Synthesis and Optical Properties of $CaLu_2Al_4SiO_{12}$ Doped by Ce^{3+}

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Introduction

The most widely applied phosphors in white LEDs are cerium doped yttrium aluminum garnet (YAG:Ce) and lutetium aluminum garnet (LuAG:Ce). They show strong absorption in the blue and broad emission band in the yellow and green spectral region, respectively. The position of Ce^{3+} emission band depends on crystal-field strength, covalency and Stokes shift. It is known that substitution of Y in dodecahedral sites by larger cations results in red shift of emission, whereas smaller cations causes blue shift. The opposite result is observed for octahedral and tetrahedral sites. The larger cation introduced into octahedral or tetrahedral site leads to blue shift of emission and smaller one – red. The other option for blue and red shift of YAG:Ce/LuAG:Ce emission band is substitution of yttrium/lutetium by divalent or tetravalent cation, respectively. However, it is quite hard to find a big enough tetravalent cation for large dodecahedral sites. On the other hand, there are plenty of divalent cations suitable for substitution of yttrium/lutetium.

We will show that substitution of Lu^{3+} by Ca^{2+} leads to blue shift of Ce^{3+} emission band. The present finding can be explained by reduction of crystal-field strength due to decrease of effective charge of dodecahedral site.

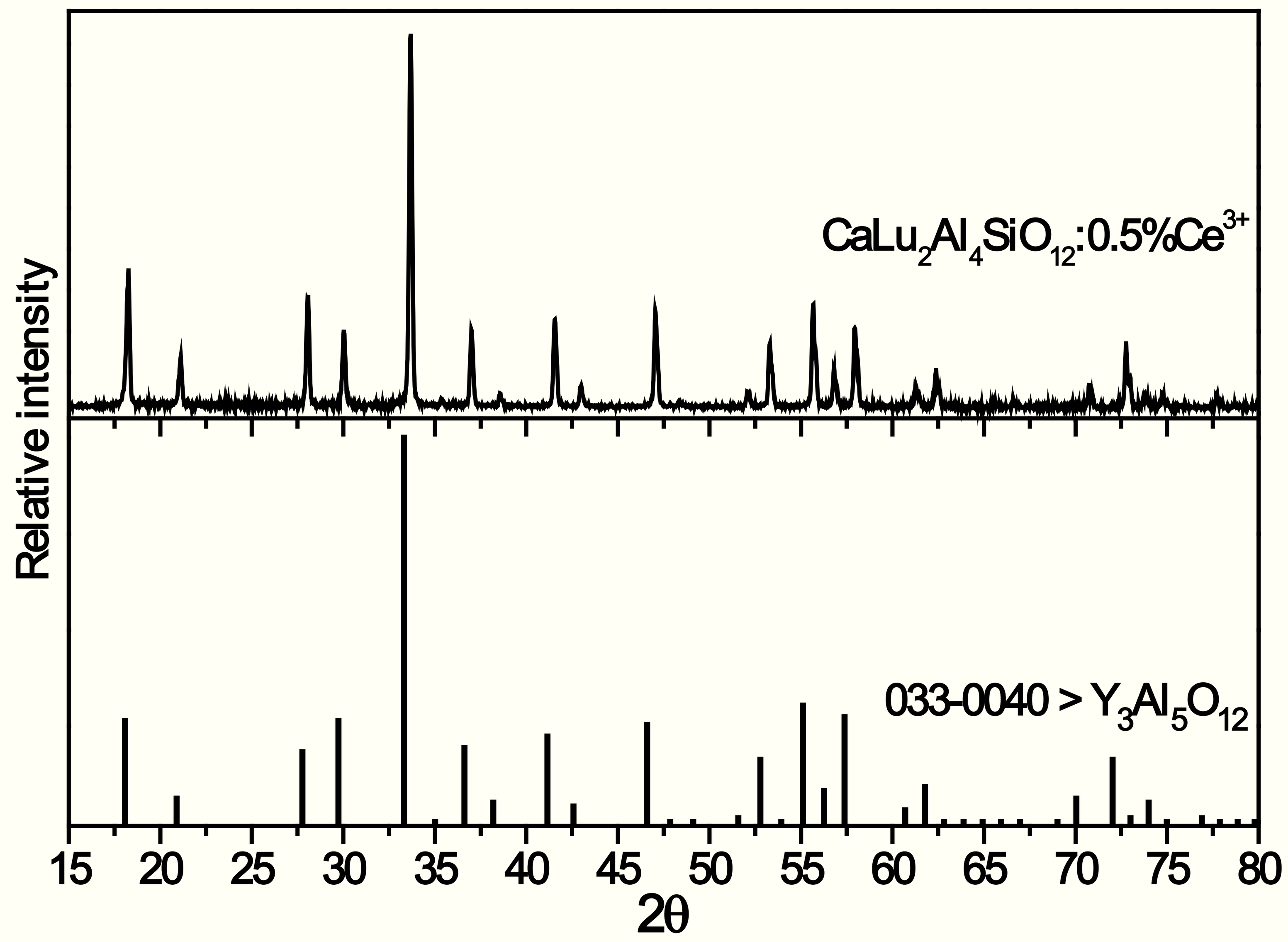

Fig. 1. XRD pattern of $CaLu_2Al_4SiO_{12}$:0.5%Ce^{3+} sample sintered at 1500 °C.

