Effect of Tb$^{3+}$ concentration on the optical and vibrational properties of YBO$_3$ tri-doped with Eu$^{3+}$, Ce$^{3+}$, and Tb$^{3+}$

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Structural and optical studies are reported of yttrium orthoborate YBO$_3$ when tri-doped with Eu$^{3+}$, Ce$^{3+}$, and Tb$^{3+}$, focusing on the role of terbium concentration. Incorporation of Tb$^{3+}$ affects emission properties for photoluminescence (PL) excited by near ultraviolet light. For constant cerium and europium concentrations, increasing the Tb$^{3+}$ results in diminished PL from the Ce$^{3+}$ and Tb$^{3+}$ color centers. Simultaneously, the PL excitation bands related to both Ce$^{3+}$ and Tb$^{3+}$ increase in intensity for red emission from the Eu$^{3+}$. Results are consistent with a Ce$^{3+}$→(Tb$^{3+}$)$_n$→Eu$^{3+}$ energy transfer scheme, where (Tb$^{3+}$)$_n$ denotes a chain incorporating $n$ terbium ions. A high red to orange PL intensity ratio is obtained, ranging from 1.34 to 2.09. Raman vibrational bands show a systematic change, with Tb$^{3+}$ concentration, in the B$_{3}$O$_9$ ring terminal oxygen bending mode coordinated with the yttrium site where dopant ions substitute. The structural changes are interpreted as variations in the local neighborhood of these sites in the YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ crystal structure. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4875914]

I. INTRODUCTION

Phosphors exhibiting narrow emission in the red wavelength range are needed for improving the color-rendering index (CRI) of white light emitting diodes (WLEDs). 1,2 Emission from YBO$_3$:Eu$^{3+}$ is attractive for solid state lighting applications due to its narrow red emission bands at wavelengths 611 and 627 nm. However, the weak and narrow f–f transitions of Eu$^{3+}$ ions in the near ultraviolet (UV) to blue range are problematic for application in phosphor-based WLEDs due to the need for strong absorption of the emission from InGaN-based LEDs. This has motivated research to incorporate dopants for sensitizing the color centers to increase the photoluminescence (PL) efficiency with near UV and blue pumping wavelengths.

Recently, utilizing energy transfer (ET) mechanisms from Ce$^{3+}$→Tb$^{3+}$ and Tb$^{3+}$→Eu$^{3+}$, the Ce$^{3+}$→(Tb$^{3+}$)$_n$→Eu$^{3+}$ (where $n$ corresponds to the number of Tb$^{3+}$ ions in a representative energy migration chain) combination has been shown to increase the luminescence efficiency of Eu$^{3+}$ emission in the YBO$_3$ host matrix using near UV excitation. 2 The concentration of Tb$^{3+}$ ions plays a crucial role in the Ce$^{3+}$→Tb$^{3+}$→Eu$^{3+}$ energy transfer and acts as a good intermediate to minimize the competing metal-metal charge transfer (MMCT) quenching between Ce$^{3+}$ and Eu$^{3+}$ ions in YBO$_3$, which reduces the red emission intensity. Despite improvement in luminescence efficiency of YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$, this phosphor shows poor chromaticity due to intense orange (O at wavelength 591 nm) and weak red (R at 611 and 627 nm) emission of Eu$^{3+}$. The orange emission is a magnetic dipole parity allowed process, while red emission is an electric dipole parity forbidden process. According to Judd–Ofelt theory, reduced local site-symmetry in the Eu$^{3+}$ ion neighborhood is one factor for increasing chromaticity. 3,4 Perturbation of the Eu$^{3+}$ color center symmetry in the host matrix may mix states which allow the electric dipole process to participate in the emission process. Because there are few ways to examine the local order of Eu$^{3+}$ ions in YBO$_3$ host matrix, this has not yet been fully studied. In a previous paper, 5 we reported changes in the PL and Raman spectra for YBO$_3$:Eu$^{3+}$ grown under different conditions. That work focused on the terminal oxygen stretching (TS) vibration, but changes were also observed in the terminal bending (TB) mode. Those changes were linked with crystal distortion near the color center and resulting changes in the PL interpreted according to Judd-Oftel theory.

Combined photoluminescence emission and excitation (PL and PLE, respectively) spectroscopic studies are powerful for obtaining information about energy transfer between impurities. Excitation of one impurity and emission from another supports identification of energy transfer. Concentrations may then be systematically varied to determine conditions most conducive to the desired transfer for improving the PL efficiency related to a particular excitation.

