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# Enhancement of Upconversion emission and Temperature Sensing of Paramagnetic Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> Phosphor via Li<sup>+</sup>/Mg<sup>2+</sup> Co-doping

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#### ABSTRACT

Herein, enhancement of upconversion emission and temperature sensing in  $\text{Li}^+/\text{Mg}^{2+}$  co-doped Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>:  $\text{Er}^{3+}/\text{Yb}^{3+}$  is reported. The upconversion emission enhancement of 53 and 21 times is observed in green (524 nm) and red (660 nm) emission bands via simultaneous co-doping of  $\text{Li}^+/\text{Mg}^{2+}$  ions and is explained in terms of radiative and non-radiative transition rates. High thermal sensitivity of the material is realized upon  $\text{Li}^+/\text{Mg}^{2+}$  co-doping by measuring the fluorescence intensity ratio of two thermally coupled energy levels ( $^2\text{H}_{11/2}$  &  $^4\text{S}_{3/2}$ ) of  $\text{Er}^{3+}$  ion. The maximum absolute sensitivity of 0.0230 K<sup>-1</sup> at 513 K is found for present material and is among the highest measured sensitivities for luminescence based thermometers. Additionally, improved magnetization and magnetic mass susceptibility is also observed on co-doping of  $\text{Li}^+/\text{Mg}^{2+}$  in the material. The result suggests that simultaneous incorporation of  $\text{Li}^+/\text{Mg}^{2+}$  is an effective approach for enhancing multifunctionality of Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>:  $\text{Er}^{3+}/\text{Yb}^{3+}$  phosphor and this material has potential applications in color displays, high temperature sensing and magnetic resonance imaging.

#### Keywords: Upconversion; Temperatures sensing; Magnetic property; Multifunctional material

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#### 1. Introduction

The last decade has seen enormous growth in the search of highly efficient upconversion nanaomaterials capable of converting near infrared (NIR) photons into visible or ultraviolet (UV) radiation. The upconversion (UC) luminescence is generally achieved in rare earth (RE) ions due to their abundant intra-4f configurational energy levels with several metastable levels [1]. The RE based upconversion phosphors have potential applications in biological imaging, optical temperature sensing, drug delivery, cancer therapy, display devices, security applications, solar light conversion etc. [2-7]. The RE ions (such as Ho<sup>3+</sup>, Er<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup> and Tm<sup>3+</sup>) doped UC phosphors as optical temperature sensors have received considerable attention in recent years because they can provide non-contact temperature measurement in nanometre to submicron scale by probing the temperature dependent fluorescence intensity ratio (FIR) of two thermally coupled energy levels [8-13]. Among all the RE ions,  $Er^{3+}$  is most popular activator for optical temperature sensors due to its two suitable thermally coupled energy levels,  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  with an energy gap of ~ 770 cm<sup>-1</sup> [14-16]. Many researchers are involved in the investigation of optical temperature sensing behavior based on the FIR technique [16-19]. Recently, Tang et al. [16] have reported temperature sensitivity as high as 0.0087 K<sup>-1</sup> for La<sub>2</sub>O<sub>3</sub> codoped with Yb<sup>3+</sup> and Er<sup>3+</sup>. Wang et al. [17] have reported improvement in temperature sensitivity of CaWO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> phosphors by doping with Li<sup>+</sup>,  $Sr^{2+}$  and  $Mg^{2+}$  ions. The effect of  $Yb^{3+}$  concentration on temperature sensing behaviour of  $Gd_2TiO_5$ :  $Er^{3+}/Yb^{3+}$  phosphor has been investigated by Liao et al. [18] and found that sensor sensitivity decreases with increasing Yb<sup>3+</sup> concentration.

It is well known that UC emission efficiency is strongly dependent on the host lattice and its interaction with the dopant ions. Generally, low phonon frequency host materials can minimize the multiphonon relaxation rate and offer high UC efficiency [16, 19]. Among various RE doped materials, molybdates with scheelite-type structure such as  $MMoO_4$  (M = Ca, Sr & Ba), RE<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (RE= Gd, Y & La), Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>, Y<sub>4</sub>MoO<sub>9</sub>, La<sub>2</sub>MoO<sub>6</sub> etc. have been extensively studied as hosts owing to their high emission efficiency, excellent chemical and thermal stability. Such materials also have broad optical transparency in the near-UV region [20-25]. These features make them suitable for applications in optoelectronics, scintillators,

catalysis etc. [22]. The  $Gd_2Mo_3O_9$  is recognized as one of the excellent up/down conversion luminescent material and is used by several researchers over the past few years [23, 26, 27]. Moreover, paramagnetic  $Gd^{3+}$  ions based host matrices are used as a contrast agents for magnetic resonance imaging [28-30]. Therefore,  $Gd_2Mo_3O_9$  is considered to be an ideal bi-functional material that exhibits luminescence as well as magnetic properties simultaneously and such combination could be used as a dual mode probe for biomedical applications [29, 30].

