Investigation of the Luminous Properties of Tb\(^{3+}\)-Substituted YAG:Ce, Gd Phosphors

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Yttrium aluminum garnet (Y\(_2\)Al\(_5\)O\(_{12}\), YAG) is an important crystallized material used as laser hosts and phosphors for its special optical properties, and it is also a candidate with good stability for high-temperature structural ceramics.\(^1\)\(^2\) YAG doped with Nd\(^{3+}\) has been known to be an outstanding solid-state laser material under room-temperature operating conditions in either continuous wave mode or pulsed emission mode.\(^2\) GaN-based, highly efficient blue InGaN light-emitting diodes (LEDs) combined with YAG phosphors can produce white light. These solid-state LED lamps have a number of advantages over conventional incandescent bulbs and halogen lamps, such as high efficiency to convert electrical energy into light, reliability, and long operating lifetime (about 100,000 h).\(^4\) For the purpose of development of highly energy-efficient white light sources, we need to produce highly efficient phosphors, which can absorb excitation energy from blue LEDs and generate emissions. The energy migration process and photoluminescent properties of YAG doped with single rare earth ion has been investigated widely. Pan et al. synthesized YAG:Ce phosphors by solid-state reaction, coprecipitation, sol-gel, and combustion methods.\(^5\) The authors showed that the particle size becomes smaller but the intensity of emission was lowered for phosphors synthesized by the chemical methods.

In this paper, we have synthesized Tb\(^{3+}\)-substituted YAG:Ce, Gd phosphors and investigated their luminescence and structural properties. Moreover, we also studied luminescence properties of these Tb\(^{3+}\)-substituted YAG:Ce, Gd phosphors using VUV excitation. The photoluminescent spectra showed interesting change when we synthesized phosphors of different Ce\(^{3+}\) and Tb\(^{3+}\) concentrations. The mechanism of the energy-transfer process in multicoloring elements systems is complicated. We propose a possible mechanism to explain the results in the work presented.

Experimental

Polycrystalline YAG-based samples can be prepared by solid-state reaction between Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\), but high temperatures are required. When the reactants are heated below 1600°C, a single phase cannot be obtained.\(^6\) In the present investigation we synthesized YAG phosphors by a three-step solid-state reaction using a mixture of metal nitrates and metal oxide instead of pure metal oxides or carbonates.

Precursors including Y(NO\(_3\))\(_3\)-6H\(_2\)O, Th\(_2\)O\(_3\), Ce(NO\(_3\))\(_3\)-6H\(_2\)O, Gd(NO\(_3\))\(_3\)-6H\(_2\)O, and Al(NO\(_3\))\(_3\)-9H\(_2\)O (ALDSH, without further purification) with the composition of (Y\(_{2.3-x}\),Tb\(_{x}\),Ce\(_{0.56}\),Gd\(_{0.44}\))Al\(_2\)O\(_12\) (x = 0, 0.575, 1.15, 1.725, and 2.3) were mixed and well ground in an agate mortar. The mixture was first calcined at 1000°C in air for 24 h. To get well-crystalline material, the calcined light yellow powders were subsequently reground and sintered in air at 1500°C for 24 h. Eventually, the crystallized powders were in turn milled and annealed in a reducing atmosphere (5% H\(_2\) in N\(_2\)) at 1500°C for 12 h in order to reduce Ce\(^{4+}\) to Ce\(^{3+}\). The final crystalline powders were yellow in color. The purpose of firing is not only to cause the solid-state reaction but also to form well-crystallized particles with an appropriate average diameter. The crystal structure and phase of the synthesized samples were analyzed by X-ray powder diffraction (XRD) with a wavelength of Cu K\(_\alpha\). The structure was refined with the program GSAS,\(^7\) and the peak shape was modeled with a pseudo-Voigt function. The full width at half maximum (fwhm) was refined as a function of 2\(\theta\), taking into account both Gaussian and Lorentzian broadening. The background was modeled as a 12-term polynomial function. Cell parameters, scale factor, and the background polynomial functions are free variables during refinements.\(^7\)

The luminescence spectra were measured by a SPEX Fluorolog-2 spectrometer using Xe lamp as light source and by a photoluminescence end station using a synchrotron as vacuum ultraviolet (VUV) radiation. The experimental setup of photoluminescence (PL) using VUV excitation is similar to that described previously.\(^8\) In brief, VUV light produced in the National Synchrotron Radiation Research Center in Taiwan was dispersed with a high-flux cylindrical grating monochromator (focal length 6 m) beam line. PL of phosphors was analyzed by a monochromator (Jobin-Yvon HR320, focal length 0.32 m) with a grating (1200 grooves/mm) blazed at 500 nm. The fluorescent intensity of the sample was detected with a photomultiplier (Hamamatsu R943-02) in a photon-counting mode.

