Synthesis and Optical Properties of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:Ce^{3+}$

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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 broad emission band in the yellow spectral region. The position of the Ce^{3+} 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 $2Al^{3+}$ by Mg^{2+} - Si^{4+} pair leads to a red shift of the Ce^{3+} emission band. The present findings can be explained by the increased covalent character of the host lattice.

Synthesis

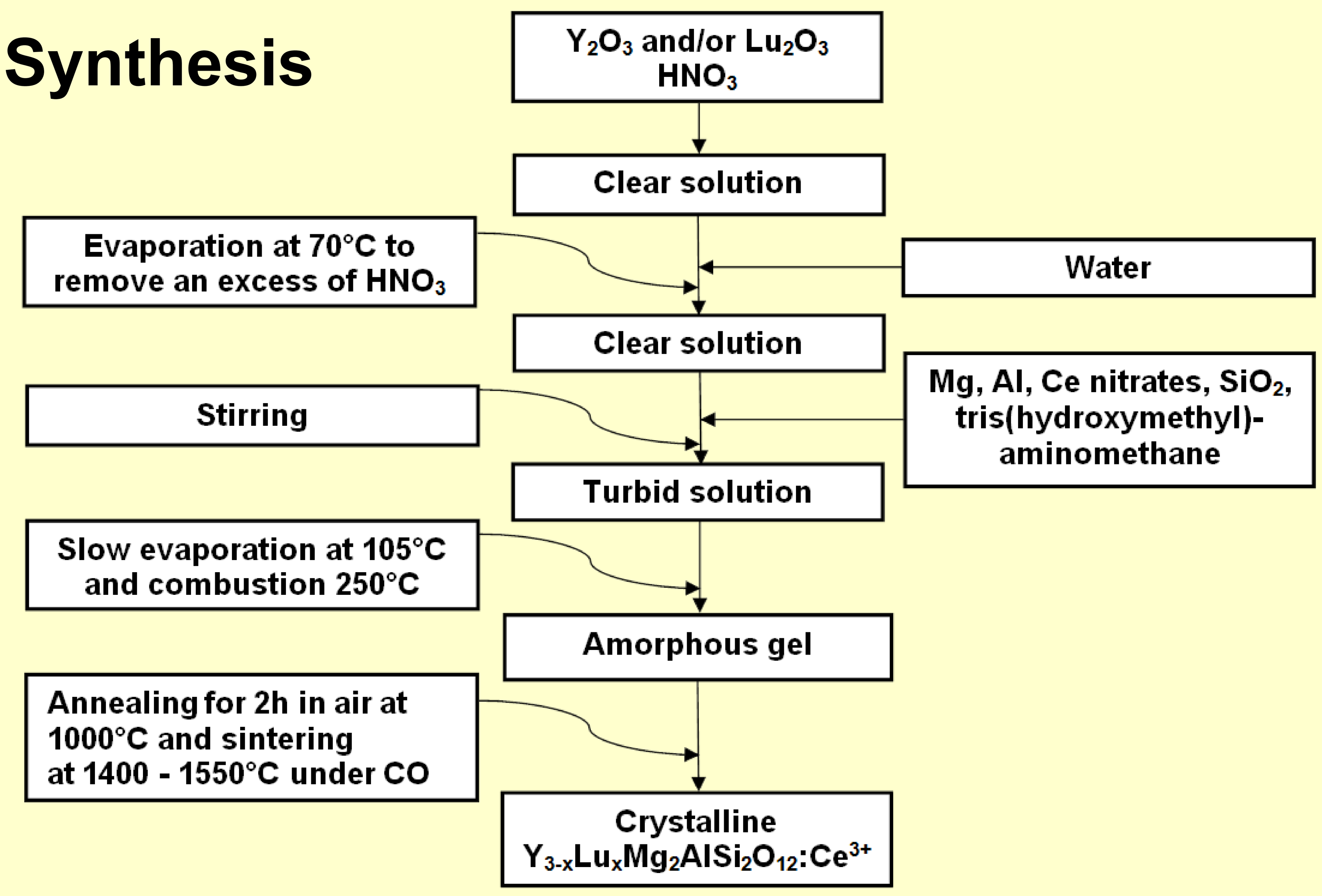

Fig.1. Scheme of the sol-gel combustion synthesis of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:Ce^{3+}$

