

Low Temperature Synthesis and Improvement in Optical Properties of MgO: Tb³⁺

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Manuscript submitted October 6, 2014; accepted June 8, 2015.

doi: 10.17706/ijmse.2015.3.2.167-174

Abstract: In current report the photoluminescence properties and enhancement of luminescence intensity in MgO: Tb³⁺ phosphor using charge compensation is reported. The MgO: Tb³⁺ synthesized by combustion synthesis. X-ray powder diffraction (XRD) analysis confirms formation of the MgO: Tb³⁺ samples with cubic structure. The PL and PLE spectra indicate that the main emission wavelength of MgO: Tb³⁺ is at 382 nm in black light region i.e. hardly visible violet region (N-UV) under 270 nm excitation. The concentration quenching is studied for Tb³⁺ in MgO occurs at 0.002 moles giving highest intensity. Further, the optimum sample studied for effect of charge compensator like (Li⁺, Na⁺, and K⁺). The results show that the emission intensity can be improved by all the three charge compensators but charge compensation using K⁺ ions gives the optimal luminescence intensity. The concentration quenching of K⁺ also studied.

Key words: Photoluminescence; charge compensation; quenching effect.

1. Introduction

Recently many researchers approached to enhance the luminescence intensity of phosphors by different ways such as use of sensitizer and charge compensator ions [1]. The magnesium is a suitable phosphor host with various applications in luminescence field when replaced by various rare earths such as Eu³⁺ activated BAM, Tb³⁺ and Ce³⁺ activated MgAl₁₁O₁₉ as blue and green components are extensively used in trichromatic lamps coated with these phosphors blends. Recently alkaline earth oxides have been studied widely because of their many industrial applications. Many times they are referred as refractory oxides which have the rock salt structure. Mainly the magnesium oxide doped with rare earth and some transition metal ions has been investigated for optical and electrical properties [2]-[6]. MgO is found important in many other applications such as glass technology [7]-[8], to detect soft X-ray from laser-heated cavities, to measure the low energy radiations in dermatology and in astronomical application [9], possible tunable material [10] and Antibacterial properties [11]. MgO is a good electrically insulating material in nuclear reactors, for optical and electronic devices and a good structural material at high temperatures. The luminescence spectra of the MgO crystal, containing impurities of transition elements (chromium, iron, manganese), shows bands in blue, orange and red regions [12]-[18]. Fast neutron irradiation produces anion vacancies, which occur in two charge states: F⁺ and F⁻ centers, corresponding to oxygen vacancies with one and two electrons, respectively. F⁺ centers have photoluminescence bands at 387 nm (3.2 eV) and F centers have photoluminescence bands at 540 nm (2.3 eV), respectively [19]-[21].

In charge compensation the above said co-dopant ions are in small amount of actual rare earth dopants but they play important role in increase the luminescence efficiency of bulk phosphors [22]. Yong-jie Chen et al reported that by using charge compensation luminescence intensity can be improved by three different approaches (i). monovalant cation acting as charge compensator like (Li⁺, Na⁺ or K⁺); (ii). Charge compensation is provided by calcium vacancy (iii). monovalent anion like (Cl⁻) [23], Probably due to the influence of charge compensation of alkali metal ions [24]. Also Y. X. Pan and G. K. Liu provide analysis of the enhancement mechanisms i.e. transformation of Mn⁴⁺-Mn⁴⁺ pairs connected with interstitial O²⁻ into isolated Mn⁴⁺ ions for charge compensation and for reducing non-radioactive relaxation using co-doping of Mg²⁺ ions [25]. Therefore, proper alkali metal ions can be co-doped to improve the emission intensity and incorporation of alkali metal ions greatly enhanced the luminescence intensity. Thus it is expected that the methods of composition modification could be applied effectively phosphor systems to prevention-pair formation for charge compensation, thereby improving luminescence efficiency.