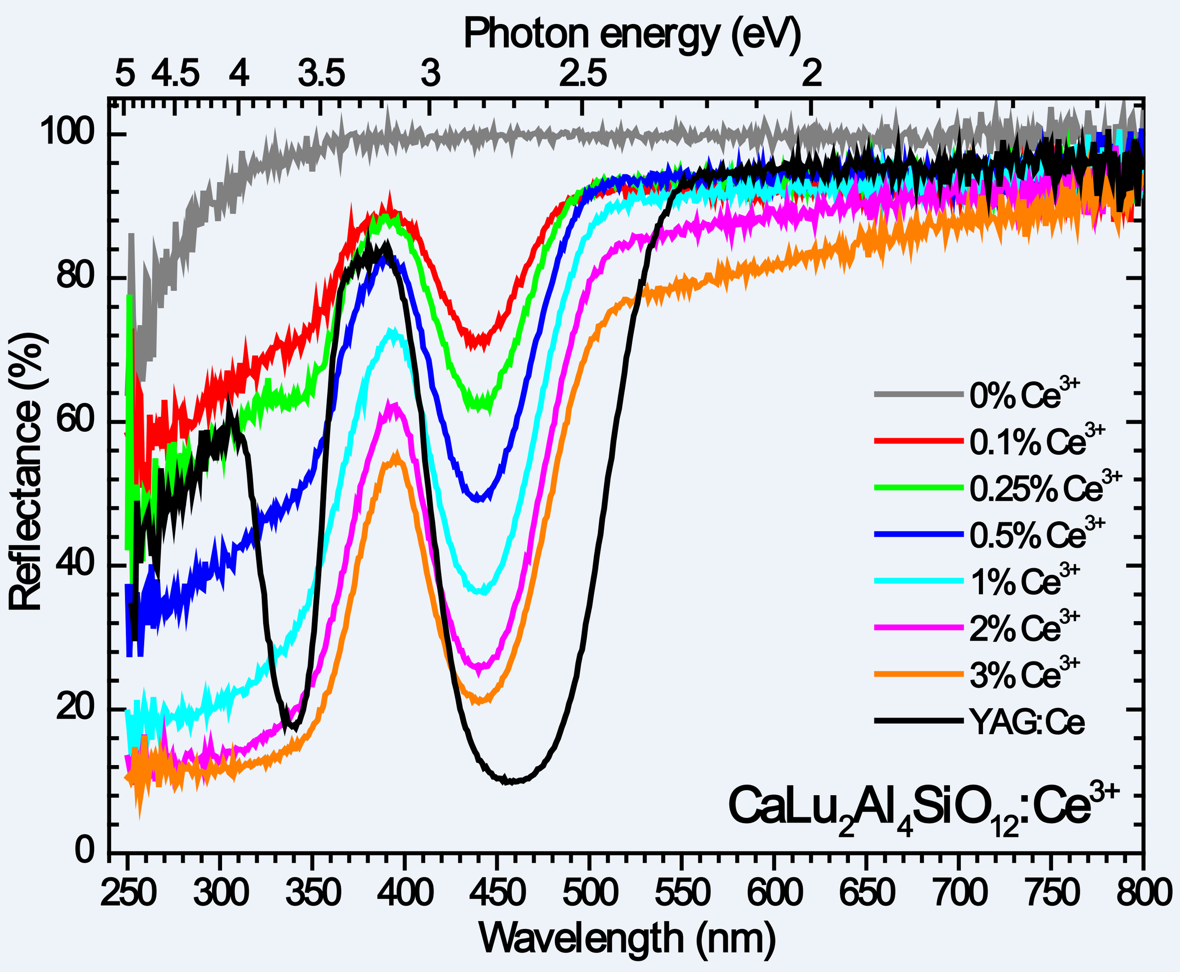

Fig. 2. Reflection spectra of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples sintered at 1400 °C.

