Optical properties of TAG co-doped with Ce and Eu

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Abstract. Nanopowder samples of terbium aluminum garnet (TAG) doped with Ce and Eu were prepared by a sol–gel technique followed by sintering in air at various temperatures (maximum of 1100°C). The investigated concentrations of both the dopants were 0.1, 0.5 and 1.0 mol%. Nine powder samples prepared by the permutation of the doping concentrations were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), powder X-ray diffraction (XRD) and optical spectroscopic techniques. SEM and TEM investigations confirmed the nano-structure of the prepared powders while EDX not only confirmed the doping of Ce and Eu in TAG but also eliminated the possibility of any interfering impurities. Powder XRD showed that the basic structure of TAG did not change on doping which was further confirmed by Fourier-transform infrared studies. However, optical absorption and Raman scattering investigations showed the distortion of the TAG lattice on doping. Emission (photoluminescence) in the spectral region of 400–700 nm was observed when excited by 280 nm radiation. The intensity of this emission showed interesting dopant concentration dependence. The emission from TAG co-doped with 0.5 mol% of both Ce and Eu is of particular interest as its calculated colour chromaticity coordinates 'x' and 'y' were found as $x = 0.35$ and $y = 0.35$ which are very close to that of sun light at noon indicating its potential as a material for the white light source.

Keywords. TAG; Ce; Eu; co-doping.

1. Introduction

The never-ending demand for the electrical power required for illumination has attracted the attention of the researchers to build more and more energy efficient white light sources. Recently, the advent of white light emitting diodes (LEDs) has been a turning point in illumination technology as the achievable energy efficiency of these LED sources can be >95%. Single colour emitting LEDs being easily available, output from three LEDs emitting the three primary colours (red-green-blue (RGB) scheme), can be mixed in an appropriate proportion to produce white light efficiently. However, the light used for illumination should reproduce the colours of the illuminating object faithfully; this property of a light source is measured in terms of a dimensionless quantity called 'colour rendering index (CRI) [1]'. Sunlight at noon being the best known light reproducing illuminating source has been assigned the CRI of 100; the next best being the filament lamp with the CRI of ~80. On the other hand, the CRI for a typical RGB LED white source being around 40 needs improvement. Therefore, there is a requirement of new materials for white light sources which can match the energy efficiency of LEDs

and have a good CRI. One such source can be based on a single material with in-built blue light emission; this blue light can also be used to excite (in the same material), green and red emission of suitable intensity resulting in white emission. Since rare earths (RE) are known for the visible light emission it is possible to generate white light by doping these elements in various hosts [2–5]. RE can be classified into two categories: (1) broad band emitters involving 5d–4f transition (Ce^{3+} and Tb^{3+}) and (2) narrow band emitters due to transition between 4f levels (Ce^{3+} , Eu^{3+} , Tb^{3+} , Er^{3+} and Nd^{3+}) [6]; rare-earth with broad emission can be co-doped with the narrow emission RE in a suitable host to produce white light. Terbium aluminum garnet, $\text{Tb}_3\text{Al}_5\text{O}_{12}$, (TAG) is one such host which is suitable for visible light emission along with devices like compact Faraday rotators and optical isolators due to its (i) high Verdet constant ($180 \text{ rad T}^{-1} \text{ m}^{-1}$, room temp., 633 nm) and (ii) broad transmission range (350–1500 nm) [7,8]. However, it is difficult to prepare single crystals of TAG due to its incongruent melting properties [9]; therefore researchers are concentrating on its applications in a powder form. Recently, a number of alternative materials have been investigated for the white light emission [10,11].

Characteristic red emission was observed when TAG was doped with Eu [12] and Ce doped TAG resulted in yellow emission [13,14]. Batentschuk *et al* found energy transfer from Ce to Eu *via* Tb [15,16] in TAG co-doped with Ce and Eu. The present study aims at investigating the optical properties of the nanopowders of TAG co-doped with Ce and Eu to assess its potential in the realization of a white light source of both the high energy efficiency and CRI.

