High homogeneity, thermal stability and external quantum efficiency of Ce:YAG single-crystal powder phosphors for white LEDs

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The properties of Ce:Y₃Al₅O₁₂ single-crystal powder phosphors, obtained by powdering single-crystals, are investigated as a function of the average grain size. It is found that single-crystal powders maintain the outstanding properties of bulky crystals, namely a high internal quantum efficiency and thermal stability. Furthermore, single-crystal powders exhibit a very high homogeneity and reproducibility, which contrasts with the large variation of emission intensity in reference ceramic powders of highest quality. The effective absorption of single-crystal phosphors increases with the grain size and it is enhanced by a treatment with HF. An effective absorption comparable with the one of reference ceramic powder phosphor is obtained, even though the Ce concentration in single-crystal phosphor powders is about one order to magnitude lower.

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1. Introduction

White light emitting diodes (wLEDs) are having nowadays a large implementation in indoor and outdoor general lighting, substituting conventional light sources. In comparison with the latter, wLEDs possess as major characteristics a superior energy efficiency and a long lifetime, among others such as non-toxicity, durability, etc. The typical design of a wLED consists of a LED encapsulated in an epoxy or resin with embedded ceramic powder phosphors (CPPs). Commercial products rely on the simplest configuration, based on a blue LED and yellow CPPs. Ce-doped Y₃Al₅O₁₂ (Ce:YAG) is the typical yellow phosphor, where the allowed 4f⁷→4f⁷ transitions of Ce³⁺ ions lead to a broad absorption band in the blue region and to a broad emission band in the yellow one. The position of these bands can be engineered to some extent by partial cation substitution. Traditionally, these yellow phosphors are synthesized as ceramics by various methods such as solid-state reaction, hydrothermal, coprecipitation, spray pyrolysis, sol–gel and combustion. It is well-known, however, that the properties of these CPPs depend not only on the composition, but also on the synthesis process, which largely determine the type of impurities, homogeneity, induced defects, microstructure, morphology, etc. Therefore, even highest quality CPPs present microstructural inhomogeneities and above all a detrimental decrease of emission efficiency with the increase of the phosphor temperature.

As alternative to conventional Ce:YAG ceramic phosphors, we have proposed the use of single-crystal phosphors (SCPs) based on Ce:YAG. These, due to their single crystalline nature, are comparatively impurity- and defect-free, and consequently these present not only a high conversion efficiency at any temperature, but also a high reproducibility and homogeneity. We have demonstrated that the SCPs are thermally very stable, with an internal quantum efficiency close to ideal till about 250°C, where the emission intensity of CPPs is already quenching. Further, we have shown that though the Ce concentration in SCPs is smaller than that of CPPs, the high absorption cross-section of blue light, with a value of 3.0 × 10⁻¹⁸ cm², guarantees an efficient absorption even with very thin plates. Although Ce:YAG SCP plates possess outstanding emission properties in comparison with CPPs, there are applications where the use of phosphors in powder form may be advantageous, e.g. favoring a light scattering in wider solid angles. To date, however, there are no reports about the properties of powdered SCPs, and therefore there is a need to determine how far the advantageous properties of SCPs are preserved after the process to reduce the size to the order of tens of micrometer. The aim of this work is to determine the optical properties of Ce:YAG SCP powders depending on the average grain size. These powders were produced from bulky SCPs grown by the Czochralski (Cz) technique.

Four different average grain sizes are analyzed, mainly in terms of emission homogeneity and quantum efficiency, in order to determine the analogies with SCPs. Likewise, the effective absorption and color coordinates are also compared to the best commercially available CPPs to assess their potential for white lighting applications.

