

Highly luminescent $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ silicate garnet nano- and microparticles with 50-70% photoluminescence quantum yields as efficient phosphor converters for white LEDs

Ievgen Levchuk* (ievgen.levchuk@fau.de), Felix Schröppel*, Lukas Römling*, Liudmyla Chepyga*, Andres Osvet*, Nicholas Khaidukov**, Yuriy Zorenko***, Rik Van Deun****, Christoph J. Brabec* and Miroslaw Batentschuk*

*Universität Erlangen-Nürnberg, Institute i-MEET, Martensstraße 7, 91058 Erlangen, Germany

**Kurnakov Institute of General and Inorganic Chemistry, RAS, 119991 Moscow, Russia

***Institute of Physics, Kazimierz Wielki University in Bydgoszcz, 85090 Bydgoszcz, Poland

****Luminescent Lanthanide Lab, Ghent University, 9000 Gent, Belgium

ABSTRACT

We present a novel synthesis method of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ nano- and microparticles with outstandingly bright photoluminescence. Nanoparticles were synthesized by the co-precipitation method, where a long-chain fatty acid salt was used as the precipitation agent for Ca, Sc and Ce water solutions in combination with SiO_2 nanoparticles or TEOS as a silica source. Further calcination in reducing atmosphere results in brightly luminescent $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ nanopowders with up to 50% photoluminescence quantum yield (PLQY). The modified conventional solid-state reaction was utilized for synthesizing microparticles. Pre-synthesis of metal and silicon oxide solid blends with subsequent high-temperature post-treatment enables to obtain $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ microparticles with the record-high PLQY of about 70%. Additionally, both kinds of samples display significantly higher thermal stability of photoluminescence in comparison to a commercial YAG:Ce phosphor.

Keywords: $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$, white LED, phosphor converter, nanopowder, co-precipitation

1 INTRODUCTION

Solid state lighting devices based on a combination of violet/blue light emitting diodes (LEDs) and phosphor convertors has created enormous commercial interest because of its potentially higher efficacies and long lifetimes. Step by step, the white light emitting diodes (WLEDs) replace the traditional light sources, due to their environmental friendliness: the efficiency of the WLEDs is higher than that of fluorescent tubes and the WLEDs do not contain mercury and other harmful elements. At present, a blue LED chip and a yellow emitting $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) phosphor is a conventional WLED device [1]. However, research is going on to optimize parameters like the color rendering index or the color correlated temperature of WLEDs. One alternative phosphor is $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ (CSS:Ce) silicate garnet phosphor. In the general, the silicate garnet phosphors are of interest,

because they show high quantum yield with a broadband emission spectra and, furthermore, a high thermal stability.

Shimomura et al. reported in 2007 [2] the synthesis and optical properties of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ silicate garnet doped with cerium for an application in white LEDs. The synthesis was done by general solid-state reaction to produce the phosphor. A broadband photoluminescence emission with a maximum at around 505nm in the green spectral region and an excitation peak at 455 nm in the blue spectral region was demonstrated and the CIE color coordinates were calculated to be $x=0.30$ and $y=0.59$. The XRD patterns showed the pure phase of CSS silicate garnet. The phosphor also showed a high thermal stability. This is very important because it is well known that due to heat generation in LEDs in normal use the luminescence can drop due to quenching effects. Compared to $(\text{Y,Gd,Ce})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ CSS:Ce shows remarkably high thermal stability up to 200°C. For example, at a temperature of 150°C it still shows a relative intensity of over 90% compared to around 55% in YAG with Gd.

Further researches has been done by Chen et al. in 2010 to estimate the effect of different fluxes on the luminescence properties of the green CSS:Ce phosphor [3]. The phosphors were produced via solid state synthesis by firing in a reducing atmosphere. Used fluxes were H_3BO_3 , LiF, CaF_2 and NH_4Cl . Also, a sample without flux was investigated. Firing without flux showed no x-ray diffraction peaks close to CSS silicate garnet. The dependence of different fluxes on photoluminescence properties was also investigated. It was shown that in terms of luminescence intensity CaF_2 shows the best result.