2. Experimental

The MgO: Tb³⁺ samples were prepared by a low cost, highly effective and time saving combustion synthesis [26]-[28]. During the synthesis, the stoichiometric amounts of precursor are mixed together in agate mortar in proper molar ratio. The precursor was crushed for 5 min by adding suitable amount of double distilled water to get homogenous solution. The solution was then heated on hot plate for 5-10 min at 80°C to get the clear solution with removal of excess of water contents. The solution was then transferred to porcelain crucible and introduced in the preheated furnace at 550 °C. Initially the solution undergoes dehydration followed by decomposition with evolution of large amount of gaseous. The mixture then foamed and wells forming foam which then ruptures with flames with incandescent color. The combustion process was completed in five minutes and results in polycrystalline powder. The resulting fine powder was heated at 750°C for 2 hr to remove the excess of impurities and carbon traces from the material. . The heated sample was directly quenched to room temperature to get the stable and highly polycrystalline powder sample. Because Tb³⁺ ions are located in Mg sites and some charge defect is built into the lattices, Li⁺, Na⁺ and K⁺ was added as charge compensator. The molar ratio and weights of the ingredients used were shown in the Table 1.

Table 1. Molar Ratio and Weights of the Ingredients for MgO:Tb³⁺

Product	Corresponding reaction with balance molar ratios of precursors
Mg _(1-x-y) O: xTb ³⁺ .y M ⁺ (M= Li, Na and K)	Mg(NO ₃) ₂ + 6 CO(NH ₂) ₂ + 10.5 NH ₄ NO ₃ + x Tb ₂ (SO ₄) ₂ {In stock solution form 1gm=100ml}+yMNO ₃ (M=Li, Na and K) = Mg _(1-x-y) O: xTb ³⁺ .yM ⁺ + Gaseous (H ₂ O, NH ₄ and NO ₂)

3. Results and Discussion

3.1. XRD of Phosphor Powders

The XRD patterns of MgO: Tb³⁺, and Mg_(1-x-y)O: xTb³⁺.yM⁺(M= Li, Na and K) are shown in Fig. 1. It can be observed from figure, the four compounds have similar features and agree well with the PDF file (ICDD, 00-004-0829), indicating that the doped Tb³⁺ and charge compensators had not caused obvious change in the host structure. The XRD shows that the formed material is completely crystalline and is in single phase with cubic structure where a=b=c=4.213, Also the symmetry allowed crystal structure properties for MgO are centro symmetric, and mineral classification halite (Group), oxide (Subgroup)

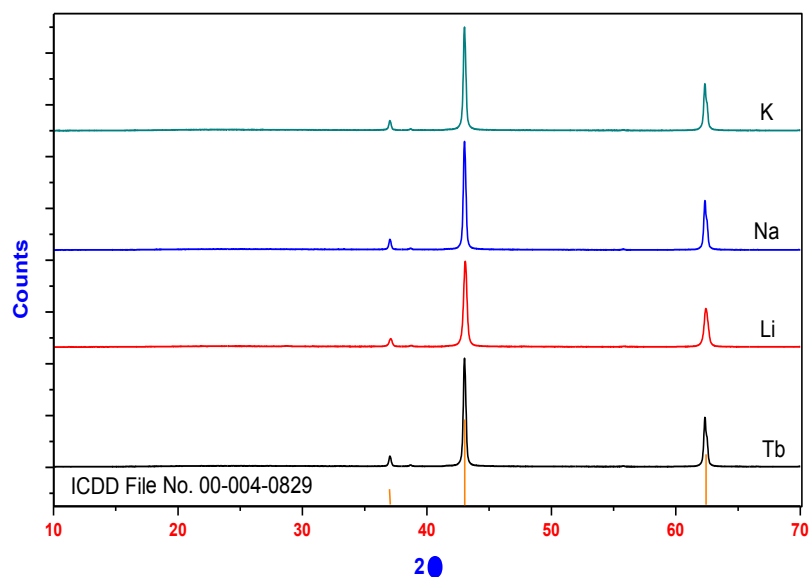


Fig. 1. XRD pattern of MgO:Tb^{3+} and $\text{Mg}(1-x-y)\text{O}:x\text{Tb}^{3+},y\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}$ and K)

3.2. Morphological of Phosphor

Fig. 2 represents the SEM photographs of representative phosphors for MgO doped with Tb and for respective charge compensator. The photograph reveals that the morphology of the sample remains quite same in all prepared phosphor and the phosphor not show any drastic change in morphology due to addition of charge compensator impurities. The phosphor shows irregular granular morphology with voids and cracks on the surface with porosity which may be occurred due to the mass flow during the combustion reaction.

