the neighboring activators (Tm³⁺ or Er³⁺) which gives rise to an efficient UC emission by the non-linear anti-stokes process [15]. The UC emission

through the anti-stokes process arises due to the intra 4f transitions of rare-earth ions, these transitions are less influenced by the crystal field due to the strong shielding of the 4f orbitals by outer (5s and 5p) orbitals [15,16].

The previous downconversion (BaMgF₄:Ce³⁺,Tb³⁺) [17] and UC studies (BaMgF₄:Yb³⁺,Tb³⁺ and BaMgF₄:Yb³⁺,Er³⁺) motivated us to further explore the UC properties in this material with different rare-earth pair doping. The Tm³⁺ doped phosphors are known for their wider emission bands which vary from the UV to infrared region [4,18,19]. Furthermore, Er³⁺/Tm³⁺ co-doped with Yb³⁺ is reported to give UC emission in the blue region under 980 nm laser excitation [20]. Keeping this in mind we doped BaMgF₄ with Yb³⁺, Tm³⁺ and Er³⁺.

In this study we report the UC luminescence of BaMgF₄ doped with Yb³⁺,Tm³⁺ and Er³⁺. For Yb³⁺-Tm³⁺ doping an intense 800 nm emission was observed for all the compositions of Yb³⁺ and Tm³⁺. The strong emission of Tm³⁺ at 800 nm suggests an efficient energy transfer from Yb³⁺ to Tm³⁺. The energy transfer mechanism responsible for 800 nm emission has been explained in detail. In addition to this the effect of Er³⁺ doping on the UC emission of Tm³⁺ and possible Tm³⁺ to Er³⁺ energy transfer/cross-relaxation (CR) is also discussed.

2. Synthesis and characterization

The experimental procedure used previously for preparation of

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BaMgF₄:Yb³⁺,Tb³⁺ and BaMgF₄:Yb³⁺,Er³⁺ was adopted for the synthesis of BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ phosphor. The starting materials used were BaCl₂, MgCl₂, NH₄F, Yb(NO₃)₃, Tm(NO₃)₃ and Er(NO₃)₃. All the reagents used were of high purity procured from Sigma-Aldrich (99.999%). Stoichiometric amounts of BaCl₂, MgCl₂ and Yb(NO₃)₃, Tm(NO₃)₃, Er(NO₃)₃ were dissolved in double distilled water, in separate beakers. In the next step stoichiometric amounts of rare earths dissolved in distilled water were added dropwise to the solution mixture. Finally, a precipitate was obtained by adding NH₄F to the mixture under continuous stirring. The obtained precipitate mixture was stirred for 2 h at 80 °C and washed several times with distilled water. The dried powder was annealed at 650 °C for 4 h in open atmosphere.

The powder X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 Advance X-ray diffractometer with a Cu target, with X-ray wavelength (λ) of 0.154 nm. The morphology of the prepared phosphors was analyzed using a JSM-7800F JEOL field emission scanning electron microscope (FE-SEM), operated at 30 kV. Energy dispersive X-ray spectroscopy (EDS) was used for the composition analysis using an Oxford instruments X-Max^N 80 detector. The UC spectra and decay curves were measured using an Edinburgh Instruments FLS-980 fluorescence spectrometer. The color coordinates were calculated by Commission Internationale de L'Eclairage (CIE) software (GoCIE).

3. Results and discussion

The prepared samples were first checked with powder XRD measurements, the XRD patterns of the samples are given in Fig. S1. The relative intensities of the diffraction peaks of the samples are consistent with the standard ICDD 84-0201 diffraction data. The XRD patterns of the doped samples did not show any impurity peaks or peaks related to some other phases of the compound for all the used concentrations of dopants.

Fig. 1 shows SEM images of the synthesized BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ sample. The agglomerated rod-shaped grains were observed in the SEM morphology with size ranging from 2 to 4 μ m. The elemental mapping

and EDS spectra shows the presence of Ba, Mg and F alongwith the dopant ions. The elemental mapping further shows that the rare-earth ion doping is homogeneous throughout the sample. The unwanted elements (Cl and Au) in the EDS spectra are originated from the chlorinated precursors used during synthesis and Au sputtering while preparing the sample for SEM.