A white LED was produced with the CSS phosphor synthesized at 1350°C with 1 wt% CaF_2 . The color correlated temperature (CCT) was determined to 4872 K and is therefore by about 1500 K lower than in common WLEDs with YAG:Ce. Moreover, the color rendering index (CRI) was estimated to be 84.0, also exceeding the CRI properties of commercial WLEDs with YAG:Ce.

Liu et al. produced CSS doped with cerium via sol gel combustion method in 2009 and compared the general and optical properties of these samples with samples produced

by usual solid state reaction [4]. XRD showed obvious CSS phase for the samples produced via gel combustion method fired in air and then fired in reducing atmosphere. The sample fired only in air showed some traces of not transformed CeO_2 .

The generation of CSS nanoparticles doped with cerium was firstly reported by Liu et al in 2010 [5]. The synthesis of the nanoparticles was done by a gel-combustion method. The SEM pictures of the as prepared samples after firing at a temperature of 900°C show grains with an average size of 200 nm. With increasing temperature the grains tend to agglomerate and grow gradually. At 1100°C the grains are dispersing well with an average grain size smaller than 1 μm .

The influence of different rare earth ion dopants on the properties of CSS have been reported by Fernandez-Gonzalez et al in 2016 in their paper on the influence of cerium and erbium co-doped CSS silicate garnet on the optical properties of the phosphor [6]. The samples were fabricated by freeze-drying precursor method and the powder grains were in μm scale.

The influence of Al^{3+} and Ce^{3+} on the optical properties of CSS was investigated and reported by Wu et al. in 2012 [7]. The phosphors were manufactured by solid-state reaction. Quantum yield of different powder samples was measured and reached 46,8 % for the optimized composition.

In this work, we present a novel synthesis method of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ nano- and microparticles with outstandingly bright photoluminescence, with the record-high PLQY of about 70%. Both kinds of samples display significantly higher thermal stability of photoluminescence in comparison to a commercial YAG:Ce phosphor.

2 EXPERIMENTAL SECTION

2.1 Synthesis procedure for microsized $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$

The modified in comparison with [3] conventional solid-state reaction was utilized for synthesizing microparticles. Pre-synthesis in air of pressed blends of CaCO_3 , Al_2O_3 and silicon oxide with subsequent high-temperature post-treatment at temperatures between 1300°C and 1400°C in $95\%\text{N}_2 - 5\%\text{H}_2$ reducing atmosphere and with additional 1% CaF_2 flux enable to obtain $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ microparticles with high quantum yield.

2.2 Synthesis procedure for nanosized $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$

Nanocrystalline $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ was synthesized *via* fatty acid assisted co-precipitation. As SiO_2 source, SiO_2 nanoparticles (NPs) solution was prepared by modified Stöber method. Representative scheme of the synthesis is shown on Fig. 1. This technique was also successfully employed for $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals synthesis (J. Phys.

Chem. C 2009, 113, 16652–16657). Our preliminary experiment has shown, that usage of Tetraethyl orthosilicate (TEOS) only in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ NPs synthesis lead to formation of low-luminescent material over micron in size. Monodisperse 40 nm SiO_2 NPs used in our method, was an ideal choice to obtain highly luminescent material. We speculate, that this spherical NPs play role as a seed for further $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ nanocrystallite formation.

First, metal nitrites $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.85 mmol, 0.673g), $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2mmol, 0.678g) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.15 mmol, 0.0651g) were dissolved in 30 mL of distilled water. Then, 20 mL water solution of SiO_2 NPs (3 mmol, 0.18g) was added. Upon continuous stirring, 30mL water solution of NaOA (12.45mmol, 3.79 g) was added drop-by-drop, to form white precipitate of metal oleates with SiO_2 NPs. The precipitate was then centrifuged (15 min 12000 rpm) and dried in vacuum oven overnight at 50°C . Then, firing of the precipitate on air (850°C , 3h) with further calcination (1200°C , 2h) in N_2/H_2 gas flow, led to formation of highly luminescent $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ NPs.

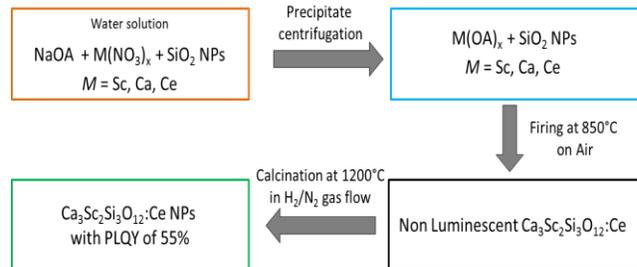


Figure 1: Schematic representation of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ NPs synthesis.