Results and Discussion

The XRD patterns of the series (Y\(_{2.3-x}\),Tb\(_x\),Ce\(_{0.56}\),Gd\(_{0.44}\))Al\(_2\)O\(_12\) (x = 0, 0.575, 1.15, 1.725, and 2.3) are shown in Fig. 1a. XRD patterns obtained for all Tb\(^{3+}\)-substituted YAG:Ce, Gd\(^{3+}\) samples are well indexable under Ia-3d lattice symmetry consistent with the standard JCPDF files (no. 79-1892 for Y\(_2\)Al\(_2\)O\(_12\) and no. 76-0111 for Tb\(_2\)Al\(_2\)O\(_12\)). It shows that the samples with different concentration of terbium ions doped into YAG:Ce, Gd are still in pure phases. In Fig. 1a we observe the highest intensity peak around 32.3°(2\(\theta\)). It is clearly observed in the expanded version of the spectra in Fig. 1b. It shows that as the contents of Tb\(^{3+}\) ions increase the peaks shift to lower 2\(\theta\) value. This observation indicates that the ionic radius of Tb\(^{3+}\) is larger than Y\(^{3+}\) and it is further confirmed by crystal refinement calculations. The combined Rietveld refinement patterns of powder XRD data of a typical sample with the chemical composition of (Y\(_{2.3-x}\),Tb\(_x\),Ce\(_{0.56}\),Gd\(_{0.44}\))Al\(_2\)O\(_12\) (x = 1.15) is shown in Fig. 2. The observed and calculated intensities are represented in the bottom of Fig. 2. The results of the refinement indicate that the position of Tb\(^{3+}\), Ce\(^{3+}\), and Gd\(^{3+}\) ions in the YAG lattice are distorted.

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of Y-Al-O system are reported as follows: (i) Y₃Al₅O₁₂, with a cubic (garnet) structure; (ii) Y₉Al₉O₁₈, with an orthorhombic (perovskite) structure; and (iii) Y₃AlO₉, with a monoclinic structure. The formation of kinetically stable Y₉Al₉O₁₈ and Y₃Al₂O₆ phases is avoided by the present three-step solid-state reaction method. XRD patterns and the refinement data confirm the cubic structure (space group \( Ia\overline{3}d \)) with the lattice constants \( a = b = c = 12.0594(1) \) Å of the \( Y_{2.35}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \) phosphor. The atomic parameters derived from the refinements are given in Table I. The lattice parameter \( a \) increases with increasing \( x \) in \( Y_{2.35-x}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \) as displayed in Fig. 3. This may be due to the chemical substitution of the larger ionic radius of \( \text{Tb}^{3+} \) [1.04 Å with CN (coordination number) = 8] into the smaller \( \text{Y}^{3+} \) (1.02 Å with CN = 8) ionic sites.\(^{10}\)

Typical excitation and emission spectra of \( Y_{2.35-x}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \) (\( x = 1.15 \)) phosphor using Xe lamp as light source are shown in Fig. 4. The excitation spectrum shows two peaks at about 350 and 470 nm. \( \text{Ce}^{3+} \) in the YAG host acted as both activator and sensitizer. Due to the spin–orbit interaction, \( \text{Ce}^{3+} \) possessing a 4f electronic configuration ground state \( J_f = 5/2 \) and \( 7/2 \) split into a doublet. On photoexcitation, the 4f electron is excited to 5d level, which is further split into various levels due to the crystal field exerted by the host ligand ions. As a result, the excitation peaks at 350 and 470 nm correspond to the absorption of \( \text{Ce}^{3+} \) ions from the 4f ground state to the two different energy levels of 5d excited states. The excitation spectrum shows that the main band is in the blue region between 400 and 520 nm. Therefore, it is clear that the YAG phosphor can be excited very well by the radiation from blue LEDs with wavelength of about 470 nm.