Here, we examine the effect of Tb$^{3+}$ ions on the structural order near Eu$^{3+}$ ions and its impact on emission properties of YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$. We synthesize the materials using the hydro(solvo)thermal method. This approach

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permits control of several parameters in the synthesis process and allows a range of impurity doping approaches. We previously used this method to produce different morphologies of YBO₃:Eu³⁺. The materials show improved chromaticity for excitation in the near UV region. Here, we extend this approach to grow YBO₃:Ce³⁺,Tb³⁺,Eu³⁺ for improving red phosphors with near UV optical pumping. We investigate structural changes in the host matrix with increasing concentration of Tb³⁺ ions using XRD and Raman spectroscopy, and the impact on optical properties using PL and PLE. Results are consistent with an energy transfer mechanism from Ce³⁺ to Eu³⁺ mediated by the Tb³⁺ ions.

II. EXPERIMENTAL DETAILS

The samples were synthesized from precursors Y(NO₃)₃·6H₂O and K₂B₄O₇·4H₂O by the hydro(solvo)thermal technique without any organic solvent or surfactant. A 1:2 molar ratio was selected for the Y and B starting precursors and a 1:1 mixture of deionized (DI) water and ethanol solvents was used in the synthesis process. Aqueous solution of 0.2 M (each) Y(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Eu(NO₃)₃·6H₂O, and Tb(NO₃)₃·5H₂O were mixed together with the water and ethanol under vigorous stirring. The samples are designated according to the volumes of each dopant precursor used in the synthesis. A dopant molar concentration of 0.2% was used for Ce³⁺ and the Eu³⁺ ion molar concentrations were fixed at 1% and 5%. The Tb³⁺ ion concentration was varied from 5% to 50%. An aqueous solution of 0.2 M K₂B₄O₇·4H₂O was added to the former solution while stirring. The precipitate appeared immediately. The pH was fixed at ~8.5 using 1 M ammonia water. The solution was stirred for 30 min before being transferred into 50 ml autoclave and kept at 180°C for 12 h. The white sample powder was formed as the final product in the autoclave. The powder samples were then repeatedly washed with DI water and ethanol followed by drying in room ambient for 24 h.

Characterization was carried out with the samples at room temperature. Samples were characterized using scanning electron microscopy (SEM, not shown) and XRD. The diffraction measurements were carried out using a Rigaku Ultima III diffractometer with Cu-Kα radiation. PL studies were performed with a custom setup. Near UV excitation was produced by an argon-ion laser at λ_ex = 363.8 nm. Emission spectra were dispersed using a scanning spectrometer and detected with a cooled photomultiplier tube. PLE measurements were performed with a commercial spectrophotometer (PTI C61/2000 m Lawrenceville, NJ). For these measurements, powder samples were suspended in DI water in quartz cuvettes under constant stirring. All PLE spectra were obtained monitoring the red Eu³⁺ emission at wavelength λ_em = 611 nm. The separately measured water background was negligible.

III. X-RAY DIFFRACTION

XRD data are shown for each sample in Fig. 1(a). Each diffraction pattern is similar confirming consistent crystal structure for all samples. In Fig. 1(b), we summarize the 2θ peak positions as a function of Tb³⁺ concentration in the sample preparation. Clear from our data is a dependence in each diffraction angle with increasing Tb³⁺ content. The position of the XRD lines is an indication of this concentration. However, we

![Figure 1](image-url)
note that the trend is not smooth, particularly for the 25% and 30% Tb³⁺ data. Since a monotonic dependence is expected with the dopant content, we consider the XRD data to be a better indicator of Tb³⁺ concentration than those based on the preparation conditions. Line widths were analyzed according to Scherrer’s formula yielding a nanocrystal size of ∼30 nm; no trend was observed with doping concentration.

IV. PHOTOLUMINESCENCE EXCITATION AND EMISSION SPECTROSCOPY

The terbium concentration is found to affect the optical properties of our materials. Figure 2 presents PLE (a–g) and corresponding PL (A–G) spectra of YBO₃:Ce³⁺,₀₂₅,Tb³⁺,₅ₓ,Eu³⁺,₅₅ for samples with varying y from 5% to 50%. Intensities are scaled for each sample, so that the PLE intensity at λₓ = 363.8 nm (λₑₐᵣ in 611 nm) matches the PL intensity at λₑᵣ = 611 nm (λₓ = 363.8 nm) and are offset vertically for clarity. The PLE spectrum of YBO₃:Ce³⁺ is also included as a reference to help identify the effects of Tb³⁺ concentration on the excitation intensities of YBO₃:Ce³⁺,Tb³⁺,Eu³⁺ in the near UV region.