2.3 Measurement of luminescent properties, quantum yield and decay time

All spectroscopic measurements were executed with a JASCO spectrofluorometer FP8500 operating with a 150W xenon lamp, integrating sphere and a photomultiplier detector. The samples were finely grinded and put in a sample holder of 5 mm diameter. For the conventional emission and excitation spectra measurements suitable long pass filters were put in front of the detection window.

The spectra and of emission intensities at high temperatures (until 300°C) were measured with an additional to JASCO equipment consisting of a heater and light fibers.

The decay curves were measured on a time-resolved photoluminescence spectrometer Fluotime 300 (PicoQuant GmbH). The excitation source was a 402 nm pulsed diode laser with a pulse width of ca 100 ps. The decay curves were recorded with a photomultiplier in time-correlated single photon counting mode.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD) measurements

Figure 2 shows the XRD pattern of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$: 0.5% Ce^{3+} μm particles fired in B_2O_3 for 4 h and in CaF_2 for 15 h.

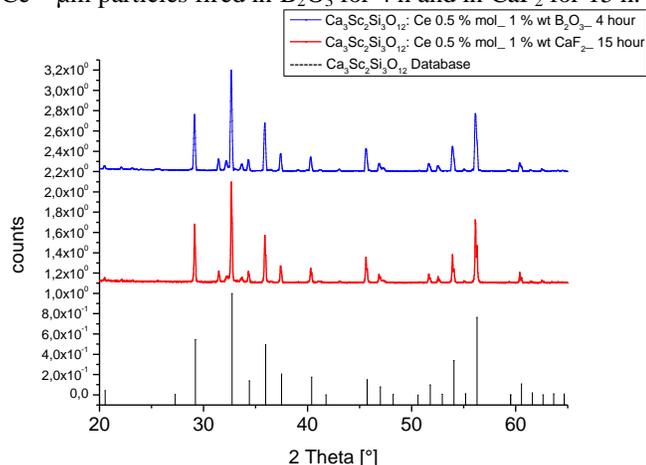


Figure 2: XRD pattern of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$: 0.5% Ce^{3+} micro-particles.

Samples prepared in CaF_2 flux show lower content of Sc_2O_3 . The phase purity of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$: Ce^{3+} is estimated by 96 %.

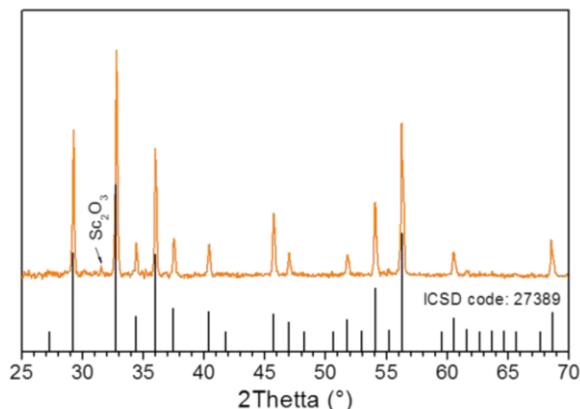


Figure 3: XRD of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce nanoparticles (NPs)

The result of a X-ray diffraction (XRD) measurement of NPs is shown in Figure 3. The high intensity of the diffraction peaks indicates good crystallinity of the nanoparticles, and the peaks are in excellent agreement with ICSD-27389. Tiny amount of Sc_2O_3 was identified in the samples, which is less than 2%.

3.2 SEM pictures of micro and nanoparticles

Several microcrystalline and nano-powder samples of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce were investigated by a Field emission scanning electron microscopy (FESEM). In the case of

microcrystals it was possible to recognize nearly cubic particles with a size distribution between 3 and 10 μm . (Figure 4). The synthesis occurs in the CaF_2 flux; therefore the growth conditions were similar to the formation of crystalline grains in melt-solutions resulting in the grain morphology similar to the unit cell.