Improving the luminescence efficiency of RE doped materials is of great importance to broaden their applications, especially in bio-medical field [31]. The UC luminescence of RE doped materials depends on the probability of their intra-4f electronic transition, which is greatly affected by the symmetry of crystal field around RE ions [32]. Thus, tailoring the local crystal field around RE ions is an effective method to improve the UC luminescence intensity and hence is the topic of recent research interest. Many researchers have reported the effect of non-RE ions (e.g.,  $Sc^{3+}$ ,  $Fe^{3+}$ ,  $Bi^{3+}$ ,  $Cd^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Li^+$ ,  $K^+$ ,  $Mn^{2+}$ ) to enhance the UC luminescence intensity [33-40]. Recently, Li et al. [33] have reported that UC luminescence intensity of BiPO<sub>4</sub>:  $Er^{3+}/Yb^{3+}$  phosphor can be enhanced by co-doping of Sc<sup>3+</sup> ions. The effect of Fe<sup>3+</sup> tri-doping on the UC luminescence of NaGdF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> nanoparticles has been studied by Ramasamy et al. [34] and have reported an enhancement of 34 and 30 times for green and red emission bands, respectively. Zhu et al. [36] have reported UC enhancement in LiYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals via co-doping of Cd<sup>2+</sup> ions. The effect of  $Mg^{2+}$  tri-doping on UC of  $\beta$ -NaGdF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals has been studied by Zhao et al. [32]. Other attempts have also been made to enhance the luminescence intensity via simultaneous co-doping of two non-RE ions or alkali metal ions [41-43]. However, this strategy has not yet been explored on variety of phosphors and hence more research is required. Recently, our group has reported the effect of simultaneous incorporation of alkali metal ions (K<sup>+</sup>/Na<sup>+</sup>) into CaMoO<sub>4</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> phosphor and has reported 36 and 5 times enhancement in green and red emission bands [41]. Astha et al. [42] have reported an enhancement in the blue UC emission intensity by co-doping of  $Zn^{2+}-Mg^{2+}$  ions in La<sub>2</sub>O<sub>3</sub>:  $Tm^{3+}/Yb^{3+}$  phosphor. The luminescence enhancement in Gd<sub>2</sub>O<sub>3</sub>: Ln<sup>3+</sup> (Ln = Yb/Er, Eu) nanocrystals by dual co-doping of  $\text{Li}^+/\text{Zn}^{2+}$  ions has been studied by Li et al. [43]. All these

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researchers have proved that co-doping of two ions (non-RE or alkali metal ions) simultaneously into the host lattice is a better approach to achieve high luminescence intensity as compared to single co-doping. The investigations on the improvement of UC efficiency by simultaneous co-doping of  $\text{Li}^+/\text{Mg}^{2+}$  has not yet been carried out to the best of authors knowledge.

Here, authors have tried to introduce  $Li^+/Mg^{2+}$  ions into  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  crystal lattice to see its effect on UC emission property. Authors have also investigated the magnetization of sample after co-doping of  $Li^+/Mg^{2+}$ . The temperature dependence of magnetization properties has studied using zero-field-cooled and field-cooled procedures in an applied magnetic field. The scope of the present work is to offer an effective way to enhance the multi-functionality of  $Gd_2Mo_3O_9$  phosphor via co-doping of  $Li^+/Mg^{2+}$  with  $Er^{3+}/Yb^{3+}$  ions.

#### 2. Experimental details

#### 2.1 Material synthesis

A series of Li<sup>+</sup>,  $Mg^{2+}$  and Li<sup>+</sup>/ $Mg^{2+}$  ions co-doped  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  phosphor was prepared via co-precipitation method using ethylene glycol (EG) as chelating agent. The compositions of the samples were chosen as follows:

 $(96.7 - x - y) Gd_2Mo_3O_9 + 0.3 mol\% Er_2O_3 + 3 mol\% Yb_2O_3 + x Li_2CO_3 + y MgCO_3$ 

Where,

$$x = 0 \text{ mol}\%$$
,  $y = 0 \text{ mol}\%$  for  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  (sample named as M)

$$x = 2, 4, 6 \text{ and } 8 \text{ mol}\%, y = 0 \text{ mol}\%$$
 for Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup>/Li<sup>+</sup> (MLi<sub>6</sub>)

x = 0 mol%, y = 2, 4, 6 and 8 mol% for  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}/Mg^{2+}$  (MMg<sub>4</sub>)

x = 1, 1.5, 2, 2.5 and 3 mol%, y = 4 mol% for  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}/Li^+/Mg^{2+}$  (MLi<sub>2</sub>Mg<sub>4</sub>)

The starting precursors,  $Gd_2O_3$  (99.99 %, Merck, India),  $Er_2O_3$  (99.99 %, Otto, India),  $Yb_2O_3$  (99.99 %, Otto, India),  $Mg_2CO_3$  (99.99 %, Merck, India),  $Li_2CO_3$  (99.99 %, Merck, India) and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (99 %, Merck, India) were taken into a stoichiometric ratio. In a typical

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synthesis process, the nitrates of the chemicals were prepared by dissolving oxides and carbonates in concentrated nitric acid (HNO<sub>3</sub>). All the prepared nitrates were mixed together and extra amount of nitric acid was removed by evaporation with addition of water under continuous stirring on a magnetic stirrer whose hot plate was kept at 80 °C. After that ammonium heptamolybdatetetrahydrate (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O solution was mixed into the above solution. To prevent the aggregation of particles, 25 ml of ethylene glycol (EG) was added as a chelating agent into the final solution. The PH of the resultant solution was kept at 9.0 and left for 12 hours to get the precipitation. After that, the precipitate was filtered and washed with de-ionized water and ethanol for several times followed by drying in an oven at 80 °C for 8 hours. Finally, the obtained powder was annealed at 800 °C for 4 hours.

#### 2.2. Characterizations

The X-ray diffraction (XRD) patterns were measured on Bruker-D8 Advanced X-ray diffractometer using CuK<sub> $\alpha$ </sub> (1.5406 Å) radiation source over the angular range  $10^{\circ} \le 2\theta \le 60^{\circ}$ . Fourier transform infrared (FTIR) spectra of the samples were recorded on FTIR spectrometer (Perkin Elmer, spectrum RXI) using KBr pellet technique in the 4000-400 cm<sup>-1</sup> spectral region. Morphologies of the samples were obtained using the ZEISS SUPPRA55 Field emission scanning electron microscopy (FESEM) equipped with the energy dispersive X-ray (EDX) spectroscopy system. Transmission electron microscopy (TEM) images were recorded on Hitachi model (H-7500). The electronic absorption spectra were recorded using a Perkin-Elmer, Lambda 950, UV-Visible-NIR spectrophotometer in the wavelength range of 200-1200 nm. The UC emission spectra were recorded on a SP2300 grating spectrograph (Princeton Instruments, USA) using a 980 nm continuous wave (CW) diode laser as excitation source. The decay curve analysis was performed by using a Lifetime spectrometer upon excitation with a Xenon flash lamp. For temperature dependent UC emission study, a thermocouple was placed close to laser spot on the sample surface and the spectra were recorded on a CCD spectrometer (Model: ULS2048X64, Avantes, USA). The laser beam power was set at 15 Wcm<sup>-2</sup> and a chopper was used to chop the CW light to avoid the direct heating of the material. Magnetic measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) in the temperature range of 2-300 K.