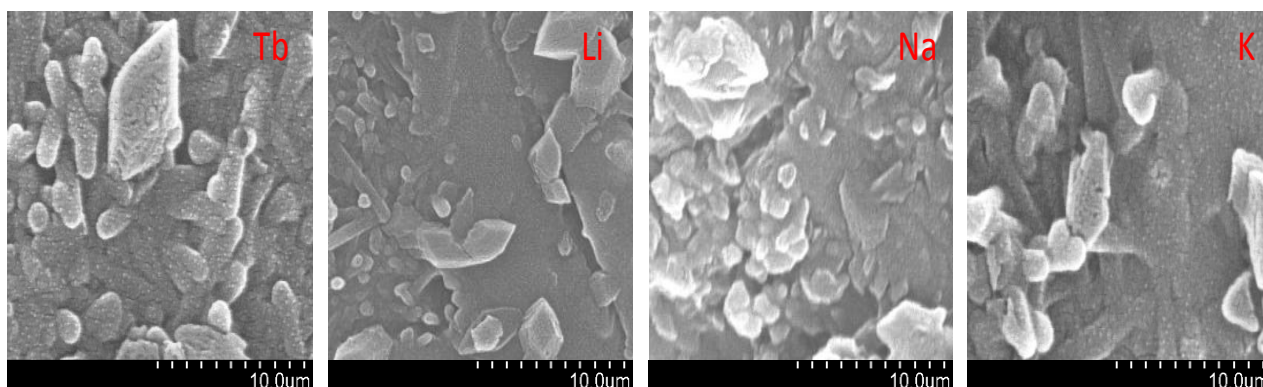


Fig. 2. photographs of representative phosphors for MgO doped with Tb and for respective charge compensator

3.3. Photoluminescence Properties

The combined excitation emission for MgO:Tb^{3+} is represented in Fig. 3. The excitation was monitored at 382 nm of emission and emission was monitored at 270 nm of excitation. In excitation spectra there is a prominent peak near 270 nm attributed to $4f-5d$ transition of Tb^{3+} in host lattice where as there are weak bands near and beyond 300 nm were corresponds to $f-f$ transition of Tb^{3+} . This implies that the $f-d$ transitions of Tb^{3+} are the allowed transition in the host material where as $f-f$ transitions are forbidden.

The emission spectra consist of number of peaks in range of 350 nm to 700 nm. The peaks from 350 nm

to 450 nm are correspond to 5D_3 to 7F_j ($J=6, 5, 4$) transition and those are in the range of 450 nm to 650 nm corresponds to 5D_4 to 7F_j ($J= 6, 5, 4$) transition of Tb^{3+} . The main emission line at 382 nm was due to 5D_3 to 7F_4 transition of Tb^{3+} ions. The material shows strong point emission at 382 nm which is attributed to 5D_3 transition of terbium ion. The emission at 544 nm attributed to 5D_4 transition is also comparable and it is nearly half of the main emission peak at 382 nm.

