Influence of Mg-to-Ce Concentration Ratio on Cathodoluminescence in LuAG and LuGAGG Single-Crystalline Films

Ondrej Lalinsky,* Petr Schauer, and Miroslav Kucera

The cathodoluminescence (CL) characterizations of Lu₃Al₅O₁₂:Ce,Mg (LuAG:Ce,Mg) and of multicomponent [Lu₀.₂₅Gd₀.₇₄]₃[G₃₂.₄₈Al₂.₅₂]O₁₂:Ce,Mg (LuGAGG:Ce,Mg) single-crystalline garnet films are supported by the optical absorption spectroscopy. Using this approach, the influence of the Mg-to-Ce concentration ratio on the CL spectra and the CL decay is analyzed. The crucial role of stable Ce⁴⁺ centers in CL is shown in Mg-rich film studies. Although the CL intensity is somewhat reduced, drastic improvements in timing performance are demonstrated, including the CL decay time as low as 4.2 ns and the afterglow as low as 0.015% at 500 ns after the e-beam excitation cutoff. These results predetermine the utilization of the LuAG:Ce,Mg and LuGAGG:Ce,Mg single-crystalline films in e-beam detection systems, where especially fast scintillator response is crucial.

1. Introduction

In applications of scintillators for electron detection, such as electron microscopy and e-beam inspection, the essential scintillator parameters are the very fast scintillation decay and high dynamic range.[1,2] Also, a high light yield (LY) is required, but more important is the high signal-to-noise ratio.[3] Recently, with the use of balanced admixture engineering in cerium-doped multicomponent garnet scintillators, the cathodoluminescence (CL) decay time as low as 28 ns and the CL afterglow as low as 0.01% at 1 μs after excitation were reported under e-beam excitation.[4] Very favorable properties were also found in photoluminescence (PL) studies of other garnet specimens, where the improvement of the LY (doubled to more than 50 000 photon MeV⁻¹) and substantial suppression of the unwanted afterglow were achieved in Gd- and Ga-substituted multicomponent garnets (LuGd)₃(GaAl)₅O₁₂:Ce (LuGAGG:Ce).[5–7]

In spite of all the aforementioned progress, the decay time in particular is still too long for some e-beam detection systems.

This problem can be solved by co-doping the garnet with Mg²⁺. This leads to additional afterglow reduction in LuGAGG:Ce,[7–9] and especially in Lu₃Al₅O₁₂:Ce (LuAG:Ce) systems,[10–12] to both rise and decay time reduction,[13] but also, unfortunately, to LY reduction at higher Mg co-doping. The afterglow suppression was explained by the Ce⁴⁺ center stabilization, competing better with electronic traps for charge capture, which resulted in practical inactivation of shallow traps. The Ce⁴⁺ center has practically the same emission characteristic as Ce³⁺.[10,14] However, the LY decrease, along with the decreasing intensity of the stable Ce⁴⁺ content, may prompt questions such as: Will the Ce⁴⁺ emission be sustained even if all the Ce ions are stabilized at the charge state of 4+, and do the stable Ce⁴⁺ centers even participate in the Ce³⁺ 5d–4f emission? These questions were positively answered in some Mg-rich single crystals,[11] but not yet in the single-crystalline films or ceramics.

Moreover, the CL has not been studied in LuAG:Ce,Mg films; only studies of the PL, radioluminescence (RL), scintillation properties (LY, scintillation decay), and related studies were conducted.[12] The PL is extremely weak in the Mg-rich films because the Ce³⁺ absorption bands disappear almost completely. The RL study could be satisfactory at this stage, but X-rays have high penetration depth so that a substrate can also be excited. The CL study solves both of these problems. First, the e-beam of 10 keV has enough energy to excite electrons across the garnet bandgap. Second, the penetration depth of the 10 keV electrons is around 1 μm in garnets,[15] which is sufficient for the study of films with thicknesses of around 10 μm.