#### 3. Results and discussion

#### 3.1 Structural studies

#### 3.1.1 X-ray diffraction analysis

The crystal structure and phase composition of the synthesized samples was determined by X-ray diffraction analysis. Fig. 1(a) shows the XRD patterns of samples named as M, MMg<sub>4</sub>, MLi<sub>6</sub> and MLi<sub>2</sub>Mg<sub>4</sub> (all annealed at 800 °C). The diffraction peaks of all the samples were well matched with the standard JCPDS file no. 33-0548 with no other impurity phases. It confirms the formation of pure tetragonal phase of Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>. It is noticed that peak positions are slightly shifted towards higher angle side with improved crystallinity for samples incorporated with  $Li^+$ ,  $Mg^{2+}$  and  $Li^+/Mg^{2+}$  ions [Fig. 1(b)]. The shifting in diffraction peak is related to the lattice contraction caused by the substitution of  $Gd^{3+}$  (93.8 pm) ions by smaller ionic radii  $Li^+$  (76 pm) and  $Mg^{2+}$  (72 pm) [44]. Furthermore, the lattice parameters and unit cell volume were calculated for M (a = b = 5.18 Å, c = 11.20 Å; unit cell volume:  $300.52 \text{ Å}^3$ ) and MLi<sub>2</sub>Mg<sub>4</sub> (a = b = 5.16 Å, c = 11.15 Å; unit cell volume: 296.87 Å<sup>3</sup>) samples. It is found that the lattice parameters and unit cell volume both decrease with the doping of Er<sup>3+</sup>/Yb<sup>3+</sup>, Li<sup>+</sup> and Mg<sup>2+</sup> ions as compared to the standard JCPDS data. This is because of larger size Gd<sup>3+</sup> (93.8 pm) ions are replaced by smaller size Er<sup>3+</sup>/Yb<sup>3+</sup> (89 pm/ 86.8 pm) and  $Li^{+}/Mg^{2+}$  (76 pm/72 pm) ions and it leads to shrinkage of unit cell volume. The strain present in the lattice was determined from the Williamson-Hall relation [27]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon\sin\theta}{\lambda}$$
(1)

where, D is the crystallite size (in nm),  $\beta$  is full width at half maximum,  $\theta$  is Bragg diffraction angle,  $\lambda$  is the wavelength of radiation (1.54 Å). The strain ( $\epsilon$ ) is calculated from the slope of  $\beta \cos\theta/\lambda$  vs.  $\sin\theta/\lambda$  plot for M and MLi<sub>2</sub>Mg<sub>4</sub> sample. The plot is given in supplementary Fig. S1. The positive slope indicates tensile strain for M sample. The slope becomes negative for Li<sup>+</sup>/Mg<sup>2+</sup> doped sample and strain goes towards compressive strain. The compressive strain is possible when ions of larger radii (Gd<sup>3+</sup>) are replaced by smaller ionic radii (Li<sup>+</sup>, Mg<sup>2+</sup>).

#### 3.1.2 Fourier Transform Infrared (FTIR) study

The FTIR spectra of as-synthesized as well as samples annealed at 800 °C are shown in Fig. 2. The as-synthesized sample shows the presence of impurity bands of organic molecules. The bands at 3640 cm<sup>-1</sup> and 3410 cm<sup>-1</sup> are attributed to the O-H asymmetric and symmetric stretching vibrations of water molecules, respectively. The band at 1637 cm<sup>-1</sup> is assigned to the H-O-H bending vibration of water absorption while the band around 1390 cm<sup>-1</sup> is attributed to the N-O mode of vibration of HNO<sub>3</sub> used in the sample preparation. The band around 2431 cm<sup>-1</sup> is assigned to the C-O vibration of CO<sub>2</sub> adsorbed at the surface of sample from the atmosphere [8]. It is clear from the Fig. 2 that when Li<sup>+</sup> and Mg<sup>2+</sup> are incorporated into the sample, the intensity of impurity bands decreases and finally bands are removed completely from MLi<sub>2</sub>Mg<sub>4</sub> sample due to annealing at 800 °C. Simultaneous co-doping of Li<sup>+</sup>/Mg<sup>2+</sup> can eliminate the organic impurities from the sample which may increase the luminescence efficiency by reducing non-radiative relaxation rates. The bands ranging from 850 to 670 cm<sup>-1</sup> are related to the lattice vibrations of Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub> host.

#### **3.1.3 Microstructure analysis**

Fig. 3[a-d] shows the FESEM images of annealed M, MMg<sub>4</sub>, MLi<sub>6</sub> and MLi<sub>2</sub>Mg<sub>4</sub> samples. Without doping of Li<sup>+</sup>/Mg<sup>2+</sup>, the sample exhibits non-uniform and irregular morphology agglomerated with each other. When Li<sup>+</sup>/Mg<sup>2+</sup> ions are incorporated into the sample, the morphology and size of the particles increases which is evident in Fig. 3(b-d). The TEM image of MLi<sub>2</sub>Mg<sub>4</sub> sample has shown in Fig. 3(e). The particles have seen connected through grain boundaries. The high resolution transmission electron microscopy (HRTEM) image [Fig. 3(f)] clearly shows the resolved lattice fringes and measures interplanar distance of 0.26 nm between the two adjacent planes, which corresponds to (200) crystal plane of tetragonal Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>. The energy dispersive X-ray spectroscopy (EDX) was further used to investigate the elemental composition and purity of annealed MLi<sub>2</sub>Mg<sub>4</sub> sample as shown in Fig. 4(a). The EDX spectrum confirms the presence of Gd, Mo, O, Er, Yb and Mg elements in expected stoichiometric proportion in the Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub> host. However, EDX detector could not be able to detect the presence of Li<sup>+</sup> ion due to its smaller atomic weight among all other elements. In addition, the elemental mapping results that all the constituent elements (Gd, Mo, O, Er, Yb

and Mg) are homogeneously distributed throughout the whole region of samples [Fig. 4(b-g)].