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2. Experimental procedure

A Ce:YAG single-crystal was grown by the Cz technique using a 30 kW RF-generator. High purity (4N) commercial oxides were weighted in stoichiometric ratio and charged into an Ir crucible. The crystal was pulled along the (111) direction at fixed pulling and rotation rates, 1 mm h⁻¹ and 10 rpm, respectively. A section of the crystal, with a Ce concentration of 0.3 mol % (i.e. relatively high as for SCPs), was crushed into powders with a mortar. These were then separated into four groups by the use of sieves pairs, which had mesh openings of 100, 70, 50, and 30 microns. Correspondingly, the SCP powders are named as P(100-70), P(70-50), P(50-30), and P(30) for the smallest remaining ones. The resulting average grain size distribution was measured with a SALD-3100 laser diffraction type particle size distribution apparatus from Shimadzu. After characterization of as-crushed powders, these were additionally treated with a 40% HF aqueous solution for 60 min at 40°C, as described elsewhere. Furthermore, a 0.3 mm thick plate was prepared as single-crystal reference. For the sake of comparison with a high quality commercial phosphor, LP-6969 from LWB (Leuchstoffwerk Breitungen GmbH) was used as Ce:YAG-type CPP reference.

Scanning electron microscopy (SEM) and cathodoluminescence (CL) were carried out with a field emission SEM S4300 from Hitachi, equipped with a CL system MP32S/M from Horiba. The acceleration voltage of the electron beam was 5 kV. Excitation and photoluminescence (PL) spectra were recorded at room temperature (RT) with a Fluorolog Jobin-Yvon spectrophotometer, using a 450 W Xe-lamp as excitation source. Quantum efficiency (QE) measurements at RT and from 50 to 300°C were performed with a Photol QE-1100 spectrometer equipped with a 150 mm diameter half-moon mirror and a Xe-lamp as excitation source. The internal QE and the effective absorbance were estimated as the ratios QEint = emitted photons/absorbed photons and Aeff = absorbed photons/excitation photons, respectively. Additionally, the CIE color coordinates were determined in the same temperature range.

3. Results and discussion

Figure 1(a) shows the grain distribution obtained for the four SCP powders. The percent P of grain sizes is presented together with the integrated percent ΣP. The corresponding median, average and standard deviation are listed up in Table 1. The average grain size varies between 24.1 and 97.79 microns, with the standard deviation increasing from 0.13 to 0.4 as the powder size decreases. The finest SCP powder size is close to typical reference CPP, with an average value of about 15 microns (according to maker specifications). The morphology of SCP powders was observed by SEM and the images obtained at ×1000 magnification are shown in Fig. 1(b) in comparison with the reference CPP. As a general impression, we can see that SCP powders have a splinter-like appearance with flat surfaces and sharp edges, which are favored by the preferential cracking along crystallographic planes during the crushing process. Instead, CPPs exhibit rounded rough surfaces, possibly as a result of the gradual grain

Table 1. Grain size distribution of SCP powders

| Sample     | Median size (µm) | Average size (µm) | Standard deviation (µm) |
|------------|------------------|-------------------|-------------------------|
| P(100-70)  | 97.79            | 98.91             | 0.13                    |
| P(70-50)   | 61.77            | 61.54             | 0.15                    |
| P(50-30)   | 34.2             | 29.4              | 0.3                     |
| P(30)      | 24.1             | 20.2              | 0.4                     |
| Reference CPP |                 |                   |                         |

Fig. 1. Comparison of SCP powders with the reference: (a) Grain size distribution of SCP powders, (b) SEM images of the surface morphology, CL intensity mappings at (c) 530 nm (yellow Ce³⁺ emission) and (d) 320 nm (UV emission band).
growth in all directions during the synthesis.

In the same way where the SEM images were obtained, cathodoluminescence was recorded. By excitation with the electron beam two broad band emissions are observed (see later Fig. 2). The first yellow band corresponds with the well-known Ce$^{3+}$ $^{2}D_{5/2} \rightarrow ^{2}F_{5/2}$ and $^{2}D_{3/2} \rightarrow ^{2}F_{7/2}$ transitions. On the other hand, the UV band has been attributed to an excitonic emission localized near the antisite defect Y$_{3}$Al$_{2}$ and therefore it can be a good probe to check the homogeneity of the YAG matrix. Luminescence intensity mappings centered on the yellow and UV bands, at 530 and 320 nm, are shown in Figs. 1(c) and 1(d), respectively. Grains of SCP powders present a quite homogeneous emission intensity, independent of grain size, clearly resembling the surface morphology of the original SEM images. Furthermore, as both UV and yellow mapping intensities correlate very well with each other, we presume that the small differences of intensities on a single mapping are related to geometric factors, such as the grain orientation and depth relative to the electron beam and the light detection system. The analogous mappings in the reference CPP show, in contrast, not only a very large difference in intensity between grains in each mapping, but also a large difference between both yellow and UV mapping intensities, indicating an inhomogeneous emission characteristic.

