Synthesis and Optical Properties of $CaY_2Al_4SiO_{12}:Ce^{3+}$

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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 Y^{3+} by Ca^{2+} leads to a blue shift of the Ce^{3+} emission band. The present finding can be explained by reduction of crystal-field strength due to a decrease of effective charge of dodecahedral site.

Synthesis

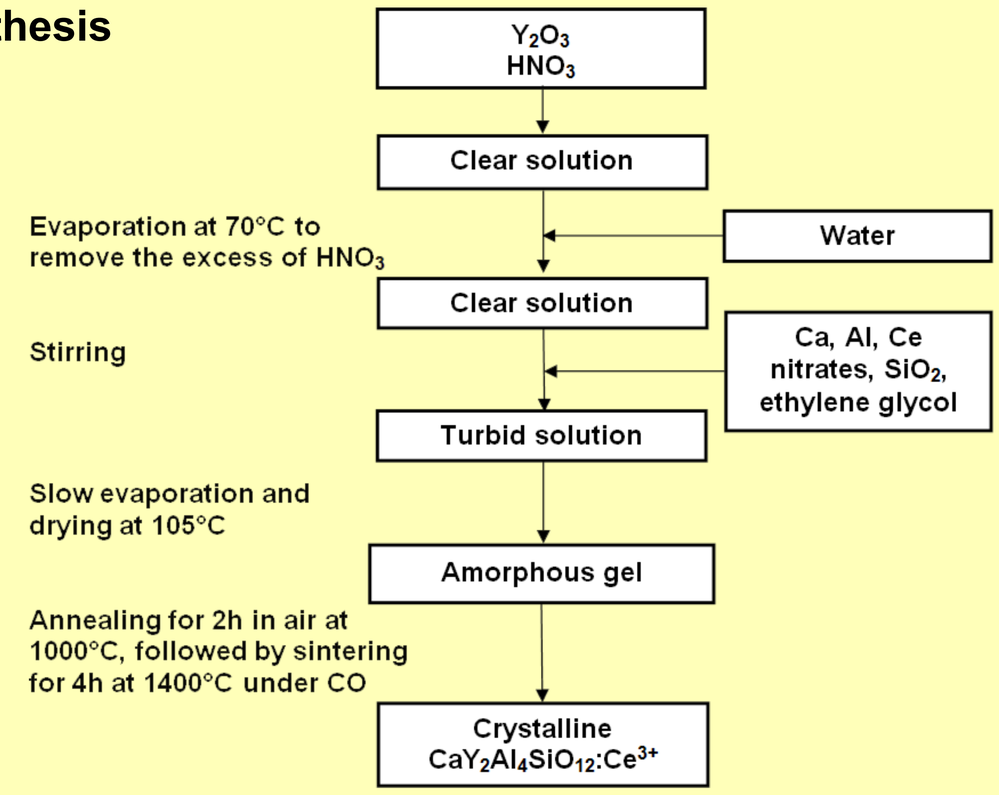

Fig.1. Scheme of the sol-gel synthesis procedure of $CaY_2Al_4SiO_{12}:Ce^{3+}$ samples

Results and Discussion

All samples were synthesized by a sol-gel method employing ethylene glycol as a chelating agent. The complete synthesis procedure is shown in **Fig. 1**. It turned out that sintering powders at 1400 C resulted in single-phase garnet materials (see **Fig. 2**). Phosphors possessed a green to yellow body color indicating the absorption in the blue what is in line with the reflection spectra represented in **Fig. 3**. As expected the absorption in the blue increased with higher Ce^{3+} concentration. However, higher Ce^{3+} amounts have led to greyish samples probably due to defect formation. Excitation and emission spectra are depicted in **Fig. 4**. The maximum excitation and emission intensity was achieved if phosphors were doped by 1% Ce^{3+}. Further increase of 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. **Fig. 5** shows the thermal quenching of the sample doped by 0.5% Ce^{3+}. It reveals that emission intensity decreases if temperature is increased. Boltzmann method was employed to calculate $TQ_{1/2}$ value ($TQ_{1/2}$ indicates the temperature at which the phosphor looses 50% of its quantum efficiency). It turned out that pending phosphor looses half of efficiency at 458 K (≈185 C). Color points of synthesized phosphors are shown in **Fig. 6**. It is obvious that the increase of Ce^{3+} concentration leads to a red-shift of the color point towards YAG:Ce, which is in line with emission spectra. Finally, quantum efficiencies were calculated and are presented in **Fig. 7**.