Specific bands are present in the PL spectrum, e.g., Fig. 2 spectrum A, related to the Ce³⁺, Tb³⁺, and Eu³⁺ ions in YBO₃:Ce³⁺,₀₂₅,Tb³⁺,₅₅,Eu³⁺,₅₅. The weak emission band from 370 to 430 nm is associated with 5d–4f states in Ce³⁺. The main Tb³⁺ emission peaks are at wavelengths 488 and 545 nm and originate from ⁵Dₓ₋⁷Fₓ (J = 6, 5) transitions. The 591 nm orange (O) and 611 and 627 nm red (R) bands from Eu³⁺ belong to allowed magnetic dipole ⁵Dₓ₋⁷Fₓ and forbidden electric dipole ⁵Dₓ₋⁷F₂ transitions, respectively. With an increase in the Tb³⁺ concentration to 10%, the Ce³⁺-related emission is no longer observed. Additionally, the Tb³⁺ emission bands decrease relative to Eu³⁺ emission in the PL spectra as shown in Fig. 2, spectrum B. This trend continues with increasing Tb³⁺ content with only a trace PL band seen at y = 50%. We also note that the R/O ratio for the Eu³⁺ emission varies with terbium concentration. We return to this point later.

The decrease in PL intensities of Ce³⁺ and Tb³⁺ bands relative to Eu³⁺ emission may be due to ET from Ce³⁺ → Tb³⁺ and Tb³⁺ → Eu³⁺. It has been previously reported that the Ce³⁺ ions do not directly transfer energy to the Eu³⁺ ions in YBO₃ host matrix. Moreover, the luminescence from the Eu³⁺ and Ce³⁺ ions is quenched due to the MMCT effect. The addition of Gd³⁺ ions to YF₃ has been shown to mediate transfer of electrons from Ce³⁺ to Eu³⁺ and to negate the MMCT quenching.

ET from Ce³⁺ → Tb³⁺ → Eu³⁺ in YBO₃ may be studied using PLE by excitation of the Ce³⁺ and Tb³⁺ ions while monitoring emission from the Eu³⁺ color centers. The PLE spectrum, for YBO₃:Ce³⁺,₀₂₅,Tb³⁺,₅ₓ,Eu³⁺,₅₅ in Fig. 2, spectrum a, is similar to that of YBO₃:Eu³⁺. The sample exhibits an intense broad deep-UV band near 241 nm (not shown) and weak intensity states in the range 310–390 nm. The deep UV feature is close to the excitation band of O → Eu charge transfer states of YBO₃:Eu³⁺. As Tb³⁺ concentration does not effectively transfer energy from Ce³⁺ to Eu³⁺, the Tb³⁺ concentration is further increased to 15% in spectrum c of Fig. 2, significant changes are observed. A weak shoulder appears near 285 nm and the near UV band from 310–390 nm increases in strength. Previous work has identified the 285 nm feature and the near UV band (310–390 nm) in the excitation spectrum to absorption by the Tb³⁺ to Ce³⁺ color centers, respectively.

These Tb³⁺ and Ce³⁺ excitation bands in the PLE spectra for Eu³⁺-related emission, and the quenching which occurs when only Ce³⁺ and Eu³⁺ are present in the YBO₃, indicate that energy transfer is taking place between the dopants according to Ce³⁺ → Tb³⁺ → Eu³⁺ and Tb³⁺ → Eu³⁺. Because the Ce³⁺ and Tb³⁺ PL intensities are simultaneously decreasing relative to the Eu³⁺ emission, we conclude that the ET mechanism is affecting the emission from these color centers in Fig. 2 spectrum C. The intensity of the PLE bands at 285 nm and near the UV range 310–390 nm are improved further with higher Tb³⁺ content (y = 20%–50%) in Fig. 2, spectra d–g. The emission intensity of Tb³⁺ further decreases...
relative to Eu$^{3+}$ in the PL spectra D–G in Fig. 2. These trends further support the ET between dopants. It has been suggested that the Tb$^{3+}$ ions form a Tb$^{3+}$-Tb$^{3+}$ energy migration chain, denoted (Tb$^{3+}$)$_n$ at higher Tb$^{3+}$ concentrations. These chains transfer energy from Ce$^{3+}$ to Eu$^{3+}$ ions minimizing the MMCT effect between these two ions. The strongest Tb$^{3+}$ (285 nm) and Ce$^{3+}$ (310–390 nm) excitation bands observed in our data are at high Tb$^{3+}$ content (y = 50%), indicating effective ET from Ce$^{3+}$ to Eu$^{3+}$ at these levels and in agreement with the Tb$^{3+}$ energy migration chain hypothesis.