A peak at around 548 nm (yellow light) in the emission spectrum is due to emission from the 5d states back to the 4f states. The emission spectrum in the 500 - 650 nm wavelength region of the serial samples of \( Y_{2.35-x}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \) (\( x = 0, 0.575, 1.15, 1.725, \) and 2.3) excited at 465 nm are shown in Fig. 5. The d-orbitals of rare earth ions are strongly host dependent. The energy gap between ground state and excited state of the metal ion then becomes smaller. This is called Nephelauxetic Effect or the electron–hole splitting of its d-d orbitals decreases.\(^{11}\) However, in our case when the larger \( \text{Tb}^{3+} \) ion substitutes the smaller \( \text{Y}^{3+} \) ion in the garnet structure; and \( \text{Y}_{2.35-x}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \) at 300 K. Observed (plus signs) and calculated (solid line) intensities. The difference plot between observed and calculated intensities is shown at the bottom.

### Table I. Atomic positions, isotropic temperature factors, and occupancies of \( Y_{2.35-x}\text{Ce}_{0.05}\text{Gd}_{0.65}\text{Al}_{2} \text{O}_{12} \)

<table>
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<th>Atoms</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Fraction</th>
<th>Uiso (Å²)</th>
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<tbody>
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<td>Y</td>
<td>0.125</td>
<td>0</td>
<td>0.25</td>
<td>0.3877</td>
<td>0.0160(3)</td>
</tr>
<tr>
<td>Tb</td>
<td>0.125</td>
<td>0</td>
<td>0.25</td>
<td>0.3831</td>
<td>0.0160(3)</td>
</tr>
<tr>
<td>Ce</td>
<td>0.125</td>
<td>0.0492</td>
<td>0.0110</td>
<td>0.0160(4)</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>0.125</td>
<td>0.25</td>
<td>0.2137</td>
<td>0.0160(3)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0160(1)</td>
</tr>
<tr>
<td>O</td>
<td>0.1495</td>
<td>-0.306</td>
<td>0.0492</td>
<td>1</td>
<td>0.0160(4)</td>
</tr>
</tbody>
</table>

Space group \( Ia\overline{3}d \)

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Reliability factors</th>
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<tr>
<td>( a = 12.0594(1) ) Å</td>
<td>( R_s = 9.96% )</td>
</tr>
<tr>
<td>( b = 12.0594(1) ) Å</td>
<td>( R_m = 13.97% )</td>
</tr>
<tr>
<td>( c = 12.0594(1) ) Å</td>
<td>( \chi^2 = 1.05 )</td>
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The f-d energy gap becomes larger in this condition. The PL spectrum is thus predicted to blue shift. Contrary to this prediction, Fig. 5 shows an opposite result, the red shift with the increase in $x$ values from 0 to 2.3. Jia et al. have showed the phonon side band of Cl$^-$-substituted CaS:Eu$^{2+}$. The coupling of activators with phonons resulted in the metastable energy state. The electrons in excited state relaxed with nonradiation processes to the phonon-coupling state and then emitted at longer wavelength. In our work, the crystal structure of YAG:Ce does not change with Tb$^{3+}$ substituted, which shows that the influence of phonons is not as high as in CaS:Eu. The real mechanism for our observation is not known clearly. Further studies are still carried on.

The excitation spectrum in the wavelength region 110-250 nm of (Y$_{2.3-x}$TbxCe$_x$Gd$_{0.65}$Al$_{12}$) phosphor monitored at 543 nm is shown in Fig. 6a, whereas, the emission spectrum in the wavelength region 450-850 nm of this phosphor excited at 173 nm is displayed in Fig. 6b. The excitation spectrum shows two broad bands from 160 to 200 nm and from 220 to 240 nm, respectively. These bands are affected by the absorption from the YAG host, not by that from Ce$^{3+}$ or Tb$^{3+}$. When the series of (Y$_{2.3-x}$TbxCe$_x$Gd$_{0.65}$Al$_{12}$) phosphors are excited by VUV range energy, both Tb$^{3+}$ and Ce$^{3+}$ become emission centers, and only Tb$^{3+}$ ion acts as a sensitizer. The energy gap between...
valence band and conduction band of YAG (without doping elements) is about 38 K cm\(^{-1}\). Previous work reported that the transition energy between the excited 4f state and the ground 4f state of Tb\(^{3+}\) is about 35 K cm\(^{-1}\), and the transition energy between the excited 5d state and the ground 4f state of Ce\(^{3+}\) is about 20 K cm\(^{-1}\). However, the energy gap between valence band and conduction band of YAG depends strongly on the substituted rare earth ions and their contents into YAG. On the other hand, the f-d transition energy of activators is also affected by crystal field of host.