2. Materials and methods

The sol–gel technique was employed for the preparation of both undoped and doped TAG nano-powders; terbium oxide (Tb_4O_7) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) being the starting materials for undoped TAG while cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) was used for doping Ce and europium oxide (Eu_2O_3) for Eu doping. The molar ratio of Tb_4O_7 to $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used in the synthesis of undoped TAG was 3:5. A clear solution of Tb_4O_7 obtained by dissolving concentrated HNO_3 in the aqueous (de-ionized water) solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. This mixture (mixture A) thus obtained was constantly stirred for about 3 h maintaining the temperature at 65°C . This was followed by the addition of the citric acid (hydrated $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) solution which was prepared by dissolving about 0.04 mol of citric acid in distilled water. The whole mixture was maintained at 65°C and stirred continuously for about 10 h to obtain the sol which turned into gel by heating over a water bath. The gel thus obtained was dried at 150°C in an oven. This dried gel was crushed into powder and sintered in air at various temperatures (maximum of 1100°C) using a home-built temperature controlled ($\pm 1^\circ\text{C}$) muffle furnace. The same method was used for doped samples where an appropriate amount of Eu_2O_3 solution prepared in concentrated HNO_3 or aqueous solution (de-ionized water) of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to mixture A and rest of the procedure as outlined above was followed exactly. Samples were characterized, as mentioned earlier, by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), ultraviolet–visible (UV–VIS) absorption spectroscopy, Raman scattering, Fourier-transform infrared (FTIR) and photoluminescence (PL) techniques. Powder XRD spectra at room temperature was recorded using a Philips X’perts X-ray spectrometer, while SEM images were recorded on a Joel JSM-7600F instrument. FTIR spectra were recorded using a Shimadzu, FTIR 8000 series spectrometer. A Shimadzu Model UV–VIS Absorption 1800 spectrometer

Figure 1. Typical powder XRD spectra of TAG co-doped with 0.1 mol% Ce and 0.5 mol% Eu sintered at 150, 300, 900 and 1100°C ; XRD spectra of TAG sintered at 1100°C are shown for comparison.

was used to record the absorption spectrum in the 200–700 nm region. The emission from the samples when excited with the radiation absorbed by it was recorded using the Varian Model Carry 8000 Spectrophotometer. Model Morrison, Microscope Olympus B $\times$ 41 Raman spectrophotometer was used to record the Raman emission excited by 514.5 nm radiation from an Ar-ion laser. A JEM 2100 FTEM mode was used to record the TEM images of the samples.

3. Results

3.1 Powder X-ray diffraction

Typical powder XRD spectra of TAG co-doped with 0.1 mol% Ce and 0.5 mol% Eu sintered at 150, 300, 900 and 1100°C as a function of sintering temperature are shown in figure 1; the XRD spectrum of TAG sintered at 1100°C is shown for

Table 1. Typical variation of the line-width (FWHM) of the diffraction peak (420) with sintering temperature.

S. no.	Sample (mol%)	2 theta ($^\circ$) (420)	FWHM ($^\circ$)
1	TAG:Ce (0.1) and Eu (0.5) sintered at 900°C	33.3	0.25
2	TAG:Ce (0.1) and Eu (0.5) sintered at 1100°C	33.3	0.13

Figure 2. Comparison of the XRD spectra of TAG single doped with 0.5 mol% of Ce and Eu with those of TAG co-doped with 0.5 mol% of Ce and Eu.

comparison. As seen in figure 1, the prepared material was amorphous in nature at 150°C, developed some crystallinities at 300°C which further improved at higher sintering temperatures. The narrowing of diffraction peaks was observed with an increase in sintering temperature and is summarized in table 1. As seen in this table the full width at half maximum (FWHM) of the diffraction peak with (*hkl*) values (420) of TAG powder (co-doped with Ce (0.1 mol%) and Eu (0.5 mol%)) sintered at 900°C almost doubled when the sintering temperature was increased to 1100°C. This is well known phenomena observed in solids mainly due to agglomeration.

The crystallite size was calculated using the Scherrer formula (equation 1)

$$D = K\lambda / B \cos \theta \quad (1)$$

where *D* is the mean crystalline size in nm, *K* is a dimensionless constant usually taken as 0.9, λ is the wavelength (nm) of X-ray radiation used to record the diffraction pattern, *B* is FWHM (rad) of any peak in the XRD pattern and θ is the angle (°) between the incident and diffracted beams.

Figure 2 shows the comparison of the XRD spectra of TAG single doped with 0.5 mol% of Ce and Eu with those of TAG co-doped with 0.5 mol% of Ce and Eu. The parameters like peak position and crystallite size for the diffraction peak (420) calculated from the analysis of the spectra shown in figure 2 are summarized in table 2. As seen in this table, the peak position of the (420) peak for undoped TAG is at 33.33° which increases to 33.36° when TAG is doped with 0.5 mol% Ce. On the other hand, in TAG:Eu (0.5 mol%) the peak position of this diffraction peak shifted by ~0.28° towards lower angle implying the significant induction of lattice distortion by 0.5 mol% doping of Eu in TAG. The observed shifts for TAG:Ce (0.5 mol%) and Eu (0.5 mol%) increase marginally compared to TAG:Eu (0.5 mol%) implying that co-doping of Ce and Eu reduced distortion compared to that of single doping.