The UC PL spectra of BaMgF₄ sample doped with Yb³⁺ and Tm³⁺ measured with 980 nm excitation wavelength using a continuous laser diode are shown in Fig. 2(a) and (b). The concentrations of Yb³⁺ and Tm³⁺ were optimized individually by preparing two-separate series of samples with varied concentration of Yb³⁺ and Tm³⁺. The maximum UC emission was obtained for 0.2 mol% and 10 mol% concentrations of Tm³⁺ and Yb³⁺, respectively. The samples co-doped with Yb³⁺ and Tm³⁺ show intense UC PL emission around 800 nm, which is nearly 85 times higher in magnitude than the UC emission in the visible region. The dominating NIR emission at 800 nm was due to the transition of ³H₄ to ³H₆ energy levels of Tm³⁺. The other UC PL peaks in the visible region were attributed to the ¹I₆ → ³F₄ (347 nm), ¹D₂ → ³F₄ (451 nm), ¹G₄ → ³F₄ (648 nm), ¹D₂ → ³H₆ (361 nm), ¹G₄ → ³H₆ (477 nm), ³F₃ → ³H₆ (700 nm) transitions [19]. The 980 nm excitation facilitates the excitation of the Yb³⁺ ions, which have a large absorption cross-section in the NIR region (around 980 nm) [21], and subsequent energy transfer from Yb³⁺ to Tm³⁺.

3.1. Energy transfer process

The UC luminescence can be achieved through a number of excitation and energy transfer processes such as ground state absorption (GSA), excited state absorption (ESA), CR energy transfer and energy transfer upconversion (ETU) [21]. The UC emission through different excitation and emissions channels is illustrated in the schematic energy level diagram of Yb³⁺ and Tm³⁺, as shown in Fig. 3. The excitation by 980 nm laser promotes electrons from the ground state (²F_{7/2}) of Yb³⁺ to the excited state (²F_{5/2}) which, while relaxing to the ground state, transfers energy (process i) and populate the ³H₅ level of Tm³⁺. The ³H₅ level can also be populated through GSA by absorbing a 980 nm NIR

Fig. 1. (a–c) SEM images, (d–i) elemental mapping, and (j) EDS spectra of BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ (Yb = 10 mol %, Tm = 0.2 mol %, Er = 0.2 mol %) annealed sample.

Fig. 2. UC PL emission spectra of (a) BaMgF₄:Yb³⁺,xTm³⁺ (Yb = 2 mol% fixed) phosphor, (b) enlarged view of the UC emission in the 300–750 nm region. UC PL emission spectra of (c) BaMgF₄:xYb³⁺,Tm³⁺ (Tm = 0.2 mol% fixed) phosphor, (d) enlarged view of the UC emission in the 300–750 nm region. The UC emission spectra were measured with 980 nm excitation wavelength, at 1 W fixed laser power.

Fig. 3. Schematic energy level model illustrating various types of excitation/emission pathways, possible energy transfer between Yb³⁺-Tm³⁺ pairs and CR mechanisms between Tm³⁺ ions.

photon, but the absorption cross-section of Tm³⁺ is weak this gives rise to a weak UC emission in singly Tm³⁺ doped phosphors. The electrons in the ³H₅ level relax to the ³F₄ level through multi-phonon emission. The energy transfer (process ii) from Yb³⁺ further pump the electrons in the ³F₄ level to the ³F₂ level, the ³F₂ level can also be populated through ESA. The multi-phonon relaxation from ³F₂ level populates the ³F₃ and ³H₄ levels, from which the electrons radiatively relax to the ³H₆ level with 700 and 800 nm UC emissions, respectively. The ³H₄ level can also be populated through ETU and CR processes, as discussed later. Two NIR photons are sufficient to populate the ³F₂ level, but excitation of higher energy levels needs more than two NIR photons. The electrons in the

populated ³H₄ level can be further excited to ¹G₄ level (process iii). The electrons in the ¹G₄ level undergo relaxation to ³F₄ and ³H₆ levels with 678 and 477 nm UC emissions. The ¹D₂ level cannot be populated through ESA due to the large energy mismatch (3500 cm⁻¹) between ¹D₂ and ¹G₄ levels [22]. Instead, the ¹D₂ level can be populated via the CR process between Tm³⁺ ions, as discussed later. The electrons from the ¹D₂ level make transition to ³F₄ and ³H₆ levels with 451 and 361 nm UC emissions [19]. The additional energy transfer from Yb³⁺ to Tm³⁺ (process iv) populates the ³P₂ level of Tm³⁺ from the ¹D₂ level. The transition from the ³P₂ level is very rarely observed in inorganic phosphors since electrons in the ³P₂ level relax non-radiatively through the ³P_{0,1} levels to the ¹I₆ level and it also requires more than four NIR photons in the excitation [22]. The electrons can undergo a radiative transition from the ¹I₆ level to the ³F₄ level with 347 nm emission. Due to the greater number of NIR photons involved in the excitation of this high energy level usually the transitions observed from this level have lower probability and hence the weak UC PL intensity [22].