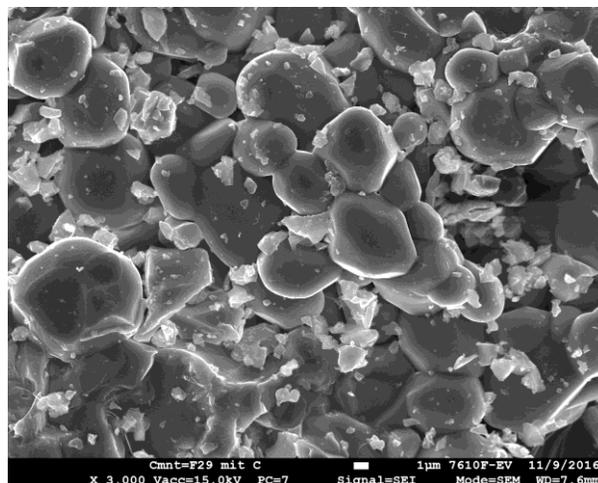


Figure 4: FESEM picture of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce micro-particles

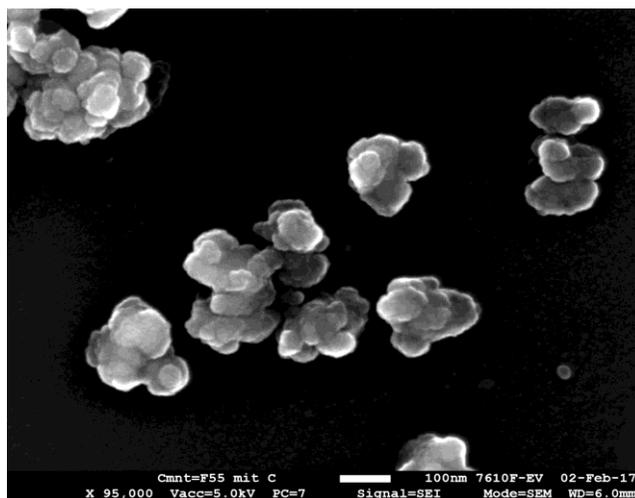


Figure 5: FESEM picture of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce nanoparticles

The obtained $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce NPs were non-uniform in shape and 100-300 nm in size (Figure 5), which makes this material applicable for thin film coating in LED technologies.

3.3 Photoluminescence and decay properties

The photoluminescence and excitation spectra of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$:Ce microcrystalline powders are known. Nevertheless it was important to compare the spectral

properties of our samples with the published data. And, first of all, it was necessary to determine the quantum efficiency/yield (QY) of the optimized samples.

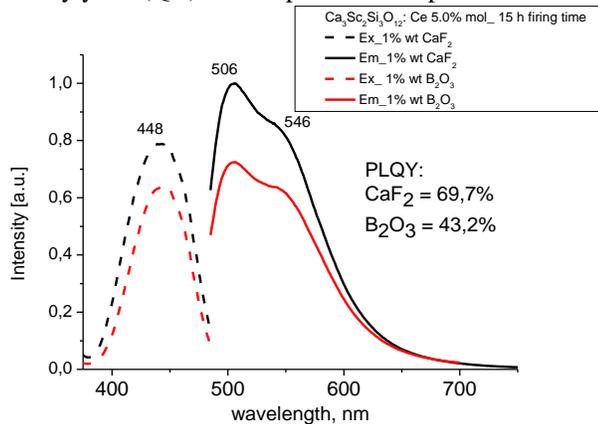


Figure 6: PL and excitation spectra of a sample in the μm scale with the nominal composition $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{5mol}\% \text{Ce}^{3+}$

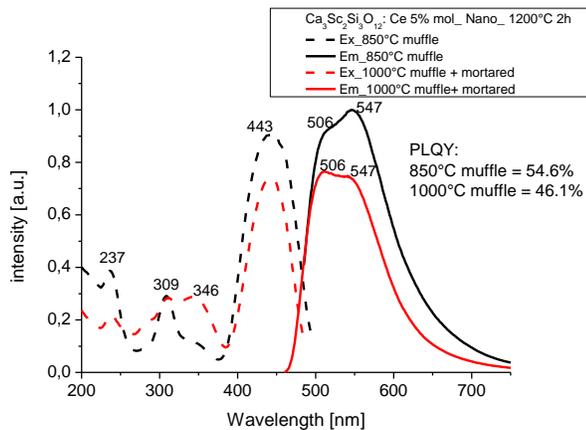


Figure 7: PL and excitation spectra of a sample in the nanometer scale with the nominal composition $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{5mol}\% \text{Ce}^{3+}$