The aim of this work is to study the influence of the Mg-to-Ce concentration ratio on CL characteristics in LuAG:Ce,Mg and in multicomponent LuGAGG:Ce,Mg in an effort to shorten the CL decay and to confirm the crucial role of the stable Ce⁴⁺ centers in the Ce³⁺ emission. For these reasons, two series of LuAG:Ce,Mg and multicomponent LuGAGG:Ce,Mg single-crystalline thin films were prepared with various concentrations of Mg²⁺ ions, including Mg-rich films.
2. Results and Discussion

The optical absorption spectra of the LuAG:Ce,Mg and LuGAGG:Ce,Mg epitaxial films are shown in Figure 1. The broad spectral bands in absorption at 440 and 345 nm correspond to the allowed 4f–5d _1_ and 4f–5d _2_ (Ce^{3+}) transitions, respectively. The intensities of both these structures gradually decrease with increasing Mg^{2+} concentration. In contrast, the intensity of the broad absorption band in the UV spectrum region (below /C25_300 nm) increases with an increase in the Mg^{2+} concentration. Such intense UV absorption originates from the charge transfer (CT) of an electron from oxygen ligands toward tetravalent Ce^{4+} ions, which arises due to the necessity of the charge compensation of the aliovalent Mg^{2+} ions embedded in trivalent sites. It is worth mentioning that the LuAG:Ce,Mg film with the highest Mg content of 0.11 at% is completely transparent in the visible range without any noticeable absorption at 445 nm, which confirms that virtually all cerium ions were stabilized in the 4+ charge state. In this film, the analyzed Mg-to-Ce stoichiometric ratio is indeed slightly higher than 1. Although the specimens were grown in the oxidizing atmosphere, the creation of oxygen vacancies cannot be excluded at higher Mg concentrations. Any F^- or F-related defect emission was not observed in the studied specimens; in contrast, there can be some stable Ce^{4+} ions even in the Mg-free specimens. The weak sharp lines observed around 275 and 310 nm in the LuGAGG:Ce, Mg spectra correspond to spin and parity forbidden 4f–4f transition, 8S → 8I, and 8S → 8P, respectively, in the Gd^{3+} ions.

The CL spectra of the studied specimens are shown in Figure 2. The spectra are dominated by a doublet with a maximum around /C25_520 nm, which corresponds to the 5d _1_–4f (Ce^{3+}) transitions. In the LuAG:Ce,Mg films, the integral intensity of the characteristic Ce^{3+} emission is still comparable with the integral intensity of the reference Bi_4Ge_3O_12 (BGO) specimen even for the highest Mg concentration (0.11 at% Mg, 1LM9) where no trivalent Ce^{3+} ions are present, as shown in Table 1 and Figure 2a. This is in agreement with the previous RL studies of LuAG:Ce,Mg single crystals. The weak broad UV emission band centered around /C25_300 nm in Mg-free specimens.
LuAG:Ce, as shown in Figure 2a, comes from the host-defect emission.\[^{[14]}\] This emission was largely suppressed by Mg co-doping.

The situation looks different in the multicomponent LuGAGG:Ce,Mg films. The Ce\(^{3+}\) 4f–5d absorption is present even in the Mg-rich 1LGM1 (0.090 at\% Mg) specimen, as shown in Figure 1b. Therefore, some Ce\(^{3+}\) ions are still present. It can be expected because the Mg/Ce concentration ratio is 0.6. However, the Ce\(^{3+}\) 5d–4f emission almost vanished in this specimen, as shown in Table 1 and Figure 2b. The noticeably decreased CL intensity of the multicomponent LuGAGG:Ce, Mg films in comparison with the LuAG:Ce,Mg films can be explained as an association of two phenomena. First, the GD\(^{3+}\) sublattice, in combination with Ce\(^{4+}\) centers, may create some nonradiative pathways that decrease the luminescence output.\[^{[8]}\] This phenomenon depends on the Mg\(^{2+}\) concentration. Second, it can be the effect of the Al/Ga and Lu/Gd substitution used in the so-called “band-gap engineering strategy.”\[^{[18]}\] The Ga\(^{3+}\) substitution shifts down the bottom of the conduction band, buries shallow electron trap levels in it, and thus diminishes their influence on the CL. The GD\(^{3+}\) substitution should prevent from doing the same to the Ce\(^{3+}\) 5d levels by shifting them down. Therefore, the CL intensity of the Ce\(^{3+}\) emission can be lower in Ga-substituted specimens due to higher probability of ionization of the Ce\(^{3+}\) excited state. This effect was observed in GAGG:Ce films in our previous study.\[^{[19]}\] The ionization of the Ce\(^{3+}\) excited state should not depend on the Mg\(^{2+}\) concentration, but can still contribute to the CL intensity decrease of all studied LuGAGG:Ce,Mg films, compared to the relative CL intensity of the 1LM1 with the 1LGM3 (Mg-free specimens) in Table 1.