In the UV-visible spectral range (300–750 nm), at lower Tm³⁺ concentration the ¹G₄ → ³H₆ (3-photon) and ³F₃ → ³H₆ (2-photon) radiative transitions have similar emission intensities, but for higher Tm³⁺ doping the 2-photon process dominated, which indicates the increase in population of the low-lying excited level ³F₃. Furthermore, for the lower Yb³⁺ concentration the 3-photon process was dominant, whereas for higher Yb³⁺ concentration the 2-photon process was dominant. In the entire UC emission range, the 800 nm emission arising from ³H₄ → ³H₆ was dominant for all the concentrations of Yb³⁺ and Tm³⁺. The BaMgF₄:Yb³⁺,Tm³⁺ has a weak 800 nm emission for lower concentration of Tm³⁺, but by increasing the Tm³⁺ concentration the intensity of 800 nm peak increased significantly, see Fig. 1(a). This is attributed to the enhanced population of the ³H₄ level due to the simultaneous occurrence of ETU and CR processes as shown in Fig. 3. The CR process

becomes more dominant when the spatial distance between neighboring Tm^{3+} ions decreases with an increase in the concentration of Tm^{3+} in the host lattice [6]. The emission intensity of this peak was further increased with increasing the concentration of Yb^{3+} ions. The increase in Yb^{3+} concentration enhances the absorption and facilitates the energy transfer induced by the decreased spatial distance between Yb^{3+} and Tm^{3+} [23]. The $^3\text{H}_4$ energy level, which is responsible for the 800 nm NIR emission, can be populated through a number of energy transfer processes. The first one is through the ESA from $^3\text{F}_4$ to $^3\text{F}_3$, which non-radiatively decays to $^3\text{H}_4$ level, as discussed earlier. The second possibility is through ETU process ($^3\text{F}_4 \rightarrow ^3\text{H}_6$ and $^3\text{F}_4 \rightarrow ^3\text{H}_4$) [24,25]. In this ETU process sequential excitation of two Tm^{3+} ions to the $^3\text{H}_4$ level takes place through absorption of two NIR photons. The excited Tm^{3+} ions transfer energy via a dipole-dipole resonant interaction through non-radiative process due to the presence of energy mismatch between the $^3\text{F}_4 \rightarrow ^3\text{H}_4$ absorption and the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission. This promotes one ion to the $^3\text{H}_4$ level and demotes the other to the $^3\text{H}_6$ level, as shown in Fig. 3. The other way to populate the $^3\text{H}_4$ level is through CR processes; the CR1 process ($^1\text{G}_4 + ^3\text{F}_4 \rightarrow ^3\text{H}_4 + ^3\text{F}_2$) [6] populates the $^3\text{F}_2$ level from which electrons non-radiatively make a transition to $^3\text{H}_4$ level and populate the $^3\text{H}_4$ level and second CR process also populates the $^3\text{H}_4$ level through CR2 ($^1\text{D}_2 + ^3\text{H}_6 \rightarrow ^3\text{F}_2 + ^3\text{H}_4$) [26,27]. The dominant 800 nm emission could be due to the contribution from all these three processes. On the other hand, the CR3 and CR4 processes play a vital role in populating the $^1\text{D}_2$ level through CR energy transfer [22,28,29], which gives rise to 361 and 451 nm emission. However, in the present phosphor the intensity of the UC emission arising from the $^1\text{D}_2$ level is weak which suggests the minor contribution of CR3 and CR4 processes in the UC emission.