In order to analyze further the homogeneity of SCP powders and to better understand the origin of the inhomogeneity of CPPs, CL spectra of the wide-area and of local-grains were recorded. As can be seen in Fig. 2(a), the normalized wide-area spectra of SCP powders systematically overlap in both the yellow and UV emission bands, indicating that the nature of the emission is intrinsic to the SCP, and therefore, that the crushing process does not induce any new defects that could distort the original local structure around the emitting Ce$^{3+}$ ions. Additionally, the CL of an undoped YAG single-crystal was measured under the same conditions. As can be seen in the inset of Fig. 2(a), the undoped sample emitted only a broad band in the UV wavelength region, clearly resembling the one observed in all Ce:YAG SCP powders. This result suggests that the influence of the Ce incorporation as dopant on the intrinsic defects of YAG single-crystals is negligible or maybe even nonexistent. The UV emission peaked at 4.19 eV and presented a shoulder at about 5.0 eV, in relatively good agreement with the reported values of 3.95 and 4.8 eV.

Furthermore, in order to confirm that the recorded CL profiles did not become similar as a result of various emissions averaged in a wide-area, several local-grains were measured separately. Once more, these led to identical emission curves (not shown), thus reconfirming the homogeneity and reproducibility of SCP powders. This result contrasted with the local-area measurements on reference CPP, whereas the emission varied largely from grain to grain. As a general trend, the yellow band dominated, with a relative emission intensity of the UV band within few percent. However, for grains with an intense UV emission, the relative intensity of the yellow emission clearly decreased. As an example, the luminescence of several of these grains, marked in Fig. 1(b), are shown in Fig. 2(b). For the sake of comparison, the spectra are normalized at the maximum of the yellow band. As indicated by the identical yellow characteristic, the Ce$^{3+}$ emission was independent of the grain measured. In contrast with the yellow emission and also with the UV band in SCP powders, the profile and the relative intensity of the UV emission varied remarkably from grain to grain, suggesting the presence of an inhomogeneous distribution of different matrix defects, which may be not only intrinsic to YAG, like in the case of single-crystals, but also related with the fabrication method of the ceramics, such as low crystallinity, incorporation of impurities, high Ce concentrations, etc. These results suggest that, although the yellow Ce$^{3+}$ emission of CPPs is reproducible, matrix defects act as efficient non-radiative recombination centers, i.e. quench the Ce$^{3+}$ emission. Therefore, these defects are responsible for the notable inhomogeneity of emission intensity in CPPs.

In order to determine precisely the color temperature of SCP powders, calibrated PL measurements were carried out. Figure 3(a) shows the excitation and photoluminescence spectra for all four SCP powders in comparison with the reference CPP at RT. The width of the blue excitation band became broader as the grain size increased. Instead, the emission spectra overlapped in the long wavelength edge, while the opposite short wavelength edge exhibited a red-shift with the increase of grain size. Taking into account the overlap of the excitation and emission spectra (in the range of 475–525 nm), this measurement indicates that the red-shift correlates with the absorption broadening, or in other words, the red-shift is just apparent, resulting from the reabsorption of a part of the blue-greenish emitted light in the own phosphor powders. Therefore, we concluded that grain size determines the average absorption path length and with it the small red-shift. The CIE color coordinates of SCP powders are then shown in Fig. 3(b), depending on grain size and temperature. As can be seen, the red-shift observed with the grain size is quite small compared with the red-shift caused by the increase in phosphor temperature. Furthermore, the relative high reabsorption and red-shift of fine-grain reference CPP, comparable to the
SCP powders of larger grain size, is due to the much higher Ce concentrations present in CPPs.