#### 3.2 Optical studies

#### 3.2.1 UV-Visible absorption spectroscopy

The UV-Visible absorption spectra of M and MLi<sub>2</sub>Mg<sub>4</sub> samples were recorded in diffuse reflectance mode against a reference standard of BaSO<sub>4</sub> compound in the 200-1200 nm wavelength range and the graph has shown in Fig. 5. The spectrum shows a broad absorption band around 300 nm assigned to the band absorption of the host [27]. The other absorptions bands are observed around 521 and 656 nm due to the  ${}^{2}H_{11/2} \leftarrow {}^{4}I_{15/2}$  and  ${}^{4}F_{9/2} \leftarrow {}^{4}I_{15/2}$  transitions, respectively of  $Er^{3+}$  ion. The band around 978 nm is observed due to the  ${}^{2}F_{5/2} \leftarrow {}^{2}F_{7/2}$  transition of Yb<sup>3+</sup> ion. It is evident from the Fig. 5 that the intensities of these absorption bands increase on the addition of Li<sup>+</sup>/Mg<sup>2+</sup> ions.

The optical band gap energy ( $E_g$ ) of the samples was estimated from the diffuse reflectance spectrum using the equation proposed by Kubelka and Munk [45]. The procedure is described in our previous report [41]. Molybdates have optical absorption governed by direct band gap transitions [46] and the Kubelka-Munk (K-M) plot has shown in the inset of Fig. 5 with best straight line fit. The value of band gap energy ( $E_g$ ) was extracted by extrapolating the linear fitted regions to  $[F(R)hv]^2 = 0$ . It is found that the value of Eg increases from 3.55 eV to 4.09 eV with the addition of Li<sup>+</sup>/Mg<sup>2+</sup> ions into the sample M. This may be due to the removal of lower lying impurity states in the sample [47].

## 3.2.2 Effect of Li<sup>+</sup>, Mg<sup>2+</sup> and Li<sup>+</sup>/Mg<sup>2+</sup> incorporation on UC properties

The UC emission spectra of samples codoped with various concentrations of  $Li^+$  and  $Mg^{2+}$  ions were studied at room temperature upon 980 nm laser light excitation with a fixed excitation power density of 25 W/cm<sup>2</sup>. First, the emission intensity was optimized by varying the concentrations of each  $Li^+$  and  $Mg^{2+}$  from 0 to 8 mol%. The resulted emission enhancement for green and red emission bands are plotted in Fig. 6(a) and (b). It is found that sample containing 6 mol%  $Li^+$  and 4 mol%  $Mg^{2+}$  show maximum enhancement in emission intensity. Beyond this optimum doping concentration, a drastic decrease in emission intensity

is observed for each sample. Fig. 6 (c) and (d) shows the comparison of the UC emission spectra of sample M with optimized codoped samples i.e. 6 mol% Li<sup>+</sup> and 4 mol% Mg<sup>2+</sup>. All the samples show green (524 nm and 548 nm) and red (660 nm) emission bands due to the  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ ,  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  transitions of  $Er^{3+}$ . It is observed that there is no change in the shape and peak positions of the emission bands on co-doping with Li<sup>+</sup> and Mg<sup>2+</sup> ions except change in emission intensity. The Li<sup>+</sup> co-doping enhances the green and red emission bands by 3.7 and 6.1 times, respectively. On the other hand, Mg<sup>2+</sup> co-doping enhances the green and red emission bands by 3.2 and 5.9 times, respectively as compared to the sample M.

In the next study, both Li<sup>+</sup> and Mg<sup>2+</sup> were simultaneously codoped in sample M. Here, concentration of Mg<sup>2+</sup> was fixed at 4 mol % and concentration of Li<sup>+</sup> (1, 1.5, 2, 2.5 and 3 mol %) was varied. Fig. 7 shows the comparison of UC emission spectra of M, MMg<sub>4</sub>, MLi<sub>6</sub> and MLi<sub>2</sub>Mg<sub>4</sub> samples measured at same excitation power of 25 W/cm<sup>2</sup>. It is found that simultaneous co-doping of Li<sup>+</sup>/Mg<sup>2+</sup> hugely enhance the emission intensity as compared to single co-doping of either  $Li^+$  or  $Mg^{2+}$ . Inset of Fig. 7 shows the variation of the green and red band intensities with an increase in Li<sup>+</sup> concentration at a fixed Mg<sup>2+</sup> concentration i.e, at 4 mol%. The optimum emission intensity is obtained corresponding to a doping of 2 mol % Li<sup>+</sup>. At this doping concentration, intensities of the green and red emission bands have increased by 53 and 21 times as compared to the sample M. The enhancement mechanisms of emission intensity with co-doping of Li<sup>+</sup> and Mg<sup>2+</sup> ions has been correlated to the distortion of the local crystal field symmetry around  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions [32, 38, 48]. Both Li<sup>+</sup> (76 pm) &  $Mg^{2+}$  (72 pm) ions have smaller ionic radii and can easily substitute the  $Gd^{3+}$  sites causing the shrinkage of the host lattice. This lattice shrinkage results decrease in lattice parameters and thus perturbing the symmetry of the local crystal field around the RE ions. According to previous studies, asymmetry surrounding of RE ions is favorable for radiative transition and consequently increasing the UC luminescence intensity [38, 49, 50]. Furthermore, beyond the optimum doping concentrations of Li<sup>+</sup> and Mg<sup>2+</sup> ions, the UC intensity has seen to quenched due to the creation of excess defect centers in the Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub> lattice. Moreover, enhancement in UC emission intensity with  $Li^+/Mg^{2+}$  co-doping may also be due to the reduction in optical quenching centers. It is evident from the FTIR spectra, OH<sup>-</sup> organic impurity is completely

removed from the  $\text{Li}^+/\text{Mg}^{2+}$  codoped samples which helps to increase the UC intensity by diminishing non-radiative relaxation rates. The improvement in crystallinity of  $\text{Li}^+/\text{Mg}^{2+}$  codoped sample as observed from XRD and FESEM analysis may also support the UC enhancement. The tensile lattice strain goes towards compressive strain upon  $\text{Li}^+/\text{Mg}^{2+}$  ions co-doping and this could also be a reason for UC enhancement [51].