The PL intensity versus laser power plots shows a gradual increase in PL intensity with increase in power, as shown in Fig. 4. The PL spectra do not show any additional peaks or degradation in the PL intensity with increase in power, see Fig. S2. The laser power dependent UC spectra were recorded to determine the number of NIR photons involved in the excitation processes, which can be estimated using the following relation

$$I_{\text{UC}} \propto P^n, \quad (1)$$

Where, I_{UC} is the integrated UC emission intensity, P is the laser power and 'n' represents the number of photons involved in the upconversion process. The value of n can be obtained from the slope of line fitted to the plot of $\log(I_{\text{UC}})$ versus $\log(P)$. The pump power variation analysis shows slopes to be 1.17, 1.28, 1.87 and 2.9 for peaks at 800, 700, 477 and 347 nm, respectively. To obtain emission from the $^1\text{I}_6$, $^1\text{G}_4$ and $^3\text{F}_3$, $^3\text{H}_4$ levels a minimum of five, three and two NIR photons are needed,

respectively, as shown in Fig. 3. However, the calculated slopes indicated the smaller number of NIR photons involved in the population of these levels. Often the multi-phonon emission and CR processes are responsible for the observed smaller values of slope [14,22]. The UC intensity versus laser power plots show saturation in the UC intensity at higher laser powers, which is attributed to the population exhaustion at the ground state and increase in the temperature of the sample at higher laser power which leads to the quenching in luminescence intensity [30, 31].

4. Decay analysis

The UC decay curves were fitted with bi-exponential function $I(t) = I(0) + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ where, A_1 and A_2 are the constants, t is time, τ_1 and τ_2 are the lifetimes, and $I(t)$ and $I(0)$ are the UC intensities at time t and the background intensity, respectively. The decay curves were fitted using the above function and the decay lifetimes were extracted, as shown in Fig. 5. The decay lifetime for the different concentrations of Yb^{3+} are given in Table 1. The decay lifetime increased continuously with an increase in Yb^{3+} concentration. The gradual increase in decay lifetime can also be correlated with the UC PL spectra where there is continuous rise in PL intensity with an increase in the Yb^{3+} concentration. The decay lifetime calculated for the different concentrations of Tm^{3+} is in the same range and showed a drop for higher concentration of Tm^{3+} which could be attributed to the concentration quenching, see Table S1 in supporting information. The decrease in decay lifetime can be either due to the formation of Yb^{3+} pairs [32] or Tm^{3+} to Yb^{3+} energy back transfer [33], both of which leads to the luminescence quenching. The quenching effect is also observed in the UC PL spectra where the UC PL emission intensity decreased with an increase in the Tm^{3+} concentration. The probability of Yb^{3+} pair formation is less as we did not see quenching in PL emission when the concentration of Yb^{3+} was varied.

5. $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+}$ doped samples

The color tunability in the UC phosphors can be obtained by either varying the dopant concentration or by doping the different rare earth ions. In present system in order to improve the emission intensities in visible region we doped the optimized composition with different concentration of Er^{3+} , also in pervious study we obtain an efficient emission from Er^{3+} , so in this study we wanted to know how the presence of Tm^{3+} influence the emission of Er^{3+} . In the $\text{Yb}^{3+}-\text{Tm}^{3+}-\text{Er}^{3+}$ co-doped sample we examined the effect of Er^{3+} and Tm^{3+} doping on UC emission. The Er^{3+} doped $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ samples show characteristic emission of Er^{3+} along with that of Tm^{3+} , as shown in Fig. 6. The emission peak at 521, 540 and 651 nm are associated with Er^{3+} emission and attributed to

Fig. 4. The logarithmic dependence of UC emission intensity as a function of logarithmic pump power for (a) $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ ($\text{Yb} = 2 \text{ mol } \%$ and $\text{Tm} = 0.2 \text{ mol } \%$) phosphor, (b) $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ ($\text{Yb} = 10 \text{ mol } \%$ and $\text{Tm} = 0.2 \text{ mol } \%$) phosphor at 800, 700, 477 and 347 nm emissions originating from the Tm^{3+} .

Fig. 5. Luminescence decay curves of BaMgF₄:Yb³⁺,Tm³⁺ phosphor under 980 nm excitation for Tm³⁺ emission at (a) 477 nm (¹G₄ → ³H₆) and (b) 800 nm (³H₄ → ³H₆), for different concentrations of Yb³⁺ at Tm³⁺ = 0.2 mol% fixed.

Table 1

Luminescence decay time calculated for BaMgF₄:Yb³⁺,Tm³⁺ (Tm = 0.2 mol%) phosphor.

