Effect of Al and Ce Ion Concentrations on the Optical Absorption and Luminescence in Gd₃(Al,Ga)₅O₁₂:Ce³⁺ Epitaxial Films

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Abstract—We have studied the effect of Al and Ce ions on the optical absorption and luminescence of single-crystal (Pb,Gd)₃₋ₓCeₓAlₓGa₅₋ₓO₁₂ (x = 2.02, 2.09, 2.13, 2.17, 2.22; y = 0.02, 0.06, 0.07) films grown on (111)-oriented single-crystal Gd₃Ga₅O₁₂ substrates by liquid-phase epitaxy from supercooled high-temperature solutions using solvents of the PbO–B₂O₃ system and growth charges containing 2.0, 2.1, or 2.2 mol % aluminum oxide and 0.03 or 0.2 mol % cerium oxide. The shift of the absorption bands of the Ce³⁺ 5d₁ and 5d₂ levels has been determined as a function of Al concentration in the films. The intensity of the Ce³⁺ luminescence bands of the films has been shown to increase with increasing Al and Ce concentrations.

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INTRODUCTION

This paper presents a continuation of a previous study [1] which showed that, in Gd₃AlₓGa₅₋ₓO₁₂:Ce³⁺ epitaxial films grown on single-crystal gadolinium gallium garnet (GGG), Gd₃Ga₅O₁₂, substrates by liquid-phase epitaxy (LPE) from supercooled high-temperature solutions using solvents of the PbO–B₂O₃ system and growth charges containing 1, 1.5, or 2 mol % Al₂O₃ and 0.03 or 0.2 mol % CeO₂, increasing the aluminum content to x = 1.9 shifted two absorption bands of the Ce³⁺ ion. Its 5d₂ level shifted by 5 nm, from 346 nm (peak absorption wavelength) in a Pb₀.₀₂Ce₀.₀₃Gd₉.₉₅Ga₀.₀₅O₁₂ (1 at % Ce³⁺) film to 341 nm in a Pb₀.₀₁Ce₀.₀₆Gd₉.₄₉Al₀.₅₁Ga₃.₅₁O₁₂ (2 at % Ce³⁺) film, and its 5d₁ level shifted from 426 to 438 nm (by 12 nm). The intensity of the Ce³⁺ luminescence band centered at 550 nm was shown to increase eight times with an increase in Al content from x = 1.1 to 1.9 [1], and the band gap of the films was shown to increase by 0.2 eV. In addition, Vasil’eva et al. [1] demonstrated a systematic increase in luminescence intensity with increasing excitation photon energy in a wide spectral range, from the UV to soft X-rays (220 eV), which points to efficient high-energy radiation conversion into luminescence.

Interest in the Gd₀.₈₇Ce₀.₀₃AlₓGa₅₋ₓO₁₂ (1 at % Ce³⁺) material has been aroused by the finding that it offers a considerable light output (up to 46000 photons/MeV), good energy resolution (4.9% at 662 keV), and high density (6.63 g/cm³) and is neither radioactive nor hygroscopic [2]. Czochralski-grown Gd₀.₈₇Ce₀.₀₃AlₓGa₅₋ₓO₁₂ crystals are used as X-ray, gamma-ray, alpha-particle, beta-particle, and neutron detectors and in medical imaging devices [3]. The optical properties of this material continue to be the subject of research with the aim of understanding how they vary with the Ga/Al concentration ratio, gaining greater insight into the processes underlying excitation energy conversion into a scintillation response, and assessing the effect of luminescence quenching on these processes [4–6].

The purpose of this work was to compare the optical properties of single-crystal Gdₓ(Al,Ga)₅O₁₂:Ce films grown from high-temperature solutions with higher aluminum oxide concentrations in comparison with previous work [1] (2.0, 2.1, and 2.2 mol %) at the same cerium oxide concentration in the growth charge (0.03 and 0.2 mol %).
Gd₃(Al,Ga)₅O₁₂:Ce epitaxial films were grown on (111)-oriented single-crystal GGG substrates by LPE from supercooled high-temperature solutions using solvents of the PbO–B₂O₃ system and growth charges containing 2.0, 2.1, or 2.2 mol % Al₂O₃ and 0.03 or 0.2 mol % CeO₂ (Table 1). The gadolinium oxide content in all of the high-temperature solutions was 0.2 mol %. The composition of the growth charge for the preparation of the epitaxial films had the following molar ratios \( R_1 \) and \( R_2 \) of their components (Table 1):

\[
R_1 = ([Ga_2O_3] + [Al_2O_3])/([Gd_2O_3] + [2CeO_2]),
\]

\[
R_2 = [PbO]/[B_2O_3].
\]

The growth charge was prepared from the following oxides: reagent-grade PbO (D/SPA), OSCh 11-3 B₂O₃, GdO-1 Gd₂O₃, TseO-SS CeO₂, OSCh 15-2 Ga₂O₃, and analytical-grade Al₂O₃.

