

Synthesis and Optical Properties of Green to Orange Tunable Garnet Phosphors for pcLEDs

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Introduction

The most widely applied phosphor in white LEDs is cerium doped yttrium aluminum garnet (YAG:Ce). It shows strong absorption in the blue and a broad emission band in the yellow spectral region. The position of the Ce³⁺ emission band depends on crystal-field strength, covalency and Stokes shift. It is known that substitution of Y at dodecahedral sites by larger cations results in a red shift of emission, whereas smaller cations causes a blue shift. The opposite result is observed for octahedral and tetrahedral sites. The larger cation introduced into octahedral or tetrahedral site leads to a blue shift of emission and a smaller one a red shift. Another option for a blue or red shift of YAG:Ce emission band is substitution of yttrium by divalent or tetravalent cation, respectively. However, it is quite hard to find a large enough tetravalent cation for the voluminous dodecahedral sites. On the other hand, there are plenty of divalent cations suitable for substitution of yttrium.

We show that substitution of 2Al³⁺ by Mg²⁺ - Si⁴⁺ pair leads to a red shift of the Ce³⁺ emission band. The present findings can be explained by the increased covalent character of the host lattice and a larger Stokes Shift.

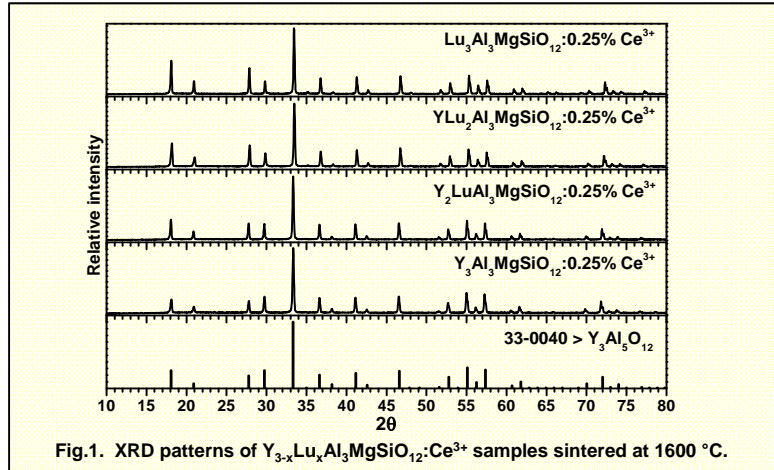


Fig.1. XRD patterns of $Y_{3-x}Lu_xAl_3MgSiO_{12}:0.25\%Ce^{3+}$ samples sintered at 1600 °C.

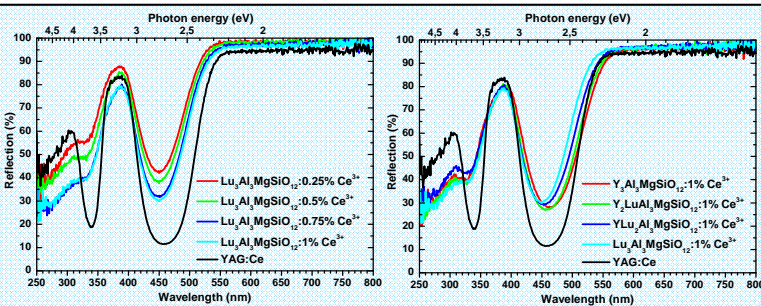


Fig. 2. Reflection spectra of $Lu_3Al_3MgSiO_{12}:Ce^{3+}$ samples

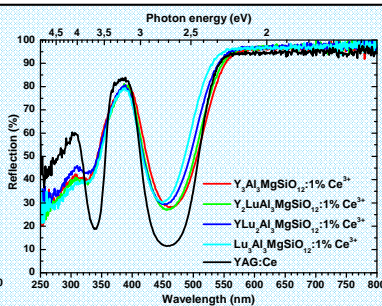


Fig. 3. Reflection spectra of $Y_{3-x}Lu_xAl_3MgSiO_{12}:1\%Ce^{3+}$ samples

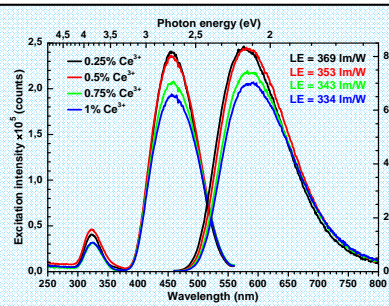


Fig. 4. Excitation and emission spectra of $Y_3Al_3MgSiO_{12}:Ce^{3+}$ samples and their lumen equivalents