Judging from the previous data, we propose that the excited state of Tb\(^{3+}\) is possibly close to the conduction band of YAG host, and it may accept energy from the YAG host and release radiation. Energy transferred from Tb\(^{3+}\) to Ce\(^{3+}\) was observed by Liu et al. for short-wavelength excitation. In emission spectrum two different emission centers of Tb\(^{3+}\) and Ce\(^{3+}\) are observed. The mechanism for nonradiative energy transfer from the 5D\(_3\) and 5D\(_4\) levels of Tb\(^{3+}\) to the lowest 5d state of Ce\(^{3+}\) was reported. In the YAG phosphor system, the Tb\(^{3+}\) (donor) emission spectrum and the Ce\(^{3+}\) (acceptor) excitation spectrum overlap considerably. The possible energy transfer process is depicted in Fig. 7. Electrons transferred from the conduction band of YAG release to the 5d and then to 4f (5D\(_3\), 5D\(_4\)) states of Tb\(^{3+}\) by a nonradiation process. Most of the electrons are going back to the ground state of Tb\(^{3+}\) and emit radiations; the others are transferred to the lower 5d excited state of Ce\(^{3+}\) by an internal crossing mechanism. The exact mechanisms of energy migration in such multicomponent doped systems still needs advanced studies.

Tb\(^{3+}\) consists of 4f-5d and 4f-4f transitions. It is proposed that the sharp peaks appearing in Fig. 6b, such as peaks at 543 and 549 nm, may be due to f-f transitions of Tb\(^{3+}\). Figure 7 also shows that the 5D\(_3\), 5D\(_4\) to 7F\(_J\) transitions of Tb\(^{3+}\) and the 7F to lowest-5d-excited-state transitions of Ce\(^{3+}\) are in resonance. Ce\(^{3+}\) in excited state releases the energy of f-d transition as shown in Fig. 7, and it shows broadband character from 500 to 700 nm in Fig. 6b. Figure 8 plots the excitation and the emission spectra of different Tb\(^{3+}\) contents obtained under same conditions in Fig. 6. Judging from the excitation spectra in Fig. 8a, we observed that the contents of Tb\(^{3+}\) do not make significant change in band shapes. Relationship between the intensities and Tb\(^{3+}\) amounts in excitation spectra is not clear. Viewing the emission spectra as shown in Fig. 8b, we found that the emission character changes with the concentration of Tb\(^{3+}\) in the phosphor system. When Tb\(^{3+}\) content is low, the emission spectrum contains both Tb\(^{3+}\) and Ce\(^{3+}\) characters; the spectrum consists of the sharp peaks emitted from Tb\(^{3+}\) and the broad bands emitted from Ce\(^{3+}\). As Tb\(^{3+}\) content increases gradually, the emission character of Tb\(^{3+}\) decreases but the emission character of Ce\(^{3+}\) increases in spectrum. We suggest that when the molar ratio of Tb\(^{3+}\) is larger than 1.15, Tb\(^{3+}\) does not serve as a doping element but becomes part of the host structure. Y\(^{3+}\) and Tb\(^{3+}\) metal ions form host structure with anions together and only Ce\(^{3+}\) and Gd\(^{3+}\) serve as doping elements. We also consider that higher Tb\(^{3+}\) concentration also increases the chance of interaction between Ce\(^{3+}\) and Tb\(^{3+}\), which helps nonradiation energy transfer from Tb\(^{3+}\) to Ce\(^{3+}\).

Conclusions

Addition of trivalent terbium ions into YAG phosphor host structure changes the chemical characteristics of the phosphor system. Excited at the wavelength in UV-visible range, the phosphor system absorbs light at about 470 nm and emits yellow light at band center 550 nm; Ce\(^{3+}\) is the only emission center in the phosphor system. When yttrium ions are substituted with terbium ions, the luminescence character changes. Excited under the the wavelength in VUV range, the emission spectrum of the phosphor system shows sharp and broad band characters, from Tb\(^{3+}\) and Ce\(^{3+}\) emission centers, respectively. The emission spectrum also depends on the content of Tb\(^{3+}\) in the phosphor system.

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