White light-emitting diode daubed via CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ nanocrystal sheets enclosed using SiO$_2$

Ha Thanh Tung$^1$, Dieu An Nguyen Thi$^2$

$^1$Faculty of Basic Sciences, Vinh Long University of Technology Education, Vinh Long Province, Vietnam
$^2$Faculty of Electrical Engineering Technology, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam

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**ABSTRACT**

Our investigation assesses the downshifting (DS), periodicity up-transmutation as well as internal light consistency from phosphor samples of CaSc$_2$O$_4$ incorporated with Ho$^{3+}$/Yb$^{3+}$ along with up-conversion from CaY$_2$O$_4$ incorporated with Ho$^{3+}$/Yb$^{3+}$. These samples are created via precursor antecedent compound technique. The generation for the crystalline samples having orthorhombic stage is validated by the X-ray powder diffraction. The dispersal reflectance spectra exhibit several lines within the zones of ultraviolet–visible–near infrared (UV-vis-NIR), resulting from the ions of Ho$^{3+}$ as well as Yb$^{3+}$. The optical band gap ($E_g$) results reach 5.69 and 5.58 eV, corresponding to CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ and CaY$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$. The CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ samples exhibit potent downshifting discharge in green hue when excited under 454 nm. CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$, as well as CaY$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$, exhibit potent discharges in green hue as well as near-infrared up-transmutation discharges in faint blue and red hues when excited under 980 nm. The spectrum hue clarity -$S_{gr}$ – for CaSc$_2$O$_4$:Ho$^{3+}$(1%)/Yb$^{3+}$(5%) reaches 0.78. The disparity in pumping force yields internal light consistency for said sample with the green discharge, being nonexistent in the CaY$_2$O$_4$:Ho$^{3+}$(1%)/Yb$^{3+}$(5%) sample. As such, CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ may prove useful when applied to up-transmutation apparatuses.

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**Corresponding Author:**
Dieu An Nguyen Thi
Faculty of Electrical Engineering Technology, Industrial University of Ho Chi Minh City
No. 12 Nguyen Van Bao Street, Ho Chi Minh City, Vietnam
Email: nguyenthidieuan@iu.edu.vn

1. **INTRODUCTION**

Phosphors incorporated with three-valence lanthanide appears to be a desirable option as they offer potent as well as distinctive power-states along with sharp f-f shifts caused by the electrons of 4f in the ions of Ln$^{3+}$ being covered via occupied exterior shells of 6s$^2$ as well as 5p$^2$. With various power states having great multiplication as well as L-results [1], [2], the ions of lanthanide exhibit strengthened multi-modal luminescence, including up-transmutation, downshifting as well as quantum cleaving, which are determined by appropriate exciting radioactivity. Downshifting (DS) complies with the Stokes rule [3], [4], turning a small wavelength photon into big wavelength photon. It should be noted that the photon up-transmutation would be one non-linear light incident, creating discharge opposed to Stokes where the successive absorptivity for at least two photons with small power causes one luminescent discharge with strong power [5]. The up-transmutation luminescence (UTL) between near-infrared and observable states in lanthanide phosphors appears to be desirable for the flexibility they offer. Internal light consistency would be when the discharge strength avoids conforming to the behavior of surging or declining pumping force causing...
hysteresis cycle [6]. The substances with light consistency can be employed for many optical apparatuses, including transistors as well as computers [7]. Different bases (fluorides, oxides, and phosphates) were thoroughly examined to gauge their luminescence. However, other substances such as scandate (Sc₂O₃) as well as yttrate (Y₂O₃) do not receive equal investigation. According to Tian’s work, the luminescence from substances derived from scandium (Sc) were assessed, leading to findings of their applications, distinctive compared to substances with rare-earth constituents. In the case of hexagon-form NaScF₃:Yb/Er nanoscopic granules yield potent UTL in red [8], distinctive compared to one from potent green discharge generated via variations for NaYF₃:Yb/Er. On the other hand, it is possible to generate the formational intersecting transmutation among orthorhombic KScF₃:Yb/Er and cube-shaped K₂NaScF₃:Yb/Er nanoscopic particles via altering the chemical response [9]. In certain works [10]–[13], the formation alterations for various substances were assessed. CaSc₂O₄, possessing orthorhombic CaFe₂O₄ formation as well as space group Pnam (62), offers certain benefits as it can act as one luminescent substance base that yields great chemical as well as heat consistency, small fluctuating periodicity, small chemical bindings (caused by tiny Sc³⁺ ion radius measured at 0.87 Å unlike other rare-earth components), small crystal field symmetry as well as potent crystal field strength. Bases with insignificant symmetry are known to yield one crystal field that possesses a greater number of bumpy constituents surrounding the doped ions, surpassing ones with significant symmetry [14], [15]. These constituents stimulate the electron joining among 4f power states and greater 4f5d settings, surging the chance of f/f shifts for the doped ions. This will validate the extra benefit from the CaSc₂O₄ base with small symmetry. The potent crystal field may cause significant Stark cleaving for power states in said ions, resulting in greater power shift performance. On the other hand, the CaY₂O₃ base exhibit one small phonon periodicity at roughly 540 cm⁻¹. It will also lessen non-radioactive multi-phonon alleviation during up-transmutation activity [16].