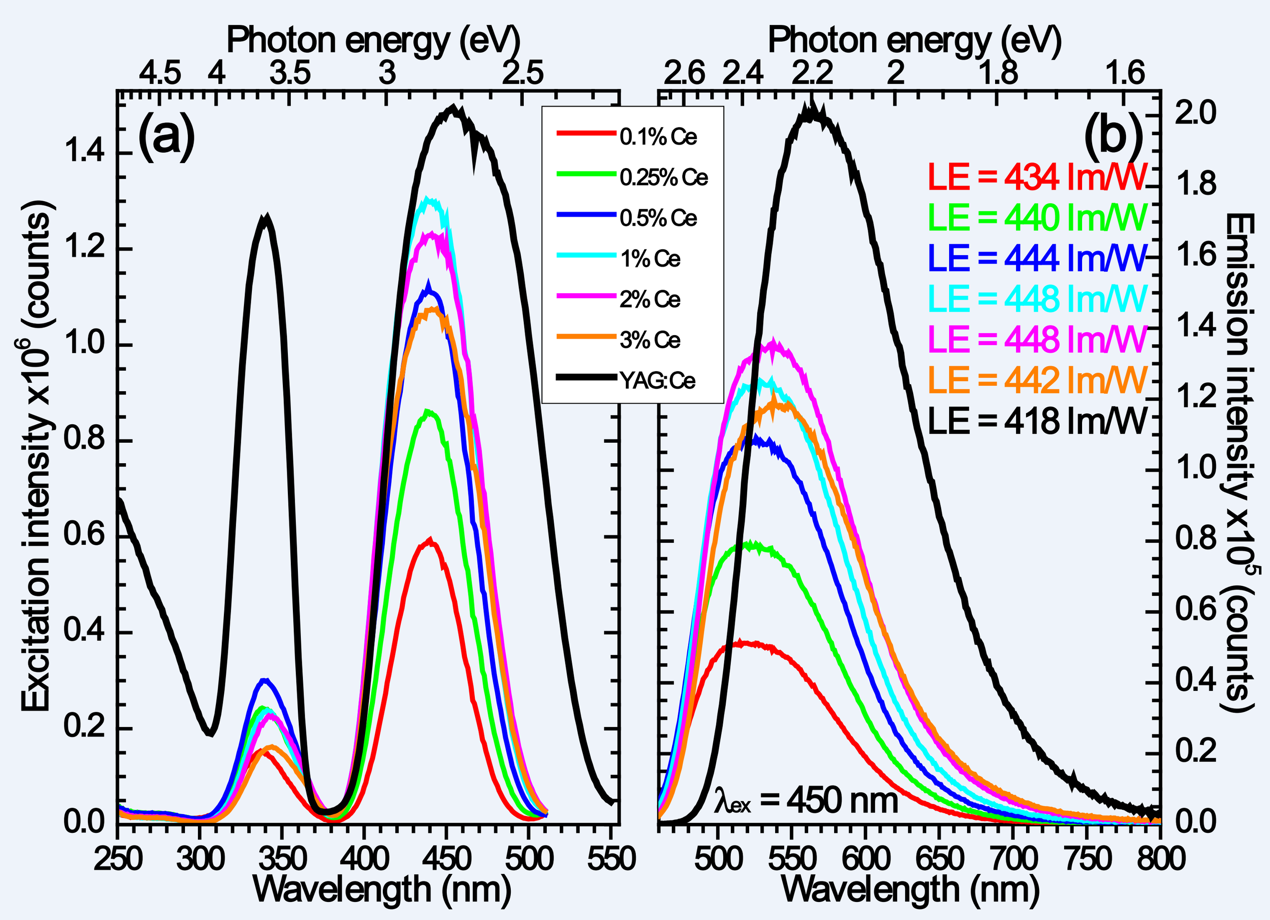

Fig. 3. Excitation (a) and emission (b) spectra of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples sintered at 1400 °C.