The free ion radius of Ce^{3+} is 101 pm while it is 93 and 97 pm for Tb^{3+} and Eu^{3+} , respectively. Since the ionic radius of Tb is very close to that of Eu while it is smaller in comparison with that of Ce. It is expected that Ce doping could introduce more lattice distortion compared to Eu while XRD analysis also showed the same result as expected that lattice distortion induced by Ce is more than that of Eu which resulted in lower degree of crystallinity in the doped TAG powder sample.

3.2 EDX

A typical EDX spectrum of TAG co-doped with (sintered at 110°C) 0.5 mol% of Ce and Eu is shown in figure 3. As seen in this figure, peaks due to Eu and Ce are prominently observed along with those of Tb and Al confirming the incorporation of the dopants in the TAG lattice. The peak due to Au is because of the gold sample holder used for recording the EDX spectrum. Also, EDX spectra did not show any interfering impurity.

Table 2. Comparison of the crystallite size of the diffraction peak (420) of TAG single doped with 0.5 mol% Ce and Eu with that of TAG co-doped with 0.5 mol% of Ce and Eu.

Sample sintered at 1100°C (mol%)	2 theta (°)	Crystallite size (nm)
TAG	33.33	40
TAG:Ce (0.5)	33.36	9
TAG:Eu (0.5)	33.13	31
TAG:Ce (0.5) and Eu (0.5)	33.11	20

Figure 3. EDX spectra of TAG co-doped with 0.5 mol% of Ce and Eu.

Figure 4. (a) Typical SEM image and (b) typical TEM image of the TAG co-doped powder sample.

3.3 SEM/TEM images

The nanostructure nature of the synthesized powder samples was investigated by SEM and TEM techniques. A typical SEM image is shown in figure 4a, while a typical TEM image is shown in figure 4b. The nanostructure nature of the powder samples of TAG co-doped with 0.5 mol% Ce and Eu is clearly seen in the SEM and TEM images. Also, from the SEM image (figure 4a), it can be concluded that the synthesized powder sample was composed of spherically-shaped particles along with some non-spherical relatively large sized particles which could be due to agglomeration and/or strain induced by Ce and Eu doping. The spherical nature of the particles of the synthesized powder is further supported by the TEM images where spherical particles are clearly visible. Similar images were observed with other dopant combinations.

3.4 FTIR

Typical FTIR spectra of TAG co-doped with Ce (0.1, 0.5 and 1.0 mol%, variable) and Eu (0.1 mol%, constant) are

Figure 5. FTIR spectra of TAG co-doped with Ce (0.1, 0.5 and 1.0 mol%, variable) and Eu (0.1 mol%, constant).

shown in figure 5; the FTIR spectrum of TAG is shown in the same figure for comparison. All the samples were sintered at 1100°C. The FTIR spectra were recorded in air using a KBr pellet. The observed absorption at 437, 680, 728 and 785 cm^{-1} could be due to Tb–O, Ce–O and Eu–O bonds while

Figure 6. Typical room temperature Raman spectra of TAG and TAG:Ce (0.1 mol%) and Eu (0.5 mol%).

Figure 7. Raman shift in the peak position of 2483 cm^{-1} in Raman spectra as a function of dopant concentration.

relatively broad absorption at 3450 cm^{-1} , which is typical of the O–H functional group, could be due to water present in air. Similarly, 1380 and 1640 cm^{-1} absorption, which is typical of the C–O functional group, could be attributed to CO_2 present in air. The main spectral features of all the spectra shown in figure 5 are almost identical implying that the basic structure of TAG did not change on co-doping with Ce and Eu.

Spectral features similar to the results shown in figure 5 were observed for TAG co-doped with Eu (0.1, 0.5 and 1.0 mol%, variable) and Ce (0.1 mol%, constant) as well as for TAG co-doped with 0.5 mol% Ce and Eu.