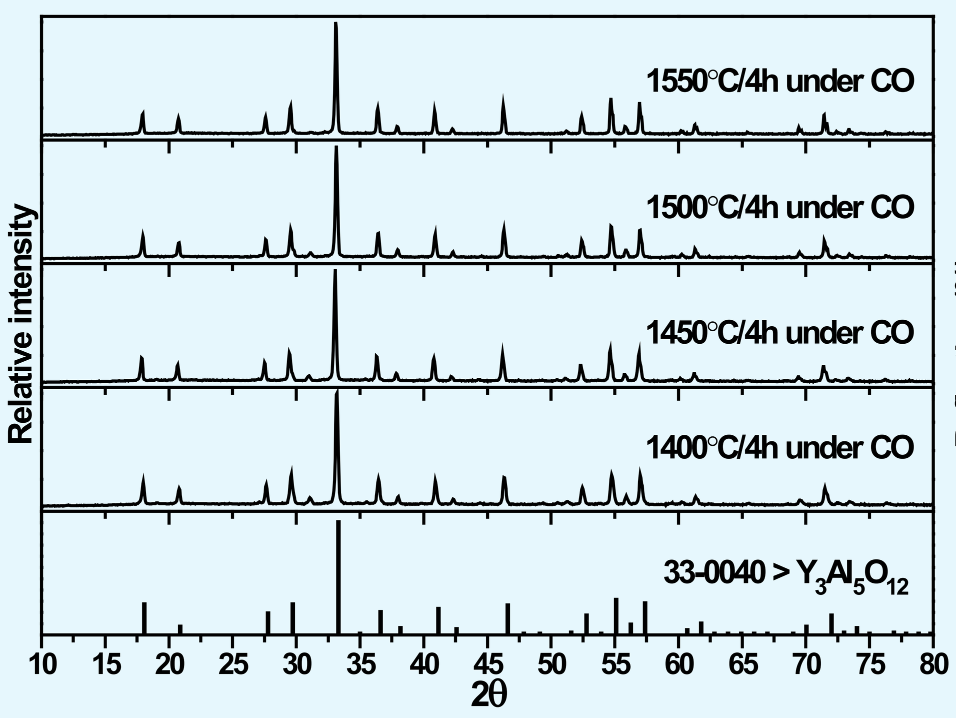

Fig. 2. XRD patterns of $Y_3Mg_2AlSi_2O_{12}:Ce^{3+}$

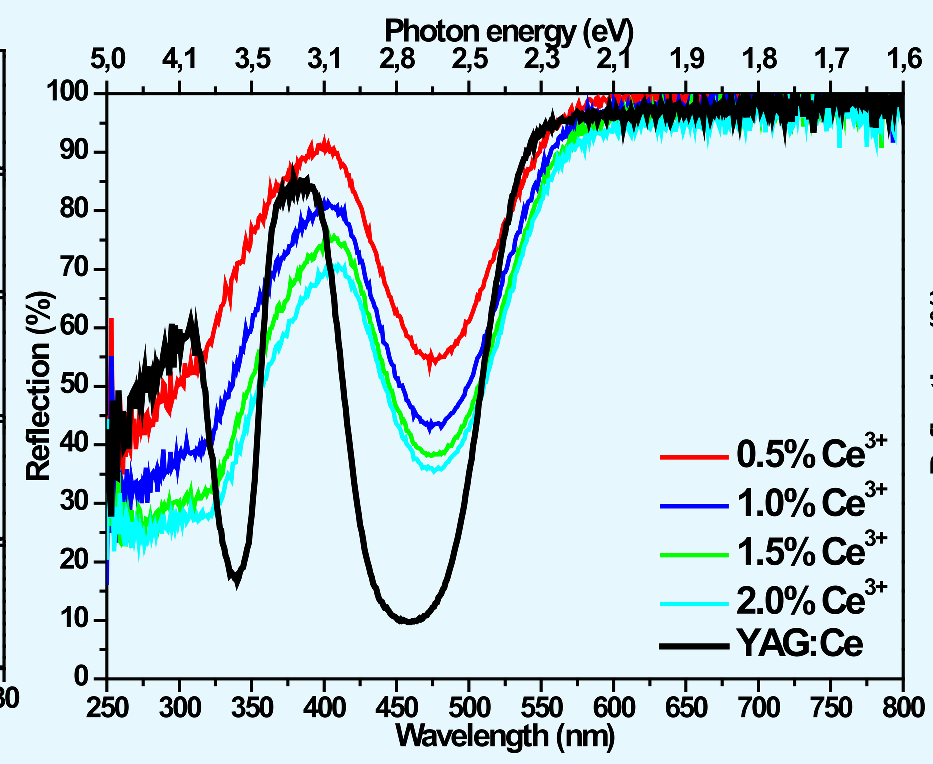

Fig. 3. Reflection spectra of $Y_3Mg_2AlSi_2O_{12}:Ce^{3+}$ samples

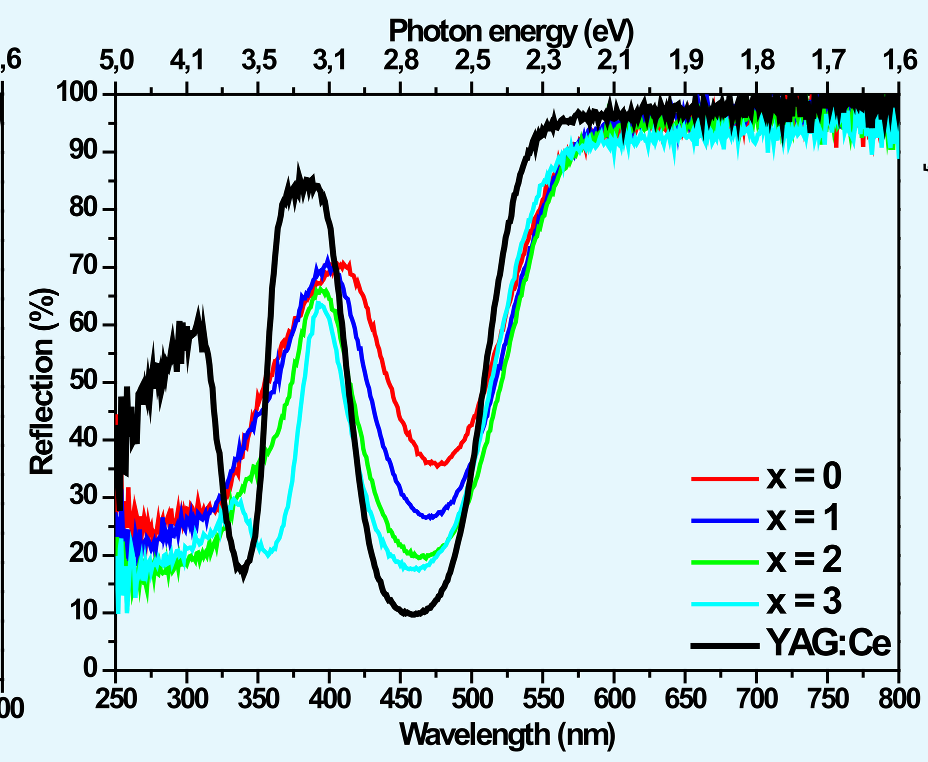

Fig. 4. Reflection spectra of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:2\%Ce^{3+}$ samples