This study will assess the formation attributes, DS as well as UTL in CaSc₂O₄:Ho³⁺/Yb³⁺ along with up-transmutation in CaY₂O₃:Ho³⁺/Yb³⁺ samples. The study will also look into the degradation kinetics for the distinctive discharges in the ions of Ho³⁺ under various Yb³⁺ content levels within the samples via employing Inokuti–Hirayama model (IH model), as well as observing DS and up-transmutation luminescence excited at 454 nm as well as 980 nm. Based on findings, CaSc₂O₄:Ho³⁺/Yb³⁺ exhibits greater up-transmutation strength, surpassing CaY₂O₃:Ho³⁺(1%)/Yb³⁺(5%), along with internal light consistency.

2. METHOD

The study will involve creating CaSc₂O₄:Ho³⁺(1%)/Yb³⁺(x%) with x values of 0, 5, 10, 20, 30 via employing the composite-derived preliminary compound technique that utilizes triethanolamine (TEA) in the form of compositing component [17]. In addition, CaY₂O₃:Ho³⁺(1%)/Yb³⁺(5%) will be created via the same technique to compare characteristics. The creation process began with making the water-bearing component, which is [Sc(NO₃)₃] (scandium nitrate) by putting [Sc₂O₃] inside one beaker, then adding dual filtered H₂O as well as HNO₃ (nitric acid). Next, the blend was fired above one magnetic mixer under a temperature of 80 °C within seven to eight hours, yielding limpid [Sc(NO₃)₃]. Next, the process involved adding various solid powders: [Ca(NO₃)₂] (calcium nitrate), [Ho(NO₃)₃] (holmium nitrate), [Yb(NO₃)₃] (ytterbium nitrate) as well as [Y(NO₃)₃] (yttrium nitrate) into dual filtered H₂O for the task of acquiring a metallic nitrates compound. Afterwards, we determined the proportions for Sc(NO₃)₃, Ca(NO₃)₂, as well as Ho³⁺/Yb³⁺(NO₃), and created a merger between TEA and nitrate compound so that the entire ratio of metallic ion: TEA particle is sustained at 1:4. Initially, TEA was precipitated, caused by the created metallic hydroxides, accompanied by metallic ions. We dissolved the product, then introduced several HNO₃ droplets to acquire one limpid compound, with pH sustained under the value of 3 to 4. Next, the vaporization of the limpid compound TEA-derived metallic nitrate was carried out using one heated plate between the temperatures of 180 °C and 200 °C, accompanied by continual mixing. Throughout the process, the nitrate ions produced in-situ oxidization condition for TEA, incompletely changing TEA hydroxyl groups to carboxylic acids. As water diminishes entirely, the nitrates degraded, exhibiting increased brown vapor from nitrogen dioxide, and yielding one preliminary powder in a great mass, which is black and organic-derived. Afterwards, we tempered this powder under a temperature of 1,200 °C within two hours for the task of acquiring the desired phosphors. This entire creation process will also apply to CaY₂O₃:Ho³⁺(1%)/Yb³⁺(5%).

Following the creation of the phosphor samples, the assessment of their attributes was carried out. Various tool was employed for the assessment task. Table 1 shows characteristics along with the tools used analyze them.