3.5 Raman scattering

Typical Raman spectra of TAG and TAG:Ce (0.1 mol%) and Eu (0.5 mol%) are shown in figure 6. As seen in this figure, Raman shifts at 2143 , 2322 , 2389 , 2483 , 2509 and 2666 cm^{-1} were observed in TAG when excited with 514.5 nm radiation from an Ar-ion laser. On doping with 0.1 mol% of Ce and 0.5 mol% of Eu, the peak position of the Raman shift at 2509 cm^{-1} did not change while it changed by $\sim 3\text{ cm}^{-1}$ in the case of the 2483 cm^{-1} shift. On the other hand, the shifts observed in TAG at 2143 , 2322 , 2389 and 2666 cm^{-1} were not observed in TAG:Ce (0.1 mol%) and Eu (0.5 mol%); new shifts at 2102 , 2414 and 2768 cm^{-1} were observed. In TAG, Raman shifts in undoped TAG are attributed to the electronic Raman of Tb^{3+} while in doped TAG, there could be contribution from Ce and Eu. Figure 6 shows the shift in the peak position of the Raman shift at 2483 cm^{-1} which is found both in TAG and in co-doped samples. As seen in figure 7, the peak position of the Raman shift at 2509 cm^{-1} did not change with the change in the dopant concentration while the other shifts at 2483 cm^{-1} changed by $\sim 4\text{ cm}^{-1}$ when TAG was co-doped with 0.1 mol% of Ce and Eu. However, this shift was almost constant with the increase in the Eu concentration maintaining the Ce concentration constant at 0.1 mol%. However, the intensity showed significant variation (figure 8) where the integrated intensity area (arbitrary units) of the Raman shift at 2483 cm^{-1} has been plotted as a function of varying (0.1, 0.5 and 1.0 mol%) Eu concentrations while maintaining the Ce concentration constant at 0.1 mol%. As seen in this figure, the intensity of this Raman shift changed almost by two orders of magnitude when TAG was co-doped with 0.1 mol% of Ce and Eu. However, the intensity reduced

Figure 8. Intensity variation of the 2483 cm^{-1} Raman shift as a function of Eu concentration; the concentration of Ce was constant at 0.1 mol%.

almost by one order of magnitude when the Eu concentration was increased to 0.5 mol% maintaining the Ce concentration at 0.1 mol% while the intensity again changed by one order of magnitude when the Eu concentration was increased to 1.0 mol% without changing the concentration of Ce which was kept constant at 0.1 mol%. The change in the intensity with 0.1 mol% co-doping of Ce and Eu shows the distortion induced in the TAG lattice due to doping as Raman scattering is very sensitive to lattice distortion; this distortion is also reflected in the shifting of the peak position of the 2483 cm^{-1} Raman shift (figure 8). The subsequent variation in intensity could be due to the surface migration of Eu with an increase in its concentration. A similar type of behaviour was observed in TAG doped with Ce (0.1, 0.5 and 1.0 mol%, variable) maintaining the Eu concentration constant at 0.1 mol%.

3.6 UV-VIS absorption

UV-VIS absorption spectra of TAG co-doped with Ce (0.1, 0.5 and 1.0 mol%, variable) and Eu (0.1 mol%, constant) are shown in figure 9. TAG, as seen in this figure, has two absorption peaks at 228 and 280 nm; both could be due to Tb^{3+} . On co-doping with 0.1 mol% Ce and Eu, its TAG absorption in the UV region (200–250 nm) increased by a factor of ~ 5 ; also the intensity of the absorption peak at 280 nm increased marginally while showing almost zero absorption at 550 nm. On the other hand, when Ce concentration was further increased to 0.5 mol% maintaining the concentration of Eu constant at 0.1 mol% a significant increase in absorption in the 200–350 nm region was observed; also an additional absorption peak at 380 nm was observed. This 380 nm absorption peak could be due to the $4f\text{--}5d$ transition of Ce. In the case of the TAG co-doped with Ce (1.0 mol%) and Eu (0.1 mol%), as seen in figure 9, the absorption was almost uniform in the spectral region of 200–350 nm, it peaked at ~ 380 nm after

Figure 9. UV-VIS absorption spectra of TAG co-doped with Ce (0.1, 0.5 and 1.0 mol%, variable) and Eu (0.1 mol%, constant).

Figure 10. UV-VIS absorption spectra of TAG co-doped with Eu (0.1, 0.5 and 1.0 mol%, variable) and Ce (0.1 mol%, constant).

which it decreased sharply till ~ 400 nm and then decreased slowly; the absorption was significant even at 600 nm. This observed absorption could be due to the $4f\text{--}5d$ transitions of Ce. Figure 10 shows the UV-VIS absorption spectra of TAG co-doped with Eu (0.1, 0.5 and 1.0 mol%, variable) and Ce (0.1 mol%, constant).