It turned out that QE gradually decreased if Ce^{3+} concentration was increased. However, QE is still too low for application in pcLEDs, but it could be improved by Ce^{3+} concentration and particle size, shape optimization..

Conclusions

In this work we demonstrated that the reduction of effective charge of dodecahedral site in YAG has led to decrease of crystal-field strength. As a consequence the emission maximum of Ce^{3+} shifted towards green spectral region (≈ 550 nm) compared with conventional YAG:Ce emitting at 560 nm.

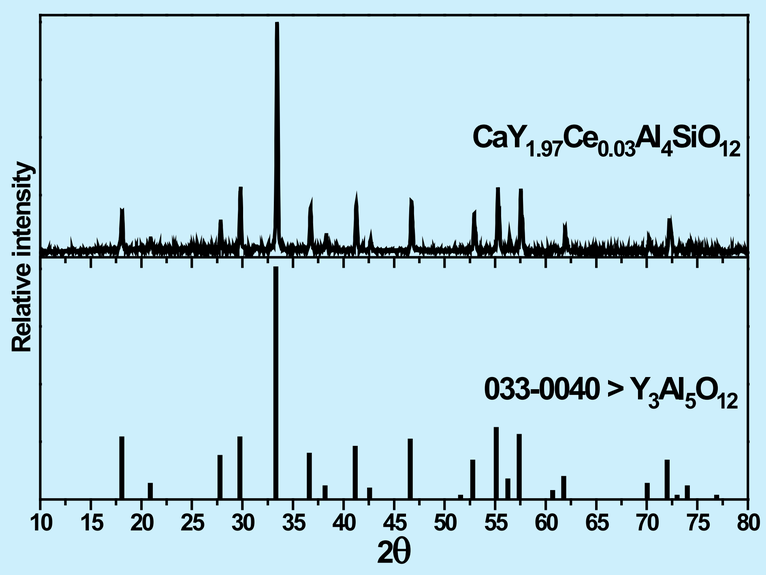

Fig. 2. XRD pattern of $CaY_{1.97}Ce_{0.03}Al_4SiO_{12}$

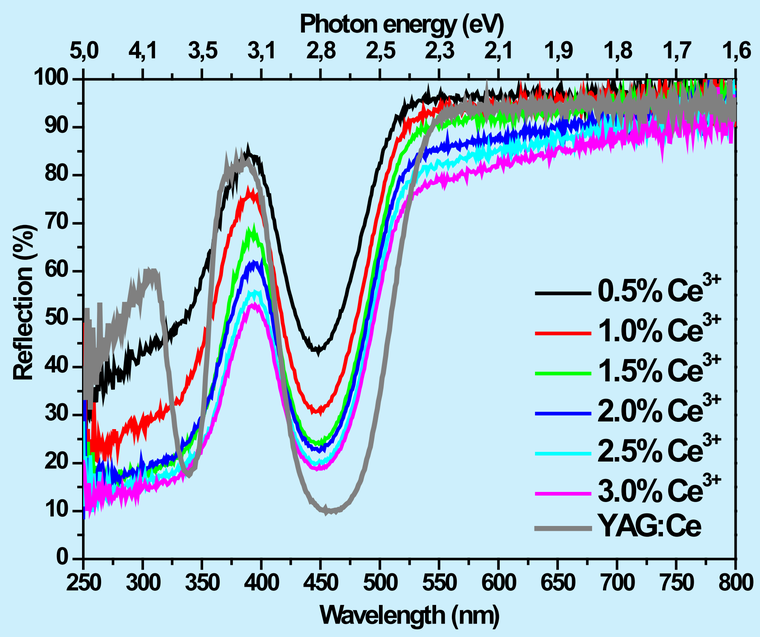

Fig. 3. Reflection spectra of $CaY_2Al_4SiO_{12}:Ce^{3+}$ samples

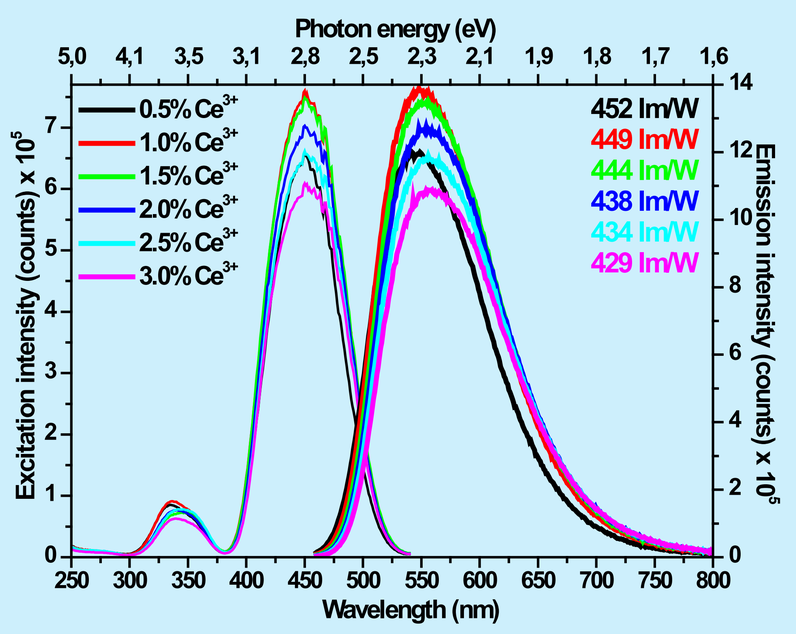

Fig. 4. Excitation and emission spectra of $CaY_2Al_4SiO_{12}:Ce^{3+}$ samples and their lumen equivalents

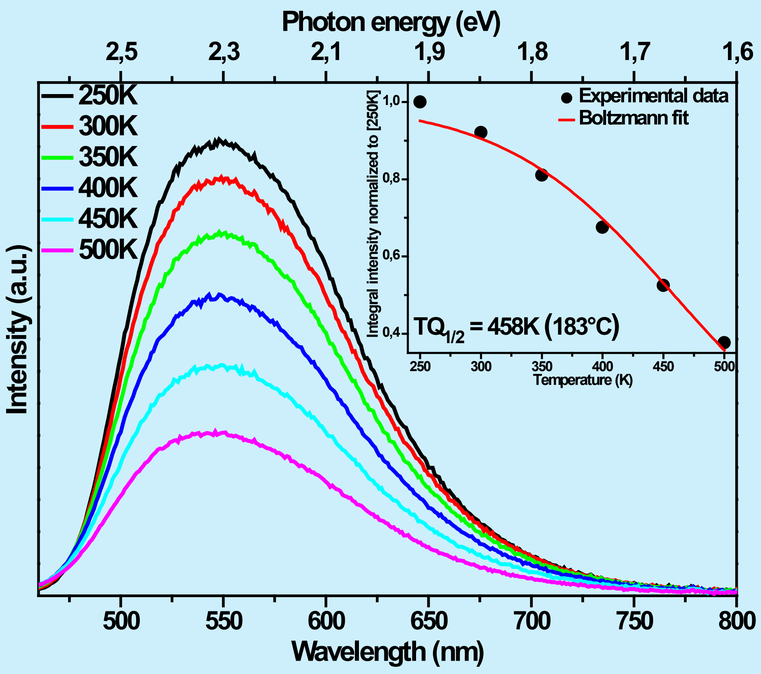

Fig. 5. Temperature dependent emission spectra of $CaY_{1.985}Ce_{0.015}Al_4SiO_{12}$