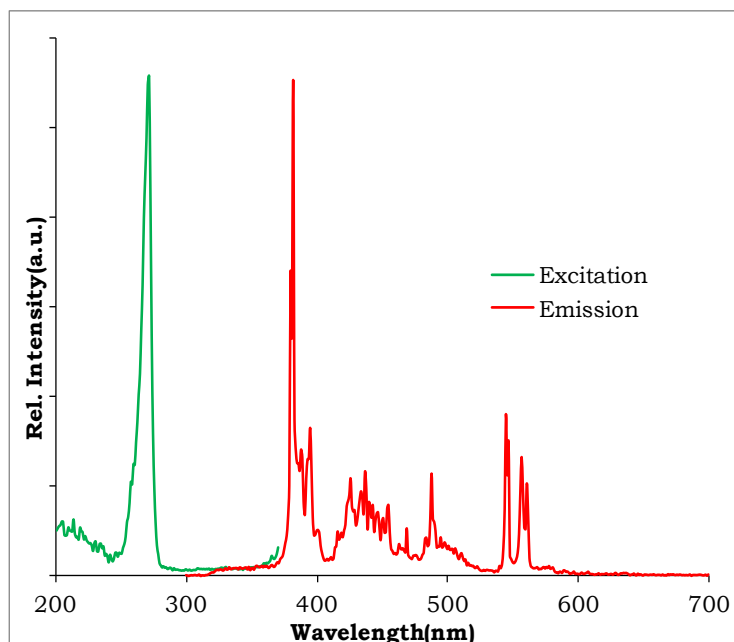


Fig. 3. Excitation and emission spectra of MgO: Tb³⁺ ($\lambda_{ex} = 270$ nm and $\lambda_{em} = 382$ nm).

3.4. Concentration Quenching of Tb³⁺ in MgO

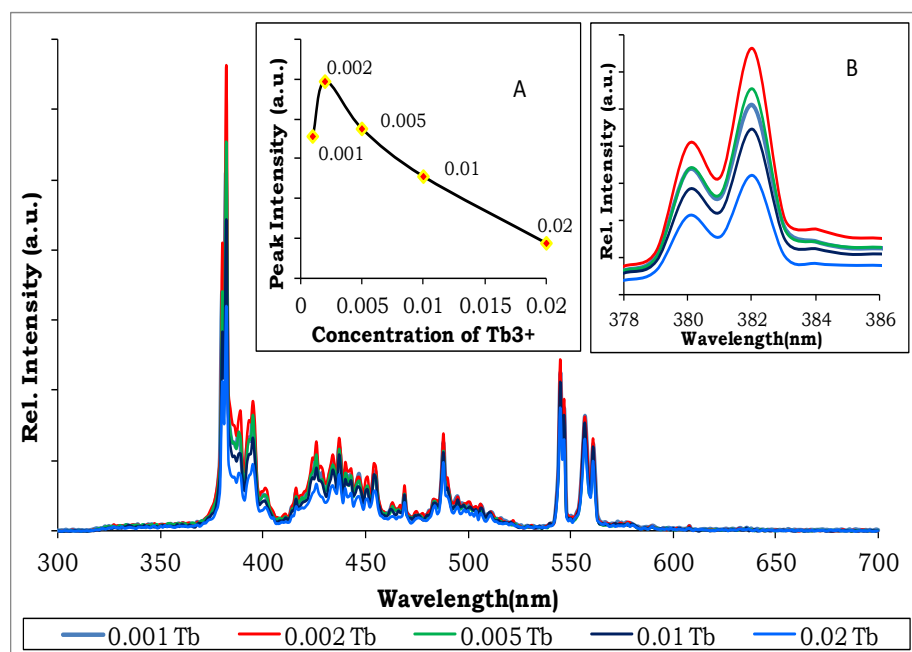


Fig. 4. Effect of the concentration of doped- Tb³⁺ on the relative luminescent intensity at 382 nm for MgO: Tb³⁺. The Inset (A) peak intensity variation with Concentration of Tb³⁺ and (B) Emission peaks variation in the range 375-390 nm

Fig. 4 shows the effect of the doped Tb³⁺ concentration in MgO: Tb³⁺. The highest intensity was found for the sample with a doping concentration of about 0.02 mol% of Tb³⁺. Higher Tb³⁺ concentration in samples led to the quenching of the luminescent intensity. A possible reason is that the quantum efficiency decreases when the content of Tb³⁺ ions is too high. The energy transfer exceeds the energy emission which can lead to the quenching of the luminescent intensity [29].