We grew 25 film–substrate–film samples 10 × 15 mm in dimensions using six batches of freshly prepared high-temperature solutions (Table 1), as described by Vasileva et al. [7]. The growth time of the epitaxial films at various supercoolings was 5, 10, 30, 60, 75, 80, 90, or 120 min. The substrate rotation rate was 50, 100, 124, or 132 rpm. For each batch of high-temperature solutions, we determined the maximum thickness of the films, \( h_{\text{max}} \), and the maximum growth rate observed in our experiments, \( f_{\text{g}}^{\text{max}} \) (Table 1). It is worth pointing out that, as the Al₂O₃ content of the growth charge was increased from 2.0 to 2.2 mol %, the film growth rate dropped in the case of the high-temperature solutions of batches I–III, containing 0.03 mol % CeO₂ (indicating that the system left the growth region), and increased in the case of the high-temperature solutions of batches IV–VI, whose growth charge contained 0.2 mol % CeO₂ (Table 1). Figure 1 shows vertical sections through the phase diagram in question, the liquidus curve (curve 1), a non-equilibrium solidus curve (curve 2), and the growth temperatures of the films. The saturation temperature was constant in the case of film growth from the high-temperature solutions of batches I–III and increased in the case of growth from batches IV–VI.

As in a previous study [1], two growth regions were identified in the case of film growth from the high-temperature solutions of batches I–III. In one region, with a relatively low supercooling (\( \Delta T < 25^\circ \text{C} \)), we obtained pale yellow films. In the other region, with large supercooling (\( \Delta T > 25^\circ \text{C} \)), pale violet films were obtained. All of the films grown from the high-temperature solutions of batches IV–VI were yellowish-green in color.

At certain supercoolings, the LPE growth of the epitaxial films was accompanied by spontaneous crystal growth on the surface of the high-temperature solution, the walls of the platinum crucible, and the surface of the platinum holder. The resultant garnet crystals were tetragon-trioktaedral in shape and had {211} faces, like in Vasileva et al. [1], with the tetragon

### Table 1. Growth charge composition and growth parameters of the Gd₃(Al,Ga)₅O₁₂:Ce epitaxial films

<table>
<thead>
<tr>
<th>High-temperature solution</th>
<th>mol % Al₂O₃</th>
<th>mol % CeO₂</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( \delta t, ^\circ \text{C} )</th>
<th>( h_{\text{max}}, \mu \text{m} )</th>
<th>( f_{\text{g}}^{\text{max}}, \mu \text{m/min} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.0</td>
<td>0.03</td>
<td>35.42</td>
<td>15.71</td>
<td>985–962</td>
<td>15.9</td>
<td>0.37</td>
</tr>
<tr>
<td>II</td>
<td>2.1</td>
<td>0.03</td>
<td>35.81</td>
<td>15.69</td>
<td>968–964</td>
<td>30.4</td>
<td>0.34</td>
</tr>
<tr>
<td>III</td>
<td>2.2</td>
<td>0.03</td>
<td>36.19</td>
<td>15.67</td>
<td>969–964</td>
<td>17.0</td>
<td>0.24</td>
</tr>
<tr>
<td>IV</td>
<td>2.0</td>
<td>0.2</td>
<td>15.35</td>
<td>15.68</td>
<td>939–934</td>
<td>17.0</td>
<td>0.28</td>
</tr>
<tr>
<td>V</td>
<td>2.1</td>
<td>0.2</td>
<td>15.52</td>
<td>15.66</td>
<td>956–937</td>
<td>20.9</td>
<td>0.34</td>
</tr>
<tr>
<td>VI</td>
<td>2.2</td>
<td>0.2</td>
<td>15.68</td>
<td>15.64</td>
<td>957–946</td>
<td>19.6</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\( \delta t \) is the temperature range where the saturation temperature was determined.