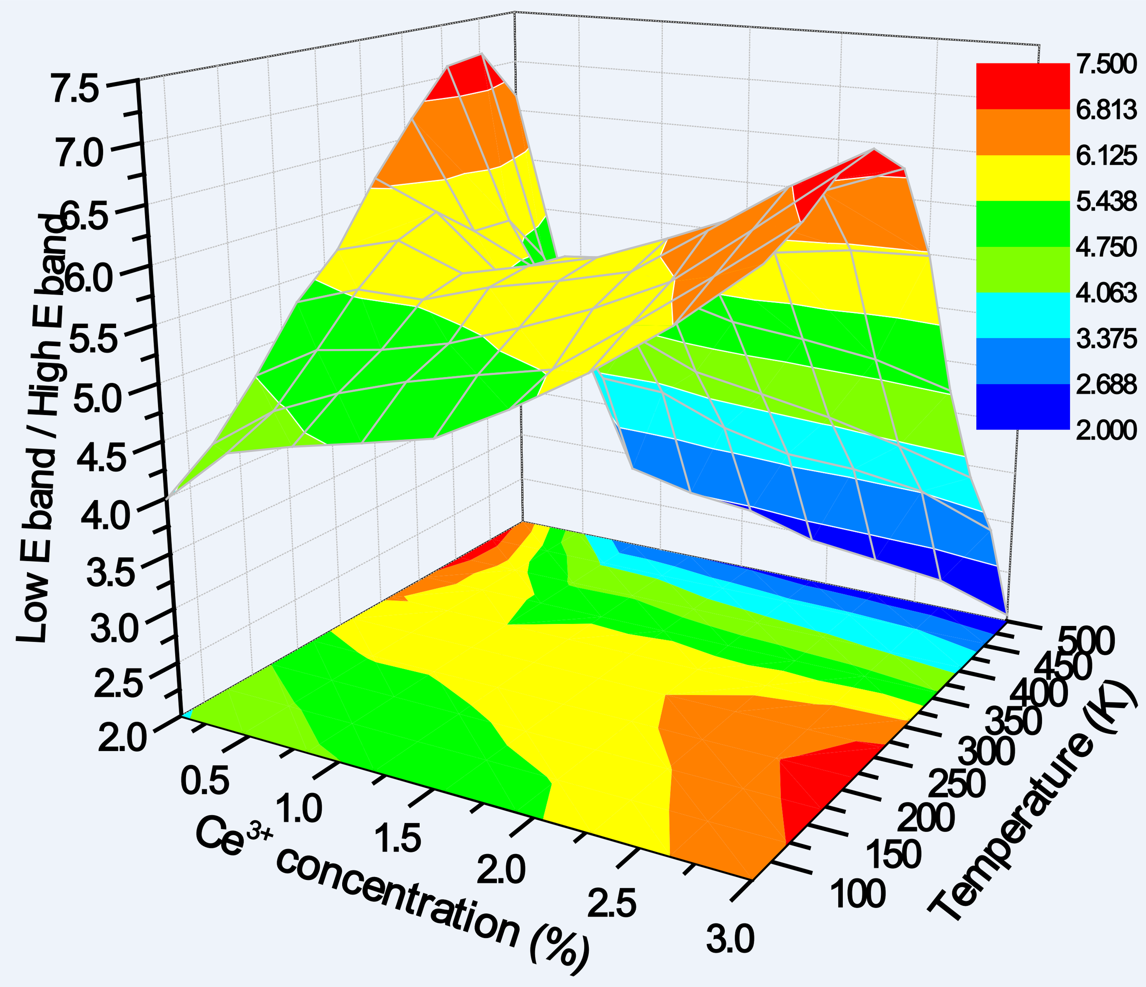

Fig. 4. Thermal quenching of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples sintered at 1400 °C.