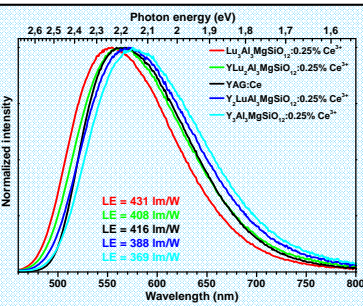


Fig. 5. Normalized emission spectra of $Y_{3-x}Lu_xAl_3MgSiO_{12}:0.25\%Ce^{3+}$ samples and their lumen equivalents

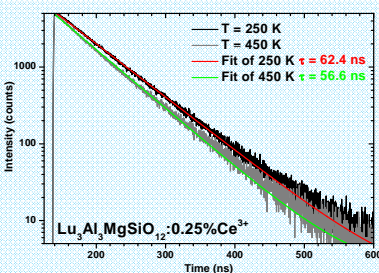


Fig. 6. Temperature dependent PLE decay times of $Lu_3Al_3MgSiO_{12}:0.25\%Ce^{3+}$

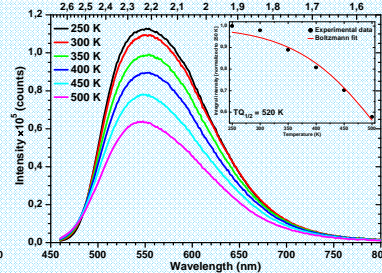


Fig. 7. Temperature dependent emission spectra of $Lu_3Al_3MgSiO_{12}:0.25\%Ce^{3+}$

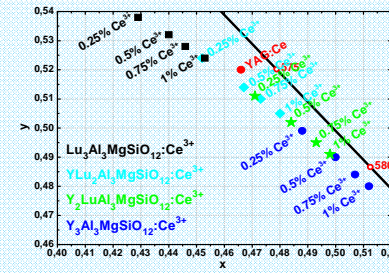


Fig. 8. CIE 1931 color points of $Y_{3-x}Lu_xAl_3MgSiO_{12}:Ce^{3+}$

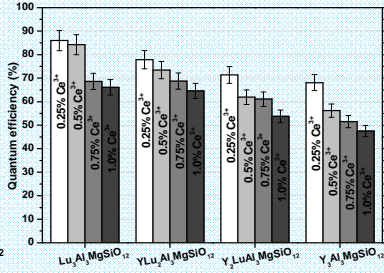


Fig. 9. Quantum efficiencies of $Y_{3-x}Lu_xAl_3MgSiO_{12}:Ce^{3+}$

Results and Discussion

All samples were synthesized by a sol-gel method employing ethylene glycol as a chelating agent. Sintering precursor powders at 1600 °C resulted in formation of single phase garnet type materials (see Fig. 1). Phosphors possessed a yellow to orange body color indicating the absorption in the blue what is in line with the reflection spectra represented in Fig. 2 and Fig. 3. As expected the absorption in the blue increased with higher Ce³⁺ concentration. Excitation and emission spectra of Y₃Al₃MgSiO₁₂:Ce³⁺ samples are depicted in Fig. 4. The maximum excitation and emission intensity was achieved if phosphors were doped with 0.25 or 0.5% Ce³⁺. Further increase of the dopant concentration led to a decrease of intensity and a

red shift of emission maximum due to re-absorption of emitted photons by the activator. It turned out that emission spectra of Ce³⁺ are a sensitive function of the Y/Lu ratio in the structure (Fig. 5). Fig. 6 depicts the temperature dependent lifetimes of Lu₃Al₃MgSiO₁₂:0.25%Ce³⁺ sample. The decay times decreases with higher temperatures indicating the drop in efficiency. Fig. 7 shows the thermal quenching of Lu₃Al₃MgSiO₁₂:0.25%Ce³⁺ sample. It reveals that emission intensity decreases if temperature is increased. It turned out that pending phosphor loses half of efficiency at 520 K (≈247 °C). Color points of synthesized phosphors are shown in Fig. 8. It is obvious that the increase of Ce³⁺ concentration leads to a red-shift of the color point, what is in line with emission spectra.

Finally, quantum efficiencies were calculated and are presented in Fig. 9. It turned out that QE gradually decreased if Ce³⁺ concentration or Y³⁺ content in the structure was increased.

Conclusions

In this work we demonstrated that the incorporation of Mg²⁺ and Si⁴⁺ ions onto the octahedral and tetrahedral sites, respectively, has led to red-shifted emission in comparison to the YAG:Ce phosphor. The synthesized phosphors possess rather high quantum efficiencies, enabling their application in pcLEDs.