In order to prove the enhancement in UC, the emission decay curves of  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transition of  $Er^{3+}$  ion for all the samples were measured under 380 nm excitation and graph has shown in Supplementary Fig. S2. The decay curves were well fitted to bi-exponential function expressed as: I (t) = A<sub>1</sub>exp (-t/\tau\_1) + A<sub>2</sub>exp (-t/\tau\_2), where I (t) is the luminescence intensity at time t. A<sub>1</sub> and A<sub>2</sub> are constants and  $\tau_1$  and  $\tau_2$  are the shorter and longer lifetime components, respectively. The fitted curves along with corresponding lifetime values for all the samples are mentioned in the Fig. S2. It is found that the lifetime ( $\tau$ ) of  ${}^{4}S_{3/2}$  level increases with the incorporation of Li<sup>+</sup> and Mg<sup>2+</sup> ions into sample M. A similar trend in intensity variation was also observed (Fig. 7). The increase in lifetime suggests the decrease of non-radiative transitions and increase of radiative emission. As we know the experimental lifetime of an excited state,  $\tau$ , is determined by the theoretical lifetime ( $\tau_{rad}$ ), the non-radiative transition rate (W<sub>NR</sub>), and the energy transfer rate (W<sub>ET</sub>), which can be expressed as  $1/\tau = 1/\tau_{rad} + W_{NR} + W_{ET}$ . This experimental larger lifetime value ( $\tau$ ) could be attributed to the tailored local environment of activators ( $\tau_{rad}$ ) and the decrease of non-radiative decay rates of excited state (W<sub>NR</sub>) [38].

Researchers have reported that addition of Li<sup>+</sup> and Mg<sup>2+</sup> ions into the RE doped materials results in a significant enhancement of the luminescence intensities [48-50]. Singh et al. [48] have reported the effect of Li<sup>+</sup> ion on the Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>:  $Er^{3+}/Yb^{3+}$  phosphor and found enhancement in the green and red emission bands by 15 and 8 times, respectively. Enhancement of about 2 and 3.3 times in green and red emission bands of  $\beta$ -NaYF<sub>4</sub>:  $Er^{3+}/Yb^{3+}$  microcrystals due to co-doping of Li<sup>+</sup> ions has been observed by Ding et al. [49]. However, the effect of Mg<sup>2+</sup> on the UC enhancement of materials has rarely been found in the literature [32, 50, 52]. In this regard, Singh et al. [50] have reported the effect of Mg<sup>2+</sup> in CaAl<sub>12</sub>O<sub>19</sub>: $Er^{3+}$ :Yb<sup>3+</sup> phosphor and observed enhancement of about 60 and 10 times in the green and red emission intensities, respectively. Herein, authors have observed maximum

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enhancement of ~ 53 and ~ 21 times for the green (524 nm) and red (660 nm) emission bands, respectively. Above observations conclude that dual co-doping of  $\text{Li}^+/\text{Mg}^{2+}$  ions simultaneously into  $\text{Gd}_2\text{Mo}_3\text{O}_9$ :  $\text{Er}^{3+}/\text{Yb}^{3+}$  improves the UC intensity significantly as compared to single co-doping of either  $\text{Li}^+$  or  $\text{Mg}^{2+}$ .

To further examine the effect of  $Li^+/Mg^{2+}$  ions on UC mechanisms, the pump power dependence of the green and red emission bands was investigated for M and MLi<sub>2</sub>Mg<sub>4</sub> samples and the plot has shown in Fig. [8(a) & (b)]. For an unsaturated UC process, it is well known that intensity of UC luminescence (I) is proportional to the nth power of input laser power (P) follows the relation  $I \propto P^n$ , where n is the number of photons involved in the UC process. Value of 'n' can be obtained from the line fitting of lnI versus lnP plot [53]. Both green and red emission bands must originate from two photon absorption processes. However, the slope 'n' values for green (548 nm) and red (660 nm) emission bands were found to decrease with  $Li^+/Mg^{2+}$  incorporation. The calculated slope values 0.71 (for 548 nm) and 0.66 (for 660 nm) are much deviated from the expected two photon values. The reduction in slope value may be due to the saturation mechanism of intermediate levels, which has been theoretically described by Pollnau et al. [53]. Despite the low slope values in Li<sup>+</sup>/Mg<sup>2+</sup> doped sample, the emission intensity has found much higher compared to Li<sup>+</sup>/Mg<sup>2+</sup> free sample. The  $Li^{+}/Mg^{2+}$  codoped sample create more and more populations in  ${}^{2}H_{11/2}$ ,  ${}^{4}S_{3/2}$  and  ${}^{4}F_{9/2}$  levels due to decrease in the non-radiative decay rates [41]. There are several theoretical modeling in literature where it has been proved that due to saturation mechanism of intermediate levels the number of photons decreases from the expected values [37, 53, 54]. The possible UC mechanism in the  $Er^{3+}-Yb^{3+}$  system upon 980 nm light excitation has schematically shown in the energy level diagram [Fig 8(c)]. The dominant UC process between  $Yb^{3+}$  and  $Er^{3+}$  is the energy transfer (ET) from the excited  ${}^{2}F_{5/2}$  level of Yb<sup>3+</sup> to the  ${}^{4}I_{11/2}$ ,  ${}^{4}F_{9/2}$  and  ${}^{4}F_{7/2}$  levels of  $\mathrm{Er}^{3+}$  ions. The whole description of the UC processes can be found in our previous reports [8, 27, 37, 55].