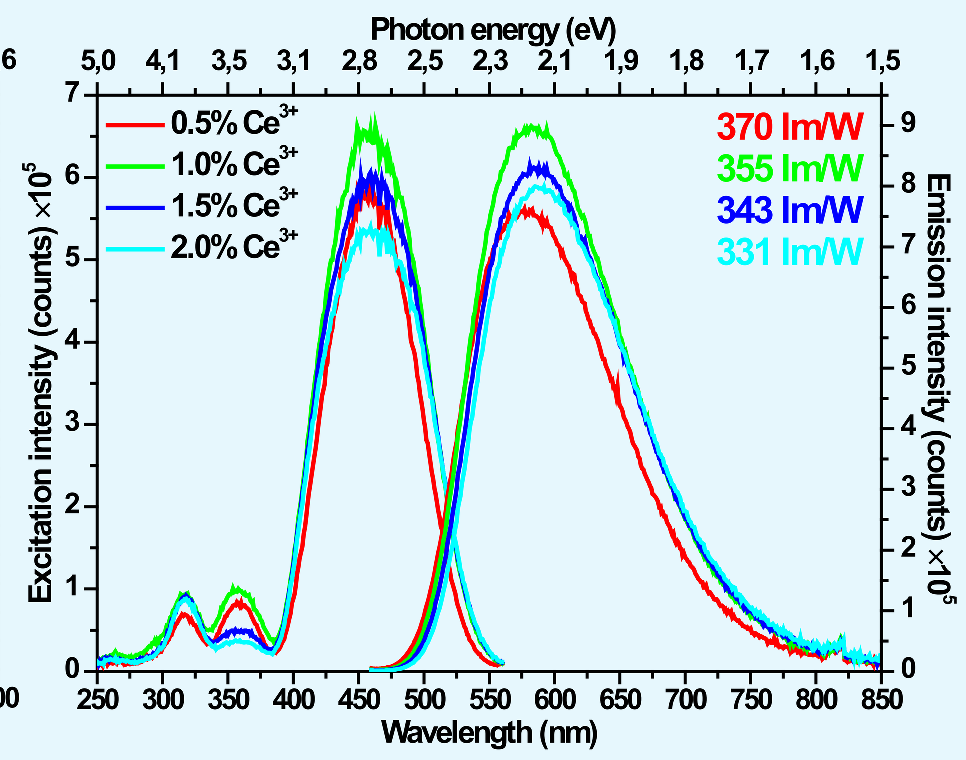

Fig. 5. Excitation and emission spectra of $Lu_3Mg_2AlSi_2O_{12}:Ce^{3+}$ samples and their lumen equivalents

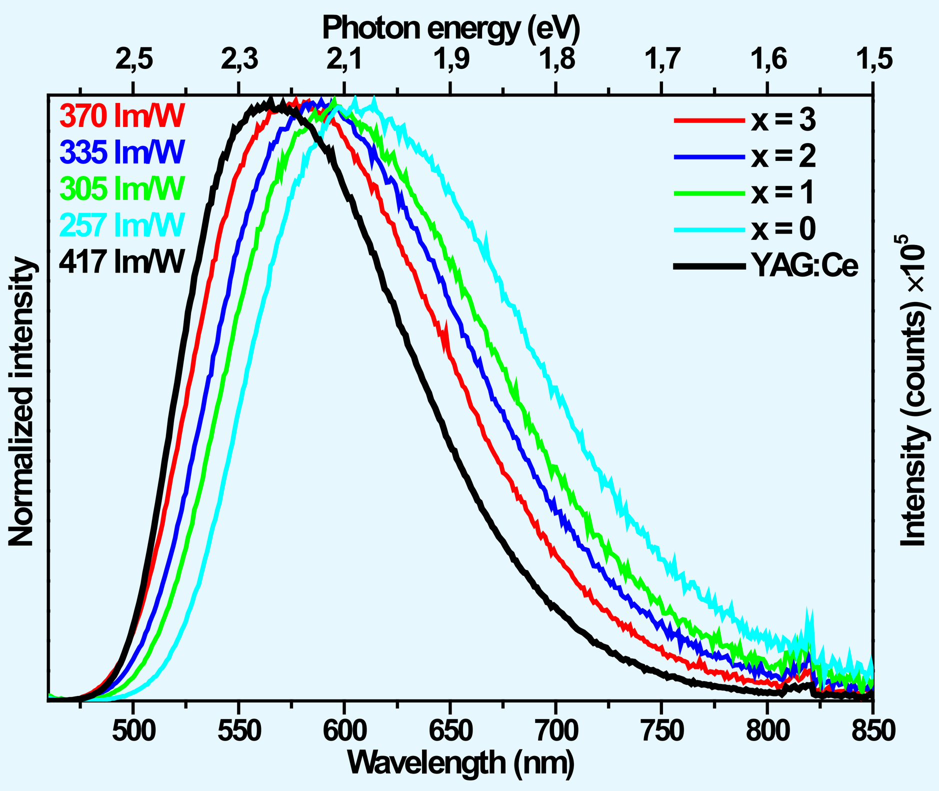

Fig. 6. Normalized emission spectra of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:0.5\%Ce^{3+}$ samples and their lumen equivalents