The QEint of SCPs and CPPs has been reported in previous publications. Independently of the grain size, SCP powders exhibit the same features as SCPs. From RT up to 250°C, the QEint has values larger than 95% and maintains values higher than 92% even at 300°C, demonstrating excellent thermal stability and even presenting a maximum efficiency at around 200°C (QEint ≈ 97%). On the other hand, the QEint of CPPs starts to quench at much lower temperatures, reaching a maximum efficiency about 80% at 300°C. Therefore, SCP powders maintain the excellent QE and thermal stability of SCPs.

The Aeff of SCP powders is given in Fig. 4. With the increase in powder size, the Aeff of as-crushed powders rises continuously from about 66 to 79%. After the powder treatment, the increase of Aeff became steeper, reaching a value of approximately 83% for the largest grain size. The monotonous increase of with the grain size is mainly related with the increase in the average absorption path length, as discussed above in connection with the reabsorption and red-shift. On the other hand, we presume that the enhancement of the Aeff after the treatment is possibly related to a surface effect. The reasoning is as follows. Figures 5(a) and 5(b) show the surface of SCP powders before and after treatment. As can be seen, before the treatment the surface is largely covered by plenty of much smaller size grains, which are widely removed after the treatment. By the elimination of the smaller particles, the total surface area can be reduced, with it also the surface scattering is diminished, and consequently the Aeff can be improved. For the finest P(30) powder, however, the effect of treatment is quite minor, due to the generally small grain size. In this case, the total surface area and corresponding surface scattering are comparable before and after treatment. The increment in Aeff varies between <1% and ~6%, with the tendency to increase with the grain size. At this point it is noteworthy to mention that larger size SCP powders can reach an Aeff comparable to the one of the reference CPP, leading consequently to a similar external QE at RT. This fact is quite remarkable if we consider that SCPs contain a Ce concentration of about one order of magnitude lower than CPPs. Furthermore, we would like to compare these results with the blue absorbance of SCP plates. Taking into account the absorption coefficient \( \alpha \) (at 450 nm) of a SCP with the same Ce concentration as the investigated SCPs, the transmittance \( T \) for a given thickness \( d \) can be calculated according to the well-known Beer–Lambert law, \( T = \exp(-\alpha d) \). The inset of Fig. 4 shows the absorbance \( 1-T \) as a function of the plate thickness. The interval of observed Aeff values in SCP

Fig. 3. (a) Normalized room temperature excitation and photoluminescence of SCP powders and the reference CPP. The inset shows a zoom of the overlapping region around 500 nm. (b) CIE color coordinates of SCP powders and the reference CPP.

Fig. 4. Aeff of SCP powders, before and after treatment. The inset shows the estimated absorbance and transmittance of the same Ce:YAG SCP in plate form as a function of thickness. The thick red line represents the effective thickness range of SCP powders.

Fig. 5. SEM images of SCP powders (a) before and (b) after treatment.
powders is marked in red and it corresponds to a plate thickness range of 0.12–0.25 mm. Therefore, we can consider that the absorbance of SCP powders is close to the saturation value.

4. Conclusions
SCP powders have been investigated as a function of the average grain size. Independently of the grain size, SCP powders exhibit an outstanding QE$_{int}$ and thermal stability, which is equivalent to that of bulky SCPs. Further, CL measurements indicated that the emission characteristic and intensity are very homogeneous and reproducible, i.e. not affected by average grain size or grain selection. Analogous CL measurements on CPPs evidence a large inhomogeneity in emission intensity, the quenching of the yellow Ce$^{3+}$ emission correlating with the rise of various UV emission bands. The CIE color coordinates of SCP powders slightly shifted towards red with the increase in powder size due to reabsorption. Further, the $A_{	ext{eff}}$ in SCP powders increased with the grain size, and it could be further improved by a treatment that eliminated the smallest particles from the surface of the predominant larger grains. An $A_{	ext{eff}}$ comparable to the one of reference CPPs was obtained, in spite of the relatively lower Ce concentrations in SCP powders.

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