Experimental data and CL decay curves obtained by the deconvolution of the data using the sum of power-law and multieponential functions

\[
I(t) = I_0 + A_0(t + t_0)^{-p} + \sum_i A_i \exp(-t/\tau_i)
\]  

are displayed in Figure 3. The \(I_0\) parameter represents the level of background electronic noise, and \(A_i\) is the relative intensity of the \(i\)-th exponential component with the decay constant \(\tau_i\). These parameters are summarized in Table 1. The parameters \(A_0\), \(I_0\), and \(p\) are related to an extra power-law function. This function was used only in the case of the 1LM1 film (Mg-free LuAG:Ce). The power-law function describes the sub-gap tunneling-driven radiative recombination between a cerium center and a nearby lying shallow electron trap in the LuAG:Ce single crystal.\[^{[20]}\] However, it possesses the physical meaning only when the value of the \(p\) parameter is within the interval of 0.95–1.5.\[^{[21]}\] Among the studied specimens, only the 1LM1 film (Mg-free LuAG:Ce) fulfilled this criterion as it shows a \(p\) parameter value of 1.49. All other films showed it to be around 2.5 (fits not shown), so only the multieponential fit was used in such a case. This may indicate that substantial tunneling from an electron trap occurs only in the 1LM1 film (Mg-free LuAG:Ce) and, with the increasing Mg content, this tunneling continuously diminishes.

The gradual suppression of the afterglow (defined here as the CL intensity at 500 ns after e-beam excitation cutoff) with the increasing Mg-to-Ce concentration ratio is observed in Figure 3a in the LuAG:Ce,Mg films. Five hundred nanoseconds was selected as a practical value for scanning (transmission) electron microscope (S(T)EM) and some other e-beam devices. The gradual decrease of decay times of all components and relative intensity decrease of slower decay components are shown in Table 1. The slow components are caused by delayed recombination at the Ce\(^{4+}\) centers of charge captured and thereafter released from the electron traps. The effect of Mg co-doping in the films was explained by the Ce\(^{3+}\) → Ce\(^{4+}\) centers stabilization, which should better compete with the shallow electron traps for electron capture.\[^{[22]}\] This diminishes also the effect of tunneling. It is not because an electron has lower probability of tunneling from a trap, but because of lower trapping probability. Then, the influence of the traps on the CL decreases with increasing Mg content and, consequently, the intensities of the slow decay components also decrease.