BaMgF ₄ :Yb _x Tm	τ (μs) @361 nm	τ (μs) @477 nm	τ (μs) @800 nm
x = 1 mol%	54	289	153
x = 2 mol%	95	392	168
x = 5 mol%	67	326	237
x = 7 mol%	84	443	460
x = 10 mol%	107	475	493

the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively. The intensity of 800 nm peak is still higher in BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ doped samples for lower concentration of Er³⁺, but for higher concentrations of Er³⁺ the emission intensity of the 800 nm peak dropped drastically, whereas the emission intensity of the peak associated with Er³⁺ goes up and increased gradually with an increase in Er³⁺ concentration. The co-doping of Er³⁺ facilitated CR processes between Tm³⁺ and Er³⁺ which altered the intensities of green/red emissions of Er³⁺ (⁴S_{3/2} → ⁴I_{15/2}/⁴F_{9/2} → ⁴I_{15/2}) and NIR (³H₄ → ³H₆) emission of Tm³⁺ [14]. Tm³⁺ emits in the blue and green regions of the visible spectrum, whereas the Er³⁺ ions have a dominant emission in the green region. The effect of Er³⁺ doping on the color tunability of the phosphor can be clearly observed in Fig. 6(b). The color of the phosphor can be tuned from bluish green to yellow with an increase in the concentration of Er³⁺. Further, it is possible to obtain a white light UC emission in this phosphor by optimizing the concentration of Er³⁺ and Tm³⁺. The increase in doping of Er³⁺ in steps of smaller concentration can lead to

white light emission, since for the first two concentrations of Er³⁺ the white light emission region in the CIE diagram lies in between these two concentrations.

In order to understand the energy transfer mechanism between Yb³⁺-Tm³⁺ and Er³⁺ the schematic energy level diagram is drawn for BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ as shown in Fig. 7. Both the rare-earth ions (Tm³⁺ and Er³⁺) can be easily excited through energy transfer from Yb³⁺ under 980 nm excitation to generate the visible/NIR UC emission. For a lower concentration of Er³⁺ in BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ there is energy transfer from Tm³⁺ to Er³⁺ which results in weak Er³⁺ emission, due to

Fig. 7. Schematic energy level model illustrating possible CR mechanisms between Tm³⁺-Er³⁺ pair.

Fig. 6. (a) UC emission spectra of BaMgF₄:Yb³⁺,Tm³⁺,Er³⁺ phosphor (Yb = 10 mol%, Tm = 0.2 mol%) with variation in Er³⁺ concentration under 980 nm excitation. (b) CIE chromaticity diagram for visualization of color tunability in BaMgF₄:Yb,Tm³⁺,Er³⁺ (Yb = 10 mol%, Tm = 0.2 mol% fixed) phosphor on varying Er³⁺ concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

lower concentration of Er^{3+} , and a strong Tm^{3+} UC emission. But, as the concentration of Er^{3+} increased, the relative UC emission of Er^{3+} enhanced with respect to Tm^{3+} emission. At higher concentration of Er^{3+} the dominating green/red emission ($^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) from Er^{3+} was evident.

Under 980 nm excitation, there is first energy transfer from Yb^{3+} to Tm^{3+} takes place which is already discussed earlier. The $^3\text{F}_4$ level of Tm^{3+} transfers its energy non-resonantly to the $^4\text{I}_{13/2}$ level of Er^{3+} through the CR1 mechanism $^3\text{H}_4(\text{Tm}) + ^4\text{I}_{15/2}(\text{Er}) \rightarrow ^3\text{F}_4(\text{Tm}) + ^4\text{I}_{13/2}(\text{Er})$ [34]. The decrease in intensity of the 800 nm peak of Tm^{3+} suggests depopulation of its $^3\text{H}_4$ level with an increase in the Er^{3+} concentration. The CR1 process populates the $^4\text{I}_{13/2}$ level of Er^{3+} , following which ESA populates the $^4\text{F}_{9/2}$ level of Er^{3+} which is responsible for the red emission. In the present case the red emission around 650 nm is due to the overlap of red emission from both Tm^{3+} ($^1\text{G}_4 \rightarrow ^3\text{F}_4$) and Er^{3+} ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$). The 650 nm emission can also be achieved through a multiphoton relaxation mediated sequential CR which involves the following CR pathways, $^4\text{I}_{13/2}(\text{Er}) + ^3\text{H}_4(\text{Tm}) \rightarrow ^4\text{I}_{9/2}(\text{Er}) + ^3\text{H}_6(\text{Tm})$ (CR2) [34], and $^1\text{G}_4(\text{Tm}) + ^4\text{I}_{15/2}(\text{Er}) \rightarrow ^3\text{F}_4(\text{Tm}) + ^4\text{F}_{9/2}(\text{Er})$ (CR3) [35]. The green emission of Er^{3+} can be achieved by populating the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels of Er^{3+} through ESA from the $^4\text{I}_{11/2}$ level of Er^{3+} . The CR4 process $^3\text{F}_2(\text{Tm}) + ^4\text{I}_{11/2}(\text{Er}) \rightarrow ^3\text{F}_4(\text{Tm}) + ^4\text{F}_{7/2}(\text{Er})$ [36] can populate the $^4\text{F}_{7/2}$ level of Er^{3+} from which an electron can non-radiatively makes transition to the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels. Green emission can be obtained when the electrons from these levels make transitions to the $^4\text{I}_{15/2}$ level.