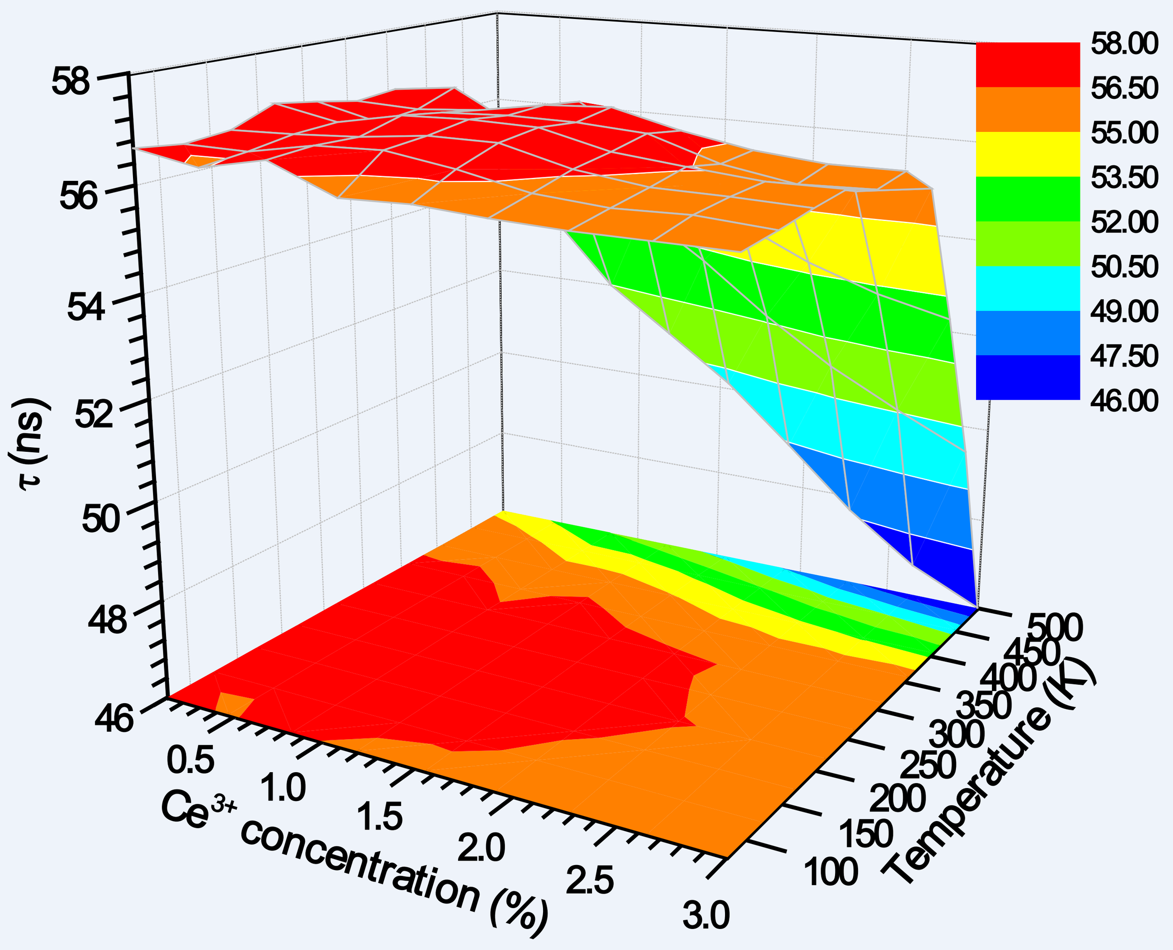

Fig. 5. Decay times $\tau_{1/e}$ of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples as a function of temperature and concentration.