### Table 1. Parameters of the LuAG:Ce,Mg (1LM) and LuGAGG:Ce,Mg (1LGM) multicomponent single-crystalline films.

<table>
<thead>
<tr>
<th>Specimen sign</th>
<th>Thickness[^{(d)}] [µm]</th>
<th>Mg concentration[^{(b)}] [at%]</th>
<th>Relative CL intensity[^{(i)}]</th>
<th>(\tau_i/A_i [\text{ns}])</th>
<th>(\tau_j/A_j [\text{ns}])</th>
<th>(\tau_k/A_k [\text{ns}])</th>
<th>(\tau_l/A_l [\mu\text{s}])</th>
<th>AC[^{(f)}] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1LM1</td>
<td>30.0</td>
<td>0</td>
<td>9.6</td>
<td>14/0.42</td>
<td>63/0.50</td>
<td>–</td>
<td>–</td>
<td>4.7</td>
</tr>
<tr>
<td>1LM4</td>
<td>22.0</td>
<td>0.011</td>
<td>7.6</td>
<td>13/0.37</td>
<td>56/0.57</td>
<td>540/0.047</td>
<td>2.0/0.011</td>
<td>2.7</td>
</tr>
<tr>
<td>1LM5</td>
<td>22.0</td>
<td>0.023</td>
<td>4.2</td>
<td>7.7/0.19</td>
<td>40/0.73</td>
<td>160/0.065</td>
<td>0.71/0.014</td>
<td>0.97</td>
</tr>
<tr>
<td>1LM7</td>
<td>17.0</td>
<td>0.045</td>
<td>2.8</td>
<td>8.2/0.43</td>
<td>41/0.56</td>
<td>260/0.011</td>
<td>–</td>
<td>0.17</td>
</tr>
<tr>
<td>1LM9</td>
<td>9.4</td>
<td>0.11</td>
<td>1.3</td>
<td>7.5/0.46</td>
<td>34/0.53</td>
<td>110/0.010</td>
<td>–</td>
<td>0.015</td>
</tr>
<tr>
<td>1LGM3</td>
<td>16.3</td>
<td>≈0[^{(d)}]</td>
<td>6.3</td>
<td>21/0.34</td>
<td>74/0.62</td>
<td>280/0.039</td>
<td>–</td>
<td>0.72</td>
</tr>
<tr>
<td>1LGM7</td>
<td>16.8</td>
<td>0.004</td>
<td>4.7</td>
<td>22/0.43</td>
<td>63/0.54</td>
<td>230/0.029</td>
<td>–</td>
<td>0.35</td>
</tr>
<tr>
<td>1LGM8</td>
<td>16.7</td>
<td>0.011</td>
<td>2.2</td>
<td>12/0.60</td>
<td>53/0.39</td>
<td>210/0.011</td>
<td>–</td>
<td>0.11</td>
</tr>
<tr>
<td>1LGM10</td>
<td>16.7</td>
<td>0.033</td>
<td>0.41</td>
<td>6.6/0.63</td>
<td>32/0.37</td>
<td>–</td>
<td>–</td>
<td>0.054</td>
</tr>
<tr>
<td>1LGM11</td>
<td>11.9</td>
<td>0.090</td>
<td>0.08</td>
<td>4.2/0.93</td>
<td>20/0.072</td>
<td>–</td>
<td>–</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\[^{(a)}\] Film thickness; \[^{(b)}\] Element concentration in the Lu\(_{2-x}\)Ga\(_x\)O\(_{2.5}\); \[^{(c)}\] Lu\(_{2-x}\)Ga\(_x\)O\(_{2.5}\):Ce,Mg (1LM) and Lu\(_{2-x}\)Ga\(_x\)O\(_{2.5}\):Ce,Mg (1LGM) films. 1LM films contain 0.11 at\% Ce, 1LGM films contain 0.15 at\% Mg. 1LM films contain 0.11 at\% Ce, 1LGM films contain 0.15 at\% Mg. \[^{(d)}\] Film thickness; \[^{(e)}\] Element concentration in the Lu\(_{2-x}\)Ga\(_x\)O\(_{2.5}\); \[^{(f)}\] Fit decay constants obtained from the fitted decay curves by Equation (1).
As the CL decay and they can act as nonradiative centers. Furthermore, at higher Mg concentrations, oxygen vacancies, constituting deep electron traps, can also be formed. The nonradiative recombination prevails in the films with higher Mg content, and it is in good agreement with the decreasing CL intensity in Figure 2 and with the increasing level of electronic noise represented by the $I_0$ parameter in Equation (1), as shown in Figure 3b.

In comparison with the CL decay of the 1LM1 film (Mg-free LuAG:Ce), the decay of the 1LM3 film ($\approx$0 at% Mg) is composed of relatively slower first and second exponential decay components, as shown in Table 1. These two exponentials are the main components of the Ce$^{3+}$ 5d–4f emission, and the slowdown of these components was interpreted in similar systems as being due to energy migration over the Gd$^{3+}$ sublattice, followed by energy transfer to Ce$^{3+}$.

As the CL decay of the studied films accelerates with the increasing Mg content, the slow components gradually disappear, and fewer exponentials to the proper data fit are required. Such a difference in the function approximation may cause a small variation in the obtained decay times. This is definitely the case of the 1LM film (0.045 at% Mg), where its decay is faster than decay of the 1LM5 film. Decay constants $\tau_c$ of the 1LM5 are shorter than that of the 1LM7. However, these two facts are not contradictory because relative amplitude $A_1$ of the fastest component is significantly higher for the 1LM7 than for the 1LM5. For the 1LM10 (0.033 at% Mg) and 1LM11 (0.090 at% Mg) specimens, fewer necessary exponentials can also be caused by the increased electronic noise level represented by the $I_0$ parameter in Equation (1) in comparison with the other curves in Figure 3. Such noise buries potentially slower components and is caused by the very low CL intensity of these films (Figure 2b), as mentioned earlier.

In previous articles, a reduction in the rise time to tens of picoseconds with the increasing Mg content was demonstrated.