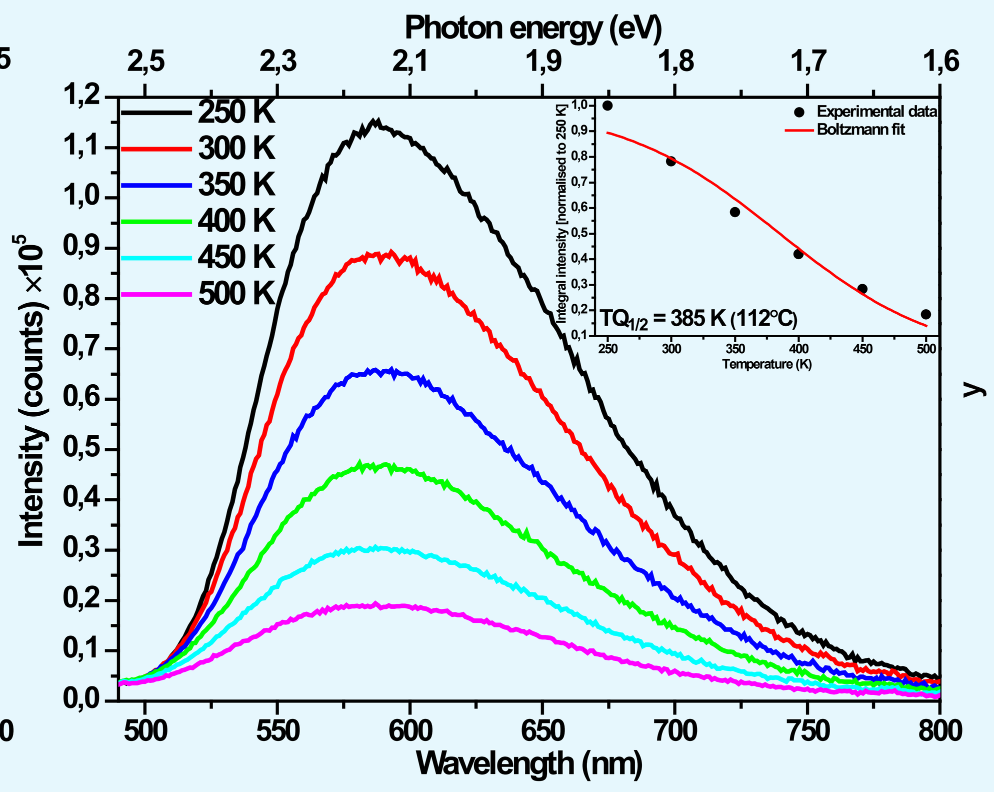

Fig. 7. Temperature dependent emission spectra of $Y_3Mg_2AlSi_2O_{12}:0.5\%Ce^{3+}$

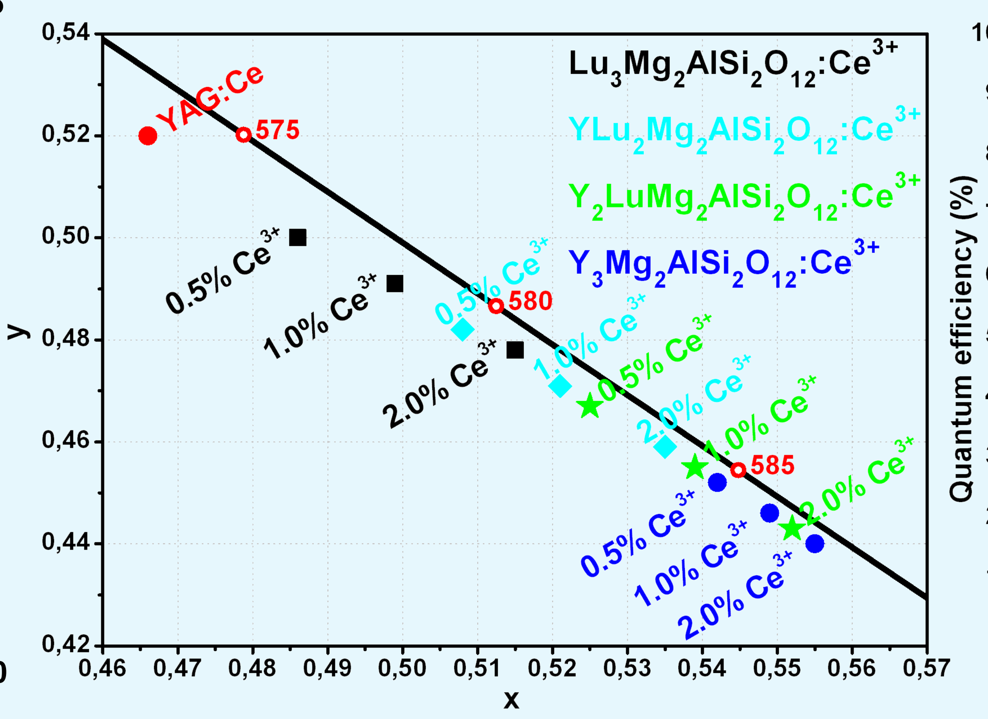

Fig. 8. CIE 1931 color points of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:Ce^{3+}$