TAG when doped with Ce (0.1 mol%) and Eu (0.5 mol%), as seen in figure 10 showed broad absorption in the 225–300 nm range with a peak at 260 nm; this is characteristic Eu absorption. However, a decrease in absorption was observed in the 225 to 300 nm region where the peak shifted to 273 nm when the Eu concentration was increased to 1.0 mol% implying the migration of Eu to the surface at higher concentrations.

Figure 13. Integrated area (arbitrary units, au) of the emission spectrum of the TAG co-doped with (a) Ce (0.1, 0.5 and 1.0 mol%, variable) and Eu (0.1 mol%, constant) and (b) Eu (0.1, 0.5 and 1.0 mol%, variable) and Ce (0.1 mol%, constant).

3.7 Photoluminescence (PL)

Figure 11 shows 280 nm excited PL spectra of TAG co-doped with Ce and Eu; the spectra of single doped Ce and Eu and those of undoped TAG have been shown for comparison.

The PL of un-doped TAG, as seen in figure 11, consists of well-defined peaks in the visible regions which could be due to Tb^{3+} as shown in figure 12. Relatively broad emission superimposed with a few peaks was observed when TAG was doped with 0.5 mol% Ce. This broad emission could be due to the 5d–4f emission of Ce while the superimposed peaks could be due to Tb present in TAG [17]. A similar type of broad emission was observed in TAG:Eu (0.5 mol%) [18] and in TAG co-doped with 0.5 mol% of both Ce and Eu. Emission lines from Tb are dominating in almost all the spectra except that of TAG co-doped with 0.1 mol% Ce and 1.0 mol% Eu where intensity falls sharply in the 400–500 nm region while Tb can be seen in the 500–700 nm region. This could be due to concentration quenching by Eu which has strong absorption in the 400–500 nm region. The variation in the intensity of the observed emission is shown in figure 11 where the integrated area (arbitrary units; au) of the emission spectrum has been

plotted as a function of the dopant concentration (figure 13a and b).

The intensity of the emission in the visible region, as seen in figure 13a, increases significantly with the increase in the concentration of Ce maintaining the Eu concentration constant at 0.1 mol%. On the other hand, in the case of the TAG co-doped Eu (0.1, 0.5 and 1.0 mol%, variable) and Ce (0.1 mol%, constant), the intensity is maximum for 0.5 mol% of Eu which decreases sharply when the Eu concentration is increased to 1.0 mol% (figure 13b). This decrease with the increase in the Eu concentration could be due to ‘concentration quenching’ and/or due to increased distortion induced by Eu as discussed while analysing the XRD data.

The suitability of any phosphor material is assessed by calculating the chromaticity colour coordinates (x , y) and colour correlated temperature (CCT) of its emission in the visible region [19]. Figure 14 summarizes these coordinates calculated for the visible emission observed from TAG co-doped with Ce and Eu.

TAG co-doped with 0.5 mol% of both Ce and Eu, as seen in figure 14, emits in the visible region which has characteristics of ‘day light’ indicating its utility in the realization of white

Figure 14. CIE diagram of TAG co-doped with Ce and Eu.

light sources; its chromaticity colour coordinates $x = 0.35$ and $y = 0.35$ along with CCT = 4812 K are very close to that of an ideal white light source which should have $x = 0.33$ and $y = 0.33$ with CCT = ~ 5000 K. On the other hand, CIE coordinates of TAG with different doping concentrations of Ce and Eu are marked on the CIE diagram [20] as shown in figure 14, emit blue-purple or blue-green shades and can be used for the fabrication of coloured light sources. However, its colour rendering index needs to be investigated to realize its full potential.

As seen in figure 14, the emission falls very well in the white light region of the CIE diagram.

4. Conclusion

Undoped and co-doped TAG were excited by 280 nm and show broad emission in the visible region. The PL spectra of undoped TAG consist of well-defined peaks in the visible regions which are due to Tb^{3+} . TAG:Ce (0.5 mol %) showed broad emission in the visible region which could be due to the 5d–4f emission of Ce along with the superimposed peaks due

to Tb present in TAG. Similar broad emission was observed in TAG:Eu (0.5 mol%) and in TAG co-doped with 0.5 mol% of both Ce and Eu. TAG co-doped with 0.5 mol% of both Ce and Eu emits in the visible region which has characteristics of ‘day light’ indicating its utility in the realization of white light sources; its chromaticity colour coordinates $x = 0.35$ and $y = 0.35$ along with CCT = 4812 K are very close to that of an ideal white light source which should have $x = 0.33$ and $y = 0.33$ with CCT = ~ 5000 K.

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