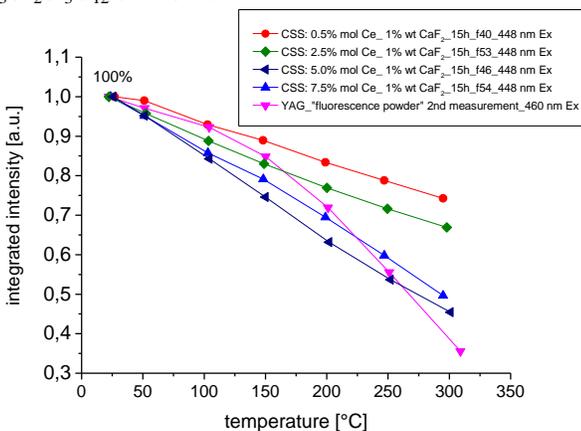


Figure 8: Temperature dependence of the integral emission of different $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ samples with grains in μm scale in the spectral region of 450-700 nm.

4 CONCLUSION AND OUTLOOK

A novel synthesis method of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ nano- and micro particles is presented. This method yields an outstandingly bright photoluminescence, with the record-high PLQY of about 70% for μm powder and 55 % for nanoparticles. Both kinds of samples display a higher thermal stability of photoluminescence in comparison to a commercial YAG:Ce phosphor.

REFERENCES

- [1] Ching-Cherng Sun, Yu-Yu Chang, Tsung-Hsun Yang, Te-Yuan Chung, Cheng-Chien Chen, Tsung-Xian Lee, Dun-Ru Li, Chun-Yan Lu, Zi-Yan Ting, Benoît Glorieux, Yi-Chun Chen, Kun-Yu Lai and Cheng-Yi Liu, "Packaging efficiency in phosphor-converted white LEDs and its impact to the limit of luminous efficacy". *Journal of Solid State Lighting*, vol. 1, 19, 2014. DOI: 10.1186/s40539-014-0019-0.
- [2] Shimomura, Y., T. Honma, M. Shigeiwa, T. Akai, K. Okamoto and N. Kijima, "Photoluminescence and Crystal Structure of Green-Emitting $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ Phosphor for White Light Emitting Diodes." *Journal of the Electrochemical Society* **154**(1), J35, 2007.
- [3] Chen, Y., M. Gong and K. W. Cheah, "Effects of fluxes on the synthesis of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ green phosphors for white light-emitting diodes." *Materials Science and Engineering: B* **166**(1): 24-27, 2010.
- [4] Liu, Y., J. Hao, W. Zhuang and Y. Hu, "Structural and luminescent properties of gel-combustion synthesized green-emitting $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor for solid-state lighting." *Journal of Physics D: Applied Physics* **42**(24): 245102, 2009.
- [5] Liu, Y., W. Zhuang, Y. Hu, W. Gao and J. Hao, "Synthesis and luminescence of sub-micron sized $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ green phosphors for white light-emitting diode and field-emission display applications." *Journal of Alloys and Compounds* **504**(2): 488-492, 2010.
- [6] Fernández-González, R., J. J. Velázquez, V. D. Rodríguez, F. Rivera-López, A. Lukowiak, A. Chiasera, M. Ferrari, R. R. Gonçalves, J. Marrero-Jerez, F. Lahoz and P. Núñez, "Luminescence and structural analysis of Ce^{3+} and Er^{3+} doped and $\text{Ce}^{3+}-\text{Er}^{3+}$ codoped $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ garnets: influence of the doping concentration in the energy transfer processes." *RSC Adv.* **6**(18): 15054-15061, 2016.
- [7] Wu, Y.-F., Y.-H. Chan, Y.-T. Nien, I.-G. Chen and J. McKittrick, "Crystal Structure and Optical Performance of Al^{3+} and Ce^{3+} Co-doped $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ Green Phosphors for White LEDs." *Journal of the American Ceramic Society* **96**(1): 234, 2013.