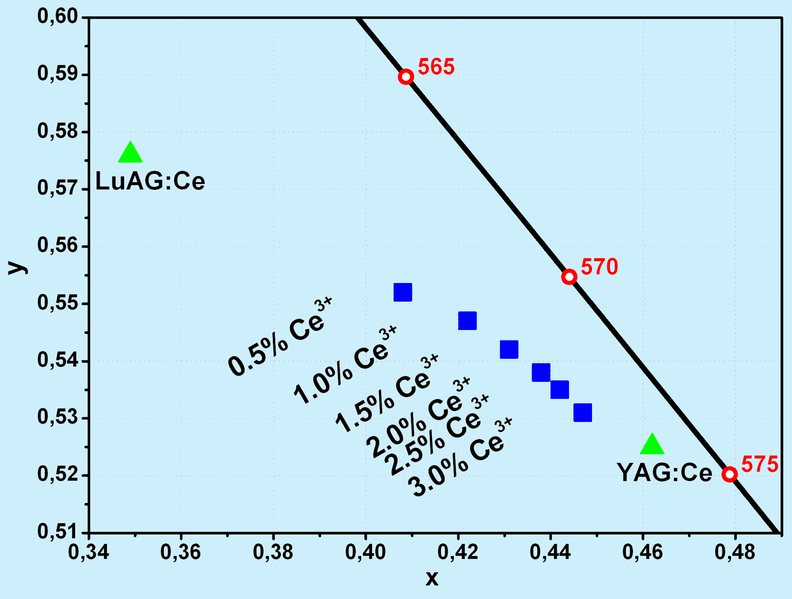

Fig. 6. CIE 1931 color points of $CaY_2Al_4SiO_{12}:Ce^{3+}$ as function of the Ce^{3+} concentration

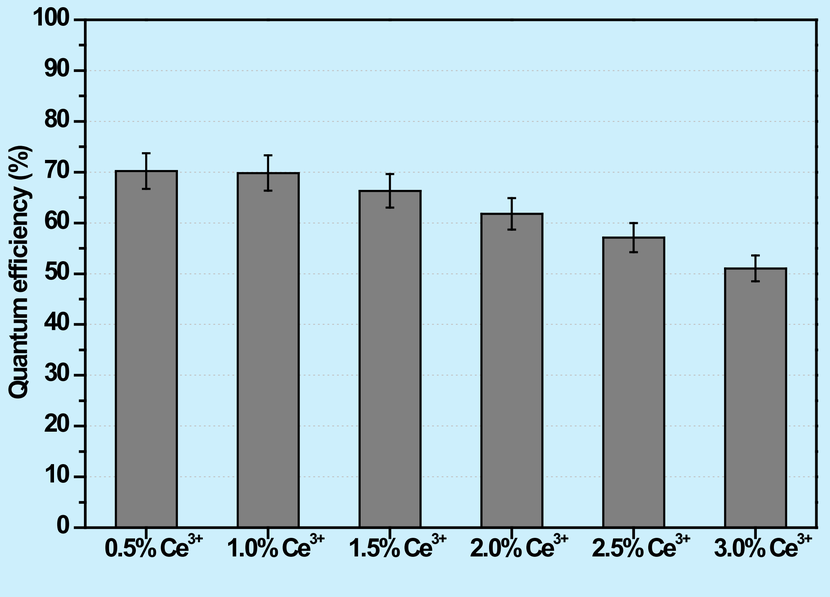

Fig. 7. Quantum efficiencies of $CaY_2Al_4SiO_{12}:Ce^{3+}$ samples