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Table 1. Assessment of phosphor characteristics

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Assessing tools</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase purity</td>
<td>X-ray diffraction (XRD) inspection using Bruker AXS D8 automatic diffractometer having Cu-Kα radioactivity (λ=1.5418 Å), under the angle scope of 20°±20°±60° subjected to 40 kilovolts as well as 40 milliamperes</td>
</tr>
<tr>
<td>Fluctuating groups</td>
<td>PerkinElmer IR spectrometer (FT-IR/FIR spectrometer Frontier) for observing Fourier transform infrared spectra (FTIR) in various phosphors</td>
</tr>
<tr>
<td>Ultraviolet–visible–near infrared</td>
<td>PerkinElmer UV–Vis–NIR spectrometer (Lambda-750)</td>
</tr>
<tr>
<td>(UV–Vis–NIR) spectra assuming</td>
<td>980 nm radiation generated by one diode laser along with an iHR320, Hamamatsu NIR-extended photomultiplier linked with one Leecroy digital storage oscilloscope</td>
</tr>
<tr>
<td>dispersal reflectance state</td>
<td>Yvon spectrometer accompanied by one photomultiplier tube</td>
</tr>
<tr>
<td>Up-transmutation discharge spectra</td>
<td>Subjecting the phosphors using an EKSPLA 10 ns pulsed optical parametric oscillator (OPO) laser, then acquiring the photoluminescence using Jobin-Yvon 320 spectrometer accompanied by one Hamamatsu NIR-extended photomultiplier linked with one Leecroy digital storage oscilloscope</td>
</tr>
<tr>
<td>Steady-state and the time-</td>
<td></td>
</tr>
<tr>
<td>resolved luminescent spectra</td>
<td></td>
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</tbody>
</table>

3. RESULTS AND DISCUSSION

The non-radioactive power shift activities cause lower luminescence if the Yb$^{3+}$ ion content surges, which is assessed by using the Inokuti-Hirayama model. With various shift characteristics assessed, it is possible to categorize the standard non-radioactive activities between the ions of Ln$^{3+}$ into two types: if the prevalent interactivity between ions results from one multipolar activity concerning the giver as well as the receiver ions, the luminescent degradation intensity posterior to the laser pulse exciting process is determined as (1) [18]:

$$I(t) = I(0) \exp \left[ -\frac{t}{\tau} - Q \left( \frac{t}{\tau} \right)^{3/5} \right]$$

$I(0)$ signifies the intensity under time $t$ value of zero. $\tau$ signifies the internal duration for the giver level subjected to excitation. $S$ signifies interactivity form among ions, assuming values of 6, 8, and 10 matching dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactivities. $Q$ will be determined as (2) [19]:

$$Q = \frac{4\pi}{3} \Gamma \left( 1 - \frac{2}{3} \right) C (C_{DA} \tau)^{3}$$

$\Gamma$ signifies the gamma function. $C$ signifies the receiver ion content. $C_{DA}$ signifies power shift between giver and receiver.

In case the prevalent interactivity results from reciprocation activity concerning the giver as well as the receiver ions, the luminescent degradation intensity correlating with time is determined as (3) [20]-[23]:

$$I(t) = I(0) \exp \left[ -\frac{t}{\tau} - \gamma^{-\frac{3}{2}} Q_{ex} g \left( e^{\gamma t} \right) \right]$$

$\gamma$ signifies one constant corresponding to the critical shift range $R_0$.