The lifetime calculated from the decay curves of the $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}, \text{Er}^{3+}$ phosphor, shown in Fig. S3, show a reduction in the lifetime of $^1\text{G}_4$, $^3\text{H}_4$ levels after Er^{3+} doping, see Table S2, in comparison to the lifetime values extracted from decay curves of the $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphor, see Table 1. This suggests energy transfer from Tm^{3+} to Er^{3+} . To our surprise the decay values for $^3\text{H}_4$ (800 nm) at higher Er^{3+} concentration again started increasing, this could be due to the backward energy transfer from Er^{3+} to Tm^{3+} .

6. Conclusion

In conclusion, we achieved dual emission (visible and NIR) through frequency upconversion in Yb^{3+} sensitized $\text{Tm}^{3+}\text{-Er}^{3+}$ doped BaMgF_4 phosphor. The $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ show characteristic UC emission peaks viz. 347, 477, 700 and 800 nm corresponding to $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{G}_4 \rightarrow ^3\text{H}_6$, $^3\text{F}_3 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$, respectively. We explored the origin of dominant 800 nm emission in the $\text{Yb}^{3+}\text{-Tm}^{3+}$ doped sample which was attributed to the prominent ETU and CR processes. The origin of color tunability in $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Er}^{3+}$ doped samples with changing the Er^{3+} concentrations was also investigated, which is influenced by the Tm^{3+} to Er^{3+} energy transfer.

Supplementary material

See supplementary materials for the XRD patterns of undoped and doped BaMgF_4 sample, variation in the upconversion emission intensity as a function of the excitation laser power for $\text{BaMgF}_4:\text{Yb}, \text{Tm}$ sample, measured decay curves of $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}, \text{xEr}^{3+}$ sample and calculated luminescence decay time of $\text{BaMgF}_4:\text{Yb}, \text{Tm}_x$ and $\text{BaMgF}_4:\text{Yb}, \text{Tm}, \text{Er}_x$ sample.

Author contributions

A.K. prepared the samples and performed optical measurement with help from R.E.K. B.P.K. conceived the project and participated in discussion to interpret the results primarily with R.E.K. and H.C.S. B.P.K. prepared the manuscript including inputs from all the authors. All authors have given approval to the final version of the manuscript.

Novelty statement

The $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphor showed a dominating UC emission at 800 nm. The optimized composition of Yb^{3+} and Tm^{3+} was further co-doped with Er^{3+} , these compositions also showed dominating 800 nm emission for lower concentrations of Er^{3+} which was gradually suppressed at higher Er^{3+} concentration. The enhancement of the visible emission of Er^{3+} in the $\text{BaMgF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}, \text{xEr}^{3+}$ doped phosphor suggests the efficient energy transfer from Yb^{3+} to Tm^{3+} and Tm^{3+} to Er^{3+} . We discussed the origin of dominant 800 nm emission in the $\text{Yb}^{3+}\text{-Tm}^{3+}$ doped sample which was attributed to the prominent ETU and CR processes. The origin of color tunability in $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Er}^{3+}$ doped samples with changing the Er^{3+} concentrations were discussed, which is influenced by the Tm^{3+} to Er^{3+} energy transfer.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2019.109511>.

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