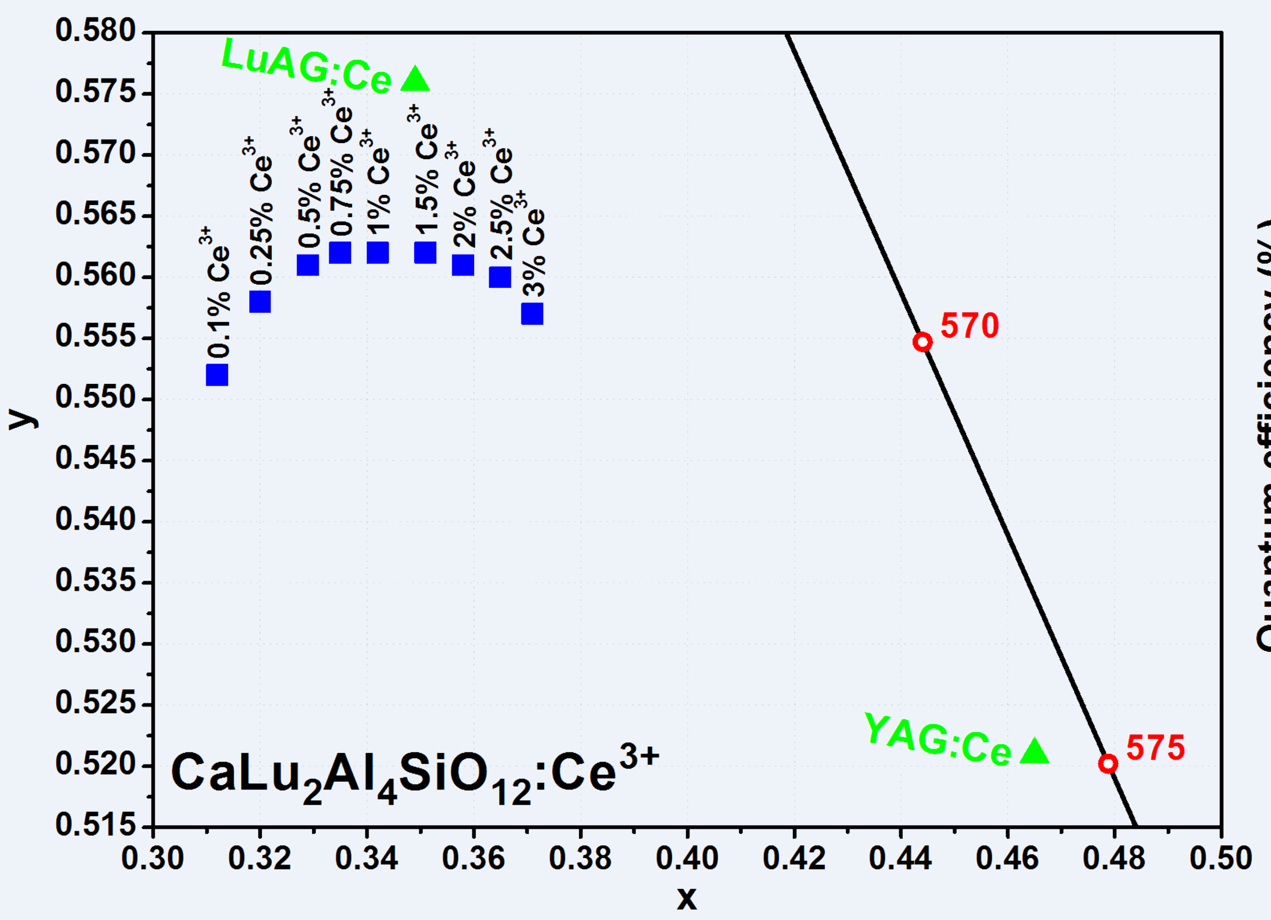

Fig. 6. CIE 1931 Color points of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples as a function of Ce^{3+} concentration.