With the assessment for power shift activity, one predetermined internal duration for the ions of Ho$^{3+}$ from the phosphor incorporated with only Ho$^{3+}$ was utilized at 75 µs. On the other hand, according to Yu’s work, surging doping content can alter the internal radioactive attributes for the functioning ions within certain matrices. For phosphors incorporated with Ho$^{3+}$ and Yb$^{3+}$, the content would be greater. If we have the fits for degradation arches for the Inokuti formula, the results for internal duration fluctuate in the 67–90 µs range, which signifies that the predetermined 75 µs result gained the phosphor with only Ho$^{3+}$ would be a decent estimation. Under greater pumping force, the ions of Yb$^{3+}$ generate dimer couples. The performance for power shift steadily diminishes, subsequently exhibiting consistent nature, then reaching a trivial level. The internal light consistency for the substances incorporated with Yb$^{3+}$ exhibited Yb$^{3+}$:Yb$^{3+}$ dimers being generated, a result of collective interactivity among the ions of Yb$^{3+}$ subjected excitation pointing out in Hehlen’s work. According to Soni’s work, the internal light consistency is caused by dimers’ generation via dipole-dipole interactivity in the ions subjected to excitation. For collective interactivity, two ions of Yb$^{3+}$ under the ground status concurrently assimilate two occurred photons under 980 nm, then reach the status of excitation. Afterwards, the ions mutually react to generate one couple–collective ion couple (dimer). As the pumping force surges, the Yb$^{3+}$ ion content subjected to excitation surges, subsequently stimulating the collective interactivity among the Yb$^{3+}$:Yb$^{3+}$ ions subjected to excitation. This potent linear interactivity will augment the internal crystal field, causing internal light consistency. Throughout this study,
the investigating team kept track of this attribute via surging or diminishing the pumping force between 0.4 W and 2 W. The relationship between scattering coefficient and wavelength is depicted by various graphs seen in Figure 1. Under all percentages, the scattering coefficient would be inversely proportional to the wavelength, noticeably diminishing under greater wavelengths.

Figure 1. Scattering coefficient of CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$@SiO$_2$ as a function of varying phosphor concentration

Figure 2 depicts the correlation concerning the number density in a vol. of 1 mm$^3$ as well as diameter measured in µm. Across all percentage levels, the dynamics exhibit similar patterns. In the range between 0.7 µm and 1 µm, the number density sees a substantial surge from 0 to 9,000,000, but plummets back its starting point under 1 µm and beyond.

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Figure 2. Number density of SrAlOCl:Bi$^{3+}$@SiO$_2$ correlating with varying phosphor concentration

Figure 3 displays the dynamics between YGA:Ce contents and SiO$_2$ granule magnitude. The dynamics appears to be an inverse correlation, as YGA:Ce content wanes with increasing SiO$_2$ particle size. Figure 4 demonstrates the correlation between the granule magnitudes and correlated color temperature (CCT) levels. In the CCT range of 2,900 K to 3,050 K, the magnitude of granules will typically fluctuate between 35 nm to 50 nm. Notably, under greater CCTs of roughly 3,150 K and 3,200 K, the granules assume the sizes of 35 nm and 0 nm, respectively. Figure 5 depicts the interaction between the hue aberration and the granule magnitude of SiO$_2$. Under magnitude ranging from 0 to 30 wt.%, the hue aberration exhibits a substantial decline going from 230 K to mere 40 K. Going up to 35 wt.%, the hue aberration sees a sudden spike, plunges at 40 wt.% then surges back up under 50 wt.%. Figure 6 exhibits the correlation between the lumen in light-emitting diode (LED) and the granule magnitude of SiO$_2$. The lumen fluctuates between 0 and 30 wt.% but experiences a huge drop from 73 Ln to 70 Ln under 40 wt.%. Afterwards, the lumen exhibits a small surge under 50 wt.%. 

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(Ha Thanh Tung)
4. CONCLUSION

The samples of CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ as well as CaY$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ were created via the preliminary compound technique. The XRD behavior validate the structure for the orthorhombic stage in CaSc$_2$O$_4$ as well as CaY$_2$O$_4$. The UV-observable spectra for the samples of CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ as well as CaY$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ exhibit various assimilation apexes caused by the ions of Ho$^{3+}$ as well as Yb$^{3+}$. The FTIR spectra correlate with the extending fluctuations for the groups Ca–O, Sc–O as well as Y–O. The DS discharge for CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ exhibit prevalent green discharge. We fitted the testing degradation arches to the Inokuti–Hirayama model for the task of assessing the interactivity among the doped ions within the samples. The untransmuted blue, green, red as well as NIR discharges for the ions of Ho$^{3+}$ when excited under 980 nm existed with CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ as well as CaY$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$. The spectrum hue clarity correlating with green hue reached 0.74 in the case of CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$. In addition, this sample generates internal light consistency in the case of green discharge. With the attributes above, CaSc$_2$O$_4$:Ho$^{3+}$/Yb$^{3+}$ can be employed in the form of a decent green discharger for photon-related sector as well as apparatuses with light consistency.

REFERENCES


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