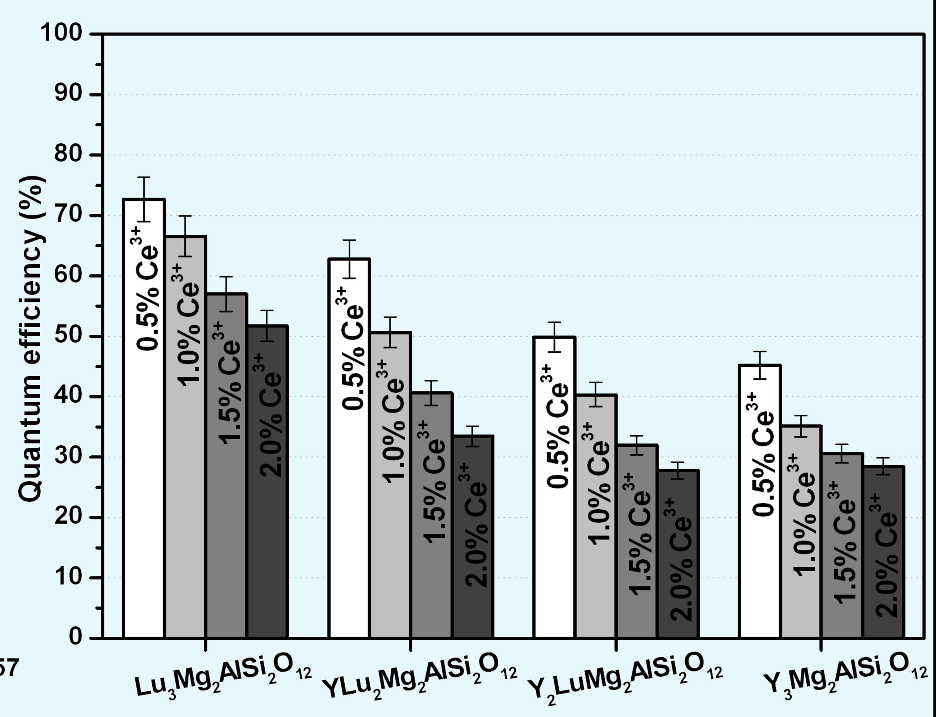

Fig. 9. Quantum efficiencies of $Y_{3-x}Lu_xMg_2AlSi_2O_{12}:Ce^{3+}$

Results and Discussion

All samples were synthesized by a sol-gel combustion method as depicted in **Fig. 1**. Sintering powders at 1400 C resulted in formation of garnet phase with solely minor impurities. A further increase of the annealing temperature resulted in reduction of impurity concentration (see **Fig. 2**). 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. 3** and **Fig. 4**. As expected the absorption in the blue increased with higher Ce^{3+} concentration. Excitation and emission spectra of $Lu_3Mg_2AlSi_2O_{12}:Ce^{3+}$ samples are depicted in **Fig. 5**. The maximum excitation and emission intensity was achieved if phosphors were doped by 1% Ce^{3+}. 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 Ce^{3+} are a sensitive function of the Y/Lu ratio in the structure (see **Fig. 6**). **Fig. 7** shows the thermal quenching of $Y_3Mg_2AlSi_2O_{12}:0.5\%Ce^{3+}$ sample. It reveals that emission intensity decreases if temperature is increased. It turned out that pending phosphors looses half of efficiency at 385 K (≈112 C). Color points of synthesized phosphors are shown in **Fig. 8**. It is obvious that the increase of Ce^{3+} 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 Ce^{3+} concentration or Y^{3+} content in the structure was increased.

Conclusions

In this work we demonstrated that the incorporation of Mg^{2+} and Si^{4+} ions onto the octahedral and tetrahedral sites, respectively, has led to red-shifted emission in comparison to the YAG:Ce phosphor. However, strong concentration and thermal quenching has been observed, which is a bottleneck to application yet.