3.5. Effect of Charge Compensation on Luminescence Intensity of Tb³⁺ in MgO:

In the MgO: Tb³⁺ crystallite, Tb³⁺ ion replace Mg²⁺ ion. It is difficult to keep charge balance in the samples Therefore; univalent charge compensator (Li⁺, Na⁺ and K⁺) was added as charge compensators in order to keep the charge balance [30]. Fig. 5 shows the effect of different change compensators on the emission intensity of MgO: Tb³⁺

It is found that all the three charge compensation increase the luminescence intensity of MgO: Tb³⁺. Whereas K⁺ ions exhibit the strongest charge compensation abilities, Na⁺ ions being the second, and Li⁺ ions are the third. It is found that the luminescence intensity of the phosphors changes with different charge compensation. The luminescence intensity of the phosphor increased observably, means by adding K⁺ as charge compensator, luminescence intensity increased 2-3 times as that of the without charge compensator. Contrarily, both Li⁺ and Na⁺ anions exhibits similar luminescent intensity and slightly stronger than of MgO: Tb³⁺. This may be because the difference between ion radii of cations charge compensator may modify the sub-lattice structure around the luminescent center ions [31]. For MgO:Tb³⁺, the doped Tb³⁺ and Mg²⁺ alkaline ions are randomly distributed, When the Li⁺, Na⁺, K⁺ added in MgO:Tb³⁺ host, the coordination conditions for Tb³⁺ will be influenced. Hence the relative excitation and emission intensity of MgO: Tb³⁺ will vary, with the difference in the alkali metal ion serving as the charge compensator [32].

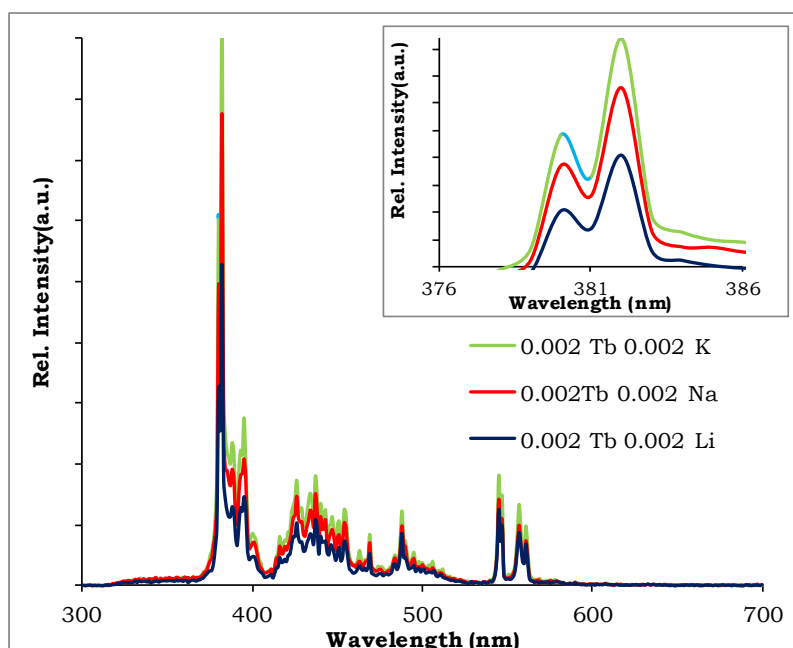


Fig. 5. Effect of different charge compensations on the emission intensity of Mg (1-x-y)O: xTb³⁺, yM⁺ (M= Li, Na and K), The inset shows variation in Peak in range 375-390 nm.

4. Conclusion

The strong and sharp UV emitting phosphor MgO: Tb³⁺ is synthesized by a simple time saving economical method of modified solution combination synthesis at comparatively lower temperature than previously reported. The synthesized phosphors show intense point NUV emission in 382 nm range under 270 nm of

excitation. The phosphor gives highest luminescence intensity for 0.002 mole of Tb^{3+} in host. For improvement in intensity of optimum sample, monovalent cations (Li^+ , Na^+ and K^+) are used as charge compensation. All the three ions show improvement in luminescent intensity through charge compensation. Especially, K^+ is the optimal charge compensator and the emitting intensity of the phosphor with K^+ as charge compensator is 2-3 times as strong as the one without charge compensator.

Acknowledgment

The authors NSB and CBP are very much thankful to the head, department of physics, SGB Amravati University, Amravati for providing all the facilities with open access and for all the needful suggestion required during the present studies.

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