Additionally, the variation of UC emission colour with excitation power density was calculated using CIE (Commission Internationale de l'Eclairage) chromaticity diagram [27]. Fig. 8(d) shows the variation of colour coordinates with excitation power for MLi<sub>2</sub>Mg<sub>4</sub>

sample. At low pump power (7 W/cm<sup>2</sup>), the emission colour is in the green region (0.28, 0.70) which is shifted to pure green region (0.17, 0.79) with increase in power density upto 65 W/cm<sup>2</sup>. This may be due to the increased population of  $\text{Er}^{3+}$  ions at  ${}^{2}\text{H}_{11/2}$  and  ${}^{4}\text{S}_{3/2}$  levels as compared to  ${}^{4}\text{F}_{9/2}$  level under high excitation power density. The green to red intensity ratio increases as the excitation power increases in the MLi<sub>2</sub>Mg<sub>4</sub> sample, indicating that green emission is more intense when the sample is excited under high pump power. The slow increase in red band correlates the lowest defects/impurities in MLi<sub>2</sub>Mg<sub>4</sub> co-doped sample.

#### 3.2.3 Temperature sensing performance

It is clear from the UC emission spectra that  $MLi_2Mg_4$  sample gives optimum green UC emission; therefore authors have chosen it to investigate temperature sensing performance. The temperature dependent green UC emission spectra of  $MLi_2Mg_4$  sample were recorded within 300-513 K temperature range. In Fig. 9(a), the normalized UC emission spectra in 505-575 nm wavelength range are plotted at different temperatures and at fixed excitation power of 15 W/cm<sup>2</sup>. It can be seen from the Fig. 9(a) that peak position of the emission bands does not shift with temperature, whereas relative intensity of the emission bands changes with temperature. Since energy gap between the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels is very small (770 cm<sup>-1</sup>), the <sup>2</sup>H<sub>11/2</sub> level can be populated from the <sup>4</sup>S<sub>3/2</sub> level via thermal excitation, resulting in the variation of UC emission intensities of the <sup>2</sup>H<sub>11/2</sub>  $\rightarrow$ <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub>  $\rightarrow$ <sup>4</sup>I<sub>15/2</sub> transitions at different temperatures. According to Boltzmann distribution theory, the fluorescence intensity ratio (FIR) of two thermally coupled levels <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> of Er<sup>3+</sup> ion can be expressed as [8]:

$$FIR = \frac{I_H}{I_s} = \frac{W_H g_H h v_H}{W_S g_S h v_S} \exp\left(\frac{-\Delta E}{k_B T}\right) = B \exp\left(\frac{-\Delta E}{k_B T}\right)$$
(2)

where,  $I_H$  and  $I_S$  are the integrated intensities corresponding to  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  (510-540 nm) and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  (540-570 nm) transitions, respectively.  $W_H$  and  $W_S$  are the radiative probabilities of the transitions,  $g_H$  and  $g_S$  are the (2J+1) degeneracy of levels  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$ respectively and  $hv_H$  and  $hv_s$  are the photon energies of the  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions respectively,  $\Delta E$  is the energy gap between the two emitting levels,  $k_B$  is the Boltzmann constant and T is the absolute temperature. Equation (2) can be expressed as follows

$$\ln(FIR) = \ln(B) + \left(-\frac{\Delta E}{k_B T}\right)$$
(3)

Inset of Fig. 9(a) shows the plot of ln(FIR) as a function of inverse absolute temperature T in the range of 300-513 K for  $MLi_2Mg_4$  sample. The experimental data is well fitted to straight line which gives slope (- $\Delta E/k$ ) and intercept (lnB) equal to 1084 cm<sup>-1</sup> and 3.58, respectively. The calculated energy gap from the slope is found to be 753 cm<sup>-1</sup>.

For temperature sensing application, it is of great importance to understand the rate at which fluorescence intensity ratio changes with temperature. This parameter is known as sensitivity. The absolute sensitivity  $(S_a)$  and relative sensitivity  $(S_r)$  are defined as [12, 56, 57]:

$$S_a = \left| \frac{dR}{dT} \right| = R \frac{\Delta E}{KT^2} \tag{4}$$

and

$$S_r = 100\% \times \left| \frac{1}{R} \frac{dR}{dT} \right| = 100\% \times \frac{\Delta E}{KT^2}$$
(5)

where all the terms have their usual meaning. The absolute and relative sensitivities were calculated as a function of temperature and the plot has shown in Fig. 9(b). It can be seen from the Fig. 9(b) that the absolute sensitivity of MLi<sub>2</sub>Mg<sub>4</sub> phosphor increases with increasing the temperature and reaches its maximum of about 23.06x10<sup>-3</sup> K<sup>-1</sup> at 513 K. The result suggests that the material is highly stable at elevated temperature and suitable for high temperature thermometry. The sensitivity was further compared with Li<sup>+</sup>/Mg<sup>2+</sup> free Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> phosphor reported in our previous work [27]. In Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> the temperature sensitivity was obtained as  $10.57 \times 10^{-3}$  K<sup>-1</sup> at 450 K. But due to co-doping of  $Li^{+}/Mg^{2+}$  into  $Gd_{2}Mo_{3}O_{9}$ :  $Er^{3+}/Yb^{3+}$  system, the temperature sensitivity increases to  $23.06 \times 10^{-3} \text{ K}^{-1}$  at 513 K. The reason behind the enhanced sensitivity in Li<sup>+</sup>/Mg<sup>2+</sup> codoped sample is expected due to the tailoring effect of crystal field environment around Er<sup>3+</sup> ion in Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub> matrix [17]. The maximum value of relative sensitivity was calculated to be 1.20 % K<sup>-1</sup> at 300 K. It is worth to compare the relative sensitivity of present material with other prominent studies of optical temperature sensors based on Er<sup>3+</sup>/Yb<sup>3+</sup> doped host materials and comparison is given in Table. 3 [14, 41, 56, 58-63]. From the comparison, it is found that sensitivity of present material is comparatively high compared to other materials reported previously. The obtained result indicates that simultaneous co-doping of  $\mathrm{Li}^{+}/\mathrm{Mg}^{2+}$ 

into  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  phosphor could be an effective approach to realize high temperature sensitivity.