V. R/O RATIO

To see the effect of the Eu$^{3+}$ concentration on the Ce$^{3+}$→(Tb$^{3+}$)$_n$→Eu$^{3+}$ energy migration chain, we decreased the concentration of Eu$^{3+}$ from 5% to 1% keeping Ce$^{3+}$ and Tb$^{3+}$ fixed at 0.2% and 50%, respectively. In Fig. 3, we show the PLE and PL spectra, obtained under identical conditions as the data in Fig. 2, but without normalizing the measured intensities. We observed an increase in PLE intensities in the near UV region, and PL intensities in Fig. 3, for the sample with lower (1%) Eu$^{3+}$ concentration. This may be due to reduced MMCT quenching effect between Eu$^{3+}$ and Ce$^{3+}$ ions at 1% when compared to the higher 5% concentration. In both cases, we obtain a high R/O intensity ratio (611 and 627 nm–591 nm), although we note that this is higher in the 5% Eu$^{3+}$ sample than for 1%. Systematic studies varying the europium content are needed to optimize the R/O ratio.

It is interesting that the R/O ratio is varied across the samples in the A–G PL spectra in Figure 2 for fixed Eu$^{3+}$ content. In all cases, the R/O ratios are greater than unity (Table I). In the YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ samples, for which we observe strong PLE in the near UV range, we obtain a R/O ratio of 1.68. The best R/O in this series of samples is for YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ (y = 5% to 50%) and YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ (y = 5% to 50%) samples. The peaks in the range 250–1150 cm$^{-1}$ are associated with different vibrational modes of the B$_2$O$_3$ ring structure in the YBO$_3$ crystal. The TB, TS, ring bending (RB), and ring stretching (RS) mode assignments are included in Fig. 4(a) according to previous investigators. The TB and TS bands are particularly important in our study because they carry information about terminal oxygen atoms in the B$_2$O$_3$ rings which comprise the bent B-O-lanthanide structure, where the lanthanide is the Y cation in the YBO$_3$ crystal structure and corresponds to the substitutional dopant site in our samples. Variations in the TB and TS vibrations are expected to carry information about the local structure of the yttrium ions. Consequently, their behavior may influence the emission, especially of the Eu$^{3+}$ dopant, since europium substitutes for yttrium in YBO$_3$. We note that the majority of the Raman bands do not show a systematic deviation with terbium concentration. However, the TB bands near 257 and 427 cm$^{-1}$ are associated with different vibrations of the Eu$^{3+}$ ions, thereby influencing the emission.

VI. RAMAN SPECTROSCOPY

To check for structural variations in our samples, beyond what is available in XRD, we carried out vibrational Raman studies. Figure 4(a) shows the Raman spectra of YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ (y = 5% to 50%) and YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ (y = 5% to 50%) samples. The peaks in the range 250–1150 cm$^{-1}$ are associated with different vibrational modes of the B$_2$O$_3$ ring structure in the YBO$_3$ crystal. The TB, TS, ring bending (RB), and ring stretching (RS) mode assignments are included in Fig. 4(a) according to previous investigators. The TB and TS bands are particularly important in our study because they carry information about terminal oxygen atoms in the B$_2$O$_3$ rings which comprise the bent B-O-lanthanide structure, where the lanthanide is the Y cation in the YBO$_3$ crystal structure and corresponds to the substitutional dopant site in our samples. Variations in the TB and TS vibrations are expected to carry information about the local structure of the yttrium ions. Consequently, their behavior may influence the emission, especially of the Eu$^{3+}$ dopant, since europium substitutes for yttrium in YBO$_3$. We note that the majority of the Raman bands do not show a systematic deviation with terbium concentration. However, the TB bands near 257 and 427 cm$^{-1}$ are associated with different vibrations of the Eu$^{3+}$ ions, thereby influencing the emission.

![FIG. 3. PLE (monitoring 611 nm) and PL ($\lambda_{ex}$ = 363.8 nm) spectra of YBO$_3$:Ce$_{0.2%}$,Tb$_{0.5%}$,Eu$_x$ samples with x = 1% and 5%.