In this article, we studied the CL properties in LuAG:Ce,Mg and multicomponent LuGAGG:Ce,Mg garnet single-crystalline films supported by the optical absorption spectra. The crucial role of the Ce$^{3+}$ ions was shown in heavily Mg$^{2+}$ co-doped specimens, where the Ce$^{3+}$ 5d–4f emission is still present under e-beam excitation, although almost all Ce ions were stabilized in the 4+ charge state. This was demonstrated in the 1LM9 specimen (0.11 at% Mg), where the Mg-to-Ce concentration ratio was $\approx$1.

3. Conclusion

In this article, we studied the CL properties in LuAG:Ce,Mg and multicomponent LuGAGG:Ce,Mg garnet single-crystalline films supported by the optical absorption spectra. The crucial role of the Ce$^{3+}$ ions was shown in heavily Mg$^{2+}$ co-doped specimens, where the Ce$^{3+}$ 5d–4f emission is still present under e-beam excitation, although almost all Ce ions were stabilized in the 4+ charge state. This was demonstrated in the 1LM9 specimen (0.11 at% Mg), where the Mg-to-Ce concentration ratio was $\approx$1.

In previous articles, a reduction in the rise time to tens of picoseconds with the increasing Mg content was demonstrated.

However, this could not be observed using our setup because minimum width of the excitation e-beam pulse was 50 ns. The rise of the scintillation signal and its faster saturation observed especially in LuGAGG:Ce,Mg system, Figure 3b, correlates well with the faster decay time in heavily Mg-doped specimens.
In the LuGAGG:Ce,Mg films, not all the Ce ions were stabilized in the $+3$ charge state because the highest Mg-to-Ce concentration ratio in the films was $\approx 0.6$ (1I2M111). Nevertheless, the Ce$^{3+}$ 5d–4f emission almost vanished in this specimen. The acceleration of the CL decay, the suppression of the afterglow, and the decrease of the CL intensity were presented as the main effects of the Mg co-doping, both in the LuAG:Ce, Mg and LuGAGG:Ce,Mg films. These effects correlate well with previous luminescence findings under X-ray and/or $\alpha$-particle excitations.[8,12] The loss of the LY is an undesirable effect for possible application, and so we admit the lower potential to apply the LuAG:Ce,Mg and the LuGAGG:Ce,Mg single-crystalline films in many areas. However, these materials can be perspective fast scintillators for applications where the fastest possible response and low afterglow are crucial, and a somewhat reduced intensity can be acceptable. Optimum Mg-doping level depends on application and it somewhat differs for LuAG:Ce,Mg and LuGAGG:Ce,Mg. The films with $\approx 0.015$ at% Mg could be perspective scintillators for detectors in real-time diagnostics in e-beam inspection systems. Higher doping level (0.030–0.045 at% Mg) could be appreciated in the detectors of high-energy particles/photons.

4. Experimental Section

Mg-co-doped LuAG:Ce0.7% and LuGAGG:Ce1% (relative concentrations in the dodecahedral sites) single-crystalline epitaxial films were grown by the isothermal dipping liquid-phase epitaxy on undoped LuAG and GAGG substrates, respectively, of (111) and (100) crystallographic orientations. The compositions of specimens, which were determined by the electron-probe microanalysis and glow-discharge mass spectrometry, and the decay times obtained from the fit are shown in Table 1. Special attention was paid to the purity of the films and the elimination of any potential impurities from the flux. The films were grown from lead-free BaO$\cdot$B$_2$O$_3$–BaF$_2$ flux. Starting raw materials of 5N purity were used. Technical details were published in previous studies.[12,28] The thicknesses of the films were 9.4–30 $\mu$m. The growth temperatures were (1030 ± 1) °C. The films had a single-crystalline and single-phase form, as proven by X-ray diffraction. The set of specimens included a reference single crystal of BGO that had an LY of 8000 photons MeV$^{-1}$. All the specimens were coated with 50 nm of Al to prevent surface charging. Optical absorption spectra, CL spectra, and CL decays were measured. The experimental setups were described in previous studies.[10,31] The CL spectra were measured under the continuous excitation of an electron beam with an energy of 10 keV and a current of 30 nA. The e-beam spot was 2 mm in diameter. For the CL decays, the electron beam was periodically deflected out of the specimen by an electrostatic deflection system, which enabled the creation of e-beam pulses with the repetition rate of 1 kHz, pulse width of 50 ns, and current of 150 nA. All the experiments were performed at room temperature.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathodoluminescence, co-doping, multicomponent garnet, scintillator, single-crystalline film

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