#### **3.2.4 Magnetic property**

Apart from the UC luminescence properties, the effect of Li<sup>+</sup>/Mg<sup>2+</sup> ions on the magnetic properties of  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  phosphor has also investigated. The magnetic field dependence of magnetization M(H) in MLi<sub>2</sub>Mg<sub>4</sub> sample was measured at three different temperatures namely 300 K, 77 K and 2 K and recorded magnetization curves have shown in Fig. 10(a). From the Fig. 10(a), one can see that material exhibit paramagnetic nature at 300 K and 77 K over a wide range of magnetic field (-90 to 90 kOe). A similar behavior was observed for  $\text{Li}^+/\text{Mg}^{2+}$  free Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> sample [27]. The paramagnetic properties of the  $Gd^{3+}$  ions in  $Gd_2Mo_3O_9$  come from the seven unpaired inner 4f electrons (4f<sup>7</sup>), which are closely bound to the nucleus and effectively shielded by the outer closed shell electrons  $5s^25p^6$  from the crystal field. The straight line crossing the origin indicates paramagnetic nature and the magnetic moments associated with the Gd<sup>3+</sup> ions are all localized and non-interacting, which led to paramagnetism of  $Gd^{3+}$  ions. The magnetic mass susceptibility of MLi<sub>2</sub>Mg<sub>4</sub> sample at 300 K and 77 K has determined to be 2.50x10<sup>-5</sup> emu/g.Oe and 8.93x10<sup>-5</sup> emu/g.Oe, respectively. The magnetization at 300 K and 77 K at 20 kOe has found to be 0.50 emu/g and 1.79 emu/g, respectively. These obtained values are higher than the Li<sup>+</sup>/Mg<sup>2+</sup> free Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>: Er<sup>3+</sup>/Yb<sup>3+</sup> sample as reported in our previous work [27]. In present study sample indicates superparamagnetic behaviour at 2 K temperature with saturation magnetization (30 emu/g) at 90 kOe magnetic field. In order to confirm paramagnetic nature, the temperature dependence of the magnetization M(T) in the zero-field-cooled (ZFC) and field-cooled (FC) regimes was done under an applied magnetic field of  $10^4$  Oe, and graph has shown in Fig. 10(b) [left scale]. It is noticed that ZFC and FC curves totally overlapped in the studied temperature range and do not show any hysteresis loop in the lowest temperature range. Such behavior confirms the characteristic of paramagnetism and obeys the Curie-Weiss law [64]. The reciprocal magnetic susceptibility,  $1/\chi$  (M/H) as a function of temperature T for fixed  $H = 10^4$  Oe has also plotted in Fig. 10(b) [right scale]. The experimental data is linear in the 2-300 K temperature range and can be well fitted to

Curie–Weiss formula  $\chi = C/(T-\Theta)$ , where  $\chi$  is magnetic susceptibility, C is curie constant and  $\Theta$  is Curie temperature. The Curie temperature  $\Theta$  is close to 0 K, confirming paramagnetic behavior of our sample [65]. The effective magnetic moment  $\mu_{eff}$  per Gd<sup>3+</sup> ion and Curie constant were determined to be 7.09  $\mu_B$  and 6.28, respectively. The value of  $\mu_{eff}$  is close to the expected value of ground state ( ${}^8S_{7/2}$ ) Gd<sup>3+</sup> free ion (7.94  $\mu_B$ ) [66]. However, the low temperature M(H) curve has indicated superparamagnetism nature but is not confirmed from ZFC and FC measurements [28, 64-66]. Similar type of observation has been reported by Szczeszak et al. [64] and Heuvel et al. [67] for Gd<sub>0.8</sub>Eu<sub>0.2</sub>VO<sub>4</sub> and Er<sub>0.3</sub>Pb<sub>0.7</sub>F<sub>2.3</sub> nanoparticles, respectively. Thus, it is concluded from the M(H) and M(T) curves the present material is found in a paramagnetic state. The strong paramagnetic behavior observed in present sample has potential for external magnetic tracking of the nanophosphor in the biological applications [29, 30].

#### 4. Conclusions

In conclusion, highly luminescent-paramagnetic  $Gd_2Mo_3O_9$ :  $Er^{3+}/Yb^{3+}$  phosphor co-doped with Li<sup>+</sup> and Mg<sup>2+</sup> ions has been successfully synthesized and characterized. The Li<sup>+</sup> and Mg<sup>2+</sup> ions have significantly enhanced emission intensity of green and red emission bands by 53 and 21 times, respectively. The enhancement is attributed to the distortion of the local crystal field around the  $Er^{3+}$  ions which was further verified by an increase in the radiative lifetimes of the emitting levels of  $Er^{3+}$  ion. Furthermore, temperature sensing of the sample has found to improve by Li<sup>+</sup>/Mg<sup>2+</sup> co-doping with a maximum absolute sensitivity of 0.0230 K<sup>-1</sup> at 513 K. Additionally, magnetization and magnetic mass susceptibility has improved by co-doping of Li<sup>+</sup>/Mg<sup>2+</sup> ions. The result indicates that intense green emitting Li<sup>+</sup>/Mg<sup>2+</sup> co-doped Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>:  $Er^{3+}/Yb^{3+}$  phosphor is an interesting thermographic phosphor and could be considered for various applications including temperature sensing, display device and magnetic resonance imaging.

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### **Figure captions**

**Fig. 1** X-ray diffraction patterns of M,  $MMg_4$ ,  $MLi_6$  and  $MLi_2Mg_4$  samples annealed at 800 °C with their standard JCPDS data; (b) Enlarged XRD patterns of (112) diffraction peak for all the samples.

**Fig. 2** Fourier transform infrared spectra of (a) as-synthesized M (b) M annealed at 800 °C (c)  $MMg_4$  annealed at 800 °C (d)  $MLi_6$  annealed at 800 °C (e)  $MLi_2Mg_4$  annealed at 800 °C.

**Fig. 3** Field emission scanning electron microscopy image of (a) M (b)  $MMg_4$  (c)  $MLi_6$  (d)  $MLi_2Mg_4$  samples annealed at 800 °C; (e) Transmission electron microscopy image of annealed  $MLi_2Mg_4$  sample; (f) High resolution transmission electron microscopy image of  $MLi_2Mg_4$  sample.

**Fig. 4** (a) Energy dispersive X-ray spectrum of MLi<sub>2</sub>Mg<sub>4</sub> sample; [b-g] Elemental mapping of Gd, Mo, O, Er, Yb and Mg in MLi<sub>2</sub>Mg<sub>4</sub> sample.