<table>
<thead>
<tr>
<th>Tb$^{3+}$ (mol. %)</th>
<th>Ce$^{3+}$, Eu$^{3+}$ (mol. %)</th>
<th>R/O ratio</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>0.2, 5</td>
<td>1.68</td>
</tr>
<tr>
<td>10</td>
<td>0.2, 5</td>
<td>1.54</td>
</tr>
<tr>
<td>15</td>
<td>0.2, 5</td>
<td>2.09</td>
</tr>
<tr>
<td>20</td>
<td>0.2, 5</td>
<td>1.91</td>
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<tr>
<td>25</td>
<td>0.2, 5</td>
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<td>30</td>
<td>0.2, 5</td>
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<tr>
<td>50</td>
<td>0.2, 5</td>
<td>1.68</td>
</tr>
<tr>
<td>50</td>
<td>0.2, 1</td>
<td>1.34</td>
</tr>
</tbody>
</table>
The intensity of this vibrational band also changes relative to RB band at 412 cm$^{-1}$ and 1 cm$^{-1}$. It is weakest in the YBO$_3$:Ce$^{3+}$0.2%,Tb$^{3+}$5%,Eu$^{3+}$5% sample and gradually grows in strength with higher Tb$^{3+}$. Based on this, we also examined the concentration dependence of the TB band near 255 cm$^{-1}$. A similar, but considerably weaker trend, is found in the data as summarized in Fig. 4(b). Based on this similar dependence, we attribute shifts in these vibrations to the same source. A plausible cause for the observed TB shift is the volume expansion implied by the XRD measurements with increasing Tb$^{3+}$ incorporation. Lattice expansion will affect bond angles in this structure more than bond length, particularly for the tetrahedral BO$_4$ building blocks of the B–O ring structure. This expansion is expected to affect the terminal oxygen vibrations since terbium substitutes for the yttrium and these ions are bonded to the corresponding oxygen atoms.

Distortion near the lanthanide cation sites may produce a different effect on the TS and TB vibrations, as illustrated in Fig. 4(c) based on Ref. 21. There are two TB vibrations, one with displacement in the plane made by the B–O–lanthanide group and one perpendicular to that plane. The TS displacement is in the B–O–lanthanide plane. The oxygen displacements of these vibrations are illustrated in Fig. 4(c). For clarity, the TS mode is located at the nominal position of the oxygen atom in YBO$_3$, and the TB vibrations are displaced to the corresponding position following the illustrated (exaggerated) bond angle distortion. The TB mode will consequently be more strongly influenced by increases in the B–O–lanthanide bond angle. Because we expect the in-plane TB vibration to have a higher energy and to be more strongly affected by the volume deformation due to doping, we associate it with the Raman feature at 427 cm$^{-1}$. The band at 255 cm$^{-1}$ may then be assigned to the TB vibration with displacement out of the B–O–lanthanide plane. The TS Raman bands in the range 900–1100 cm$^{-1}$ also vary with terbium doping, although they do not show a particular trend with Tb$^{3+}$ concentration. This may simply be due to the diminished interaction with the dopant as the distortion increases and the identity of TS and TB become blurred. We also see no dopant substitutional effect on the RB and RS bands. Since these modes are primarily internal to the ring structure they will be less affected by dopant perturbations due to their relative rigidity in the YBO$_3$ structure.

**VII. SUMMARY**

We have synthesized YBO$_3$:Eu$^{3+}$ tri-doped with Ce$^{3+}$ and Tb$^{3+}$, while systematically varying the terbium concentration. The XRD data in Fig. 1(b) shows a trend with Tb$^{3+}$ concentration confirming the incorporation of this dopant in our
materials. The Tb$^{3+}$ concentration influences PL emission when excited by near UV light. Increasing the Tb$^{3+}$ concentration results in diminished PL from the Ce$^{3+}$ and Tb$^{3+}$ color centers for constant cerium and europium content, as seen in Fig. 2. The PL excitation bands related to both Ce$^{3+}$ and Tb$^{3+}$ increase in intensity for red emission from the Eu$^{3+}$ with increasing terbium concentration. Results are consistent with a \( \text{Ce}^{3+} \rightarrow (\text{Tb}^{3+})_n \rightarrow \text{Eu}^{3+} \) energy transfer scheme. A high R/O PL intensity ratio is obtained, ranging from 1.34 to 2.09. Several Raman bands in Fig. 4 show a systematic change, with Tb$^{3+}$ concentration, in the TB mode related to the host lattice site which corresponds to yttrium position where the dopant ions substitute. The structural changes are interpreted as variations in the local neighborhood of these sites in the YBO$_3$:Ce$^{3+}$,Tb$^{3+}$,Eu$^{3+}$ crystal structure. The Raman measurements confirm variations of the local order near the Eu$^{3+}$ color centers induced by the terbium doping.