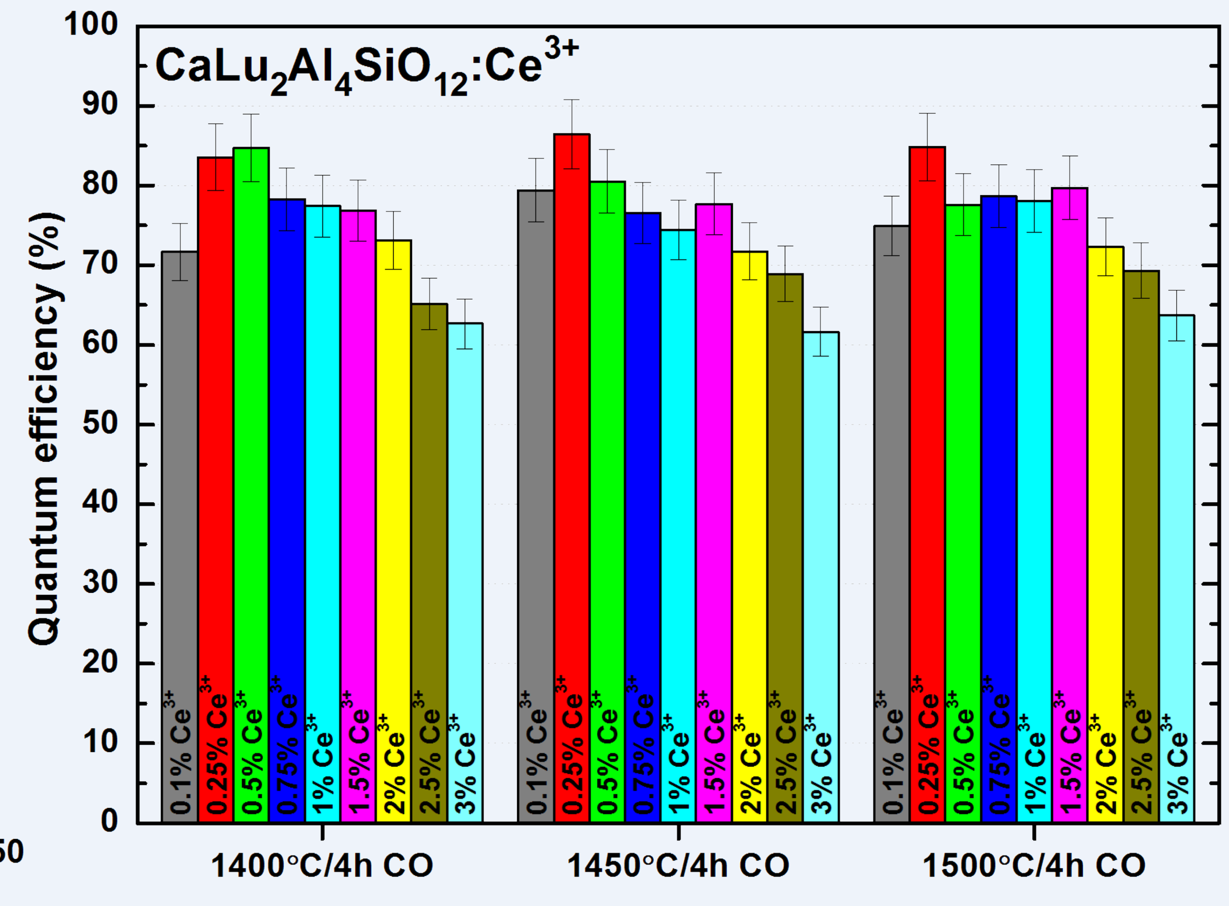

Fig. 7. Quantum efficiencies of $CaLu_2Al_4SiO_{12}:Ce^{3+}$ samples as a function of Ce^{3+} concentration and sintering temperature.

Conclusions

In this work, we demonstrated that a modification of the YAG host by Lu and Ca results in strong changes with respect to the luminescence spectra of Ce^{3+} located onto dodecahedral lattice site. Ce^{3+} in YAG:Ce and LuAG:Ce emits at 560 and 540 nm, respectively. Replacement of Lu by Ca resulted in emission maximum shift to higher energy (≈520 nm). The blue shift of emission maximum is caused by the reduction of the effective charge of dodecahedral site leading to lower crystal field strength. Another interesting feature of pending phosphors is their particular thermal quenching behavior. The low Ce^{3+} concentration edge (Fig. 5) at higher temperatures represents luminescence quenching by tunneling of electrons from excited state to the ground state. On the other hand, the high Ce^{3+} concentration edge shows quenching by re-absorption (energy transfer towards the quenching site). Phosphors possess strong absorption in the blue spectral region and relatively high quantum yields making them considerably attractive for application in phosphor converted LEDs (pcLEDs).

Acknowledgement

Authors are grateful to Merck KGaA for financial support.