Fig. 5 UV-Visible absorption spectrum in diffuse reflectance mode of M and  $MLi_2Mg_4$ ; Inset of Fig. 5 shows Kubelka-Munk plots to calculate optical band gap for M and  $MLi_2Mg_4$  sample.

**Fig. 6** (a) Variation of green and red UC emission intensity at different  $\text{Li}^+$  concentration (b) Variation of green and red UC emission intensity at different  $\text{Mg}^{2+}$  concentration (c) Comparison of UC emission spectrum of M sample with 6 mol%  $\text{Li}^+$  doped M sample (d) Comparison of UC emission spectrum of M sample with 4 mol%  $\text{Mg}^{2+}$  doped M sample under 980 nm laser excitation.

**Fig. 7** Comparison of UC emission spectra of optimized M, MMg<sub>4</sub>, MLi<sub>6</sub> and MLi<sub>2</sub>Mg<sub>4</sub> samples. Inset of Fig. 7 shows the variation of UC intensity of green and red emission bands

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as a function of  $Li^+$  concentration at a fixed Mg<sup>2+</sup> concentration at 4 mol%.

**Fig. 8** Pump power dependence of green and red emission bands in (a) M (b)  $MLi_2Mg_4$  phosphors; (c) Schematic energy level diagram of  $Er^{3+}$  and  $Yb^{3+}$  ions and the proposed UC mechanisms under 980 nm laser light excitation; (d) CIE chromaticity diagram for  $MLi_2Mg_4$  sample (variation of emission colour with excitation power densities).

**Fig. 9** (a) Temperature dependent green UC emission spectra for  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transitions of MLi<sub>2</sub>Mg<sub>4</sub> phosphor excited by 980 nm excitation. Inset of Fig. 9(a) shows monolog plot of FIR (I<sub>H</sub>/I<sub>S</sub>) as a function of inverse absolute temperature; (b) variation of absolute sensitivity (S<sub>a</sub>) and relative sensitivity (S<sub>r</sub>) as a function of temperature.

Fig. 10 (a) Magnetization versus applied magnetic field (M-H) curves in as-synthesized  $MLi_2Mg_4$  sample at 2 K, 77 K and 300 K (b) zero-field-cooled (ZFC) and field-cooled (FC) curves versus temperature (left scale) and the reciprocal of magnetic susceptibility (1/ $\chi$ ) versus temperature (right scale) at fixed magnetic field of 10<sup>4</sup> Oe.

## **FIGURES**



Fig. 1 X-ray diffraction patterns of M,  $MMg_4$ ,  $MLi_6$  and  $MLi_2Mg_4$  samples annealed at 800 °C with their standard JCPDS data; (b) Enlarged XRD patterns of (112) diffraction peak for all the samples.



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**Fig. 3** Field emission scanning electron microscopy image of (a) M (b)  $MMg_4$  (c)  $MLi_6$  (d)  $MLi_2Mg_4$  samples annealed at 800 °C; (e) Transmission electron microscopy image of annealed  $MLi_2Mg_4$  sample; (f) High resolution transmission electron microscopy image of  $MLi_2Mg_4$  sample.



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**Fig. 7** Comparison of UC emission spectra of optimized M,  $MMg_4$ ,  $MLi_6$  and  $MLi_2Mg_4$  samples. Inset of Fig. 7 shows the variation of UC intensity of green and red emission bands as a function of  $Li^+$  concentration at a fixed  $Mg^{2+}$  concentration at 4 mol%.



**Fig. 8** Pump power dependence of green and red emission bands in (a) M (b)  $MLi_2Mg_4$  phosphors; (c) Schematic energy level diagram of the  $Er^{3+}$  and  $Yb^{3+}$  system; (d) CIE chromaticity diagram for  $MLi_2Mg_4$  sample (variation of emission colour with excitation power densities).



**Fig. 9**(a) Temperature dependent green UC emission spectra for  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transitions of MLi<sub>2</sub>Mg<sub>4</sub> phosphor excited by 980 nm excitation. Inset of Fig. 9(a) shows monolog plot of FIR (I<sub>H</sub>/I<sub>S</sub>) as a function of inverse absolute temperature; (b) variation of absolute sensitivity (S<sub>a</sub>) and relative sensitivity (S<sub>r</sub>) as a function of temperature.



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Materials	Temperature range	Relative sensitivity (S <sub>r</sub> )	References
	( <b>K</b> )	(% K <sup>-1</sup> )	
Er-Yb : YNbO <sub>4</sub>	298-673	0.85	[14]
Er-Yb-K-Na : CaMoO <sub>4</sub>	306-513	1.27	[41]
Er-Yb : BaLa <sub>2</sub> (MoO <sub>4</sub> ) <sub>4</sub>	305-475	1.05	[56]
Er-Yb : NaYF <sub>4</sub> glass-ceramic	298-693	1.24	[58]
Er-Yb : GdVO <sub>4</sub>	307-473	1.11	[59]
Er-Yb: CaSc <sub>2</sub> O <sub>4</sub>	298-623	1.28	[60]
Er-Yb : YVO <sub>4</sub>	300-485	0.78	[61]
Er-Yb: TeO <sub>2</sub> -WO <sub>3</sub> glass	300-690	1.08	[62]
Er-Yb: La <sub>2</sub> O <sub>3</sub>	303-600	0.91	[63]
Er-Yb-Li-Mg: Gd <sub>2</sub> Mo <sub>3</sub> O <sub>9</sub>	300-513	1.20	This work

**Table 1** The comparison of maximum value of temperature sensitivity in  $\text{Er}^{3+}$  based materials by FIR technique.

- Emission intensity of green and red bands increases via Li<sup>+</sup>/Mg<sup>2+</sup> ions codoping.
- The maximum relative thermal sensitivity of 1.2 %  $K^{-1}$  at 300 K was achieved.
- The effect of Li<sup>+</sup>/Mg<sup>2+</sup> ions on the magnetization of the sample was investigated.
- The present material is suitable for high temperature sensing and display devices.