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On the Temperature Dependent Excitation and Reflection Spectra of $Ln_3Al_5O_{12}:Ce^{3+}$ Ceramics (Ln = Y, Lu) for White LEDs

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Abstract

Yttrium aluminum garnet (YAG) and Lutetium aluminum garnet (LuAG) doped with Ce^{3+} are widely applied phosphor powders or ceramics for the conversion of blue into green to yellow light in the rapidly expanding market of white light emitting high power LEDs. Surprisingly, the temperature dependent reflection and excitation spectra of these well-established materials have not been investigated until today. In this work, we report the temperature dependence of the reflection and excitation spectra of Ce^{3+} doped YAG and LuAG in the temperature range from 300 to 800 K.

Keywords

Temperature-Dependent Reflection, Excitation Spectra, Garnet Phosphor Ceramics, Thermal Population

1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) and Lutetium aluminum garnet ($Lu_3Al_5O_{12}$) doped with Ce^{3+} are widely used luminescent materials with a rather long history. Already in 1967 Blasse and Bril reported on Ce^{3+} doped YAG as a new phosphor for flying spot cathode ray tubes (CRTs). Its unique properties like very high quantum efficiency, a short luminescence lifetime in the ns range, and an emission spectrum that matches well with the eye-sensitivity curve, brands the material as ideally suited for this application [1]. However, in the last 20 years light emitting diodes (LEDs) have attracted much attention due to their many benefits over other light sources like gas discharge and incandescent lamps. The main advantages of LED are a longer lifetime, a higher wall plug efficiency, and a better color rendering as observed for gas discharge lamps [2]-[4]. Since the publica-

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tion of the first high brightness blue (In, Ga)N LED by Nakamura *et al.* in 1993, YAG:Ce and LuAG:Ce are the most common phosphors, which are applied to blue LED chips for white light application [5]. Due to these circumstances a lot of studies have been done in the past on this material and has not stopped until today [6]. Nevertheless, to the best of our knowledge, temperature dependent reflection and excitation spectra were not recorded for YAG and LuAG doped with Ce^{3+} so far.

2. Experimental Section

Precursors for the ceramic synthesis of $(Lu_{0.99}Ce_{0.01})_3Al_5O_{12}$(LuAG:Ce) and $(Y_{0.99}Ce_{0.01})_3Al_5O_{12}$ (YAG:Ce) were prepared by a sol-gel combustion method. The gels were prepared by using Lu_2O_3 (Treibacher 99.99%), Y_2O_3 (Treibacher 99.99%), $(Al(NO_3)_3{\cdot}H_2O$ (Aldrich 99.9%) and tris(hydroxymethyl)-aminoethane (tris) acting as a complexing agent and fuel at the same time. Starting materials were dissolved in diluted HNO_3 and heated to 65˚C - 75˚C. Then, under continuous stirring, tris was added with a molar ratio 2:1 (to all metal ions). The solutions were stirred for additional 1 h at the same temperature. Next, after concentrating the mixtures by slow evaporation, sols turned into transparent, highly viscous gels. Afterwards, the temperature was raised to 250˚C to start the self-sustaining gel combustion process which was accompanied by the development of a large amount of gas. The resulting products were dried at 120˚C for several hours and ground to fine powders, which were heated for 4 h at 1000˚C in air to remove the organic residue after the combustion process. For the fabrication of the ceramics the precursor was first uniaxial pressed at 120 MPa into discs of 10 mm in diameter and 0.8 mm thickness. Secondly, to reduce pores, the obtained green bodies were isostatically pressed at 300 MPa. The powder compacts were sintered at 1700˚C at ambient pressure in air. Excitation and reflectance spectra were recorded in ranges 250 - 550 nm and 250 - 800 nm, respectively, on Edinburgh Instruments fluorescence spectrometer equipped with 450 W Xe arc lamp and cooled (−20˚C) single-photon photomultiplier (Hamamatsu R2658P). $BaSO_4$ (99.999% Sigma-Aldrich) was used as reflectance standard. Temperature dependent measurements were carried out in a self-constructed heatable sample holder in the range from 300 to 800 K.

3. Results and Discussion

3.1. Diffuse Reflection Spectra

The diffuse reflection spectra relative to $BaSO_4$ of the YAG:Ce and LuAG:Ce ceramics were recorded in the temperature range from 300 to 800 K (shown in **Figure 1** & **Figure 2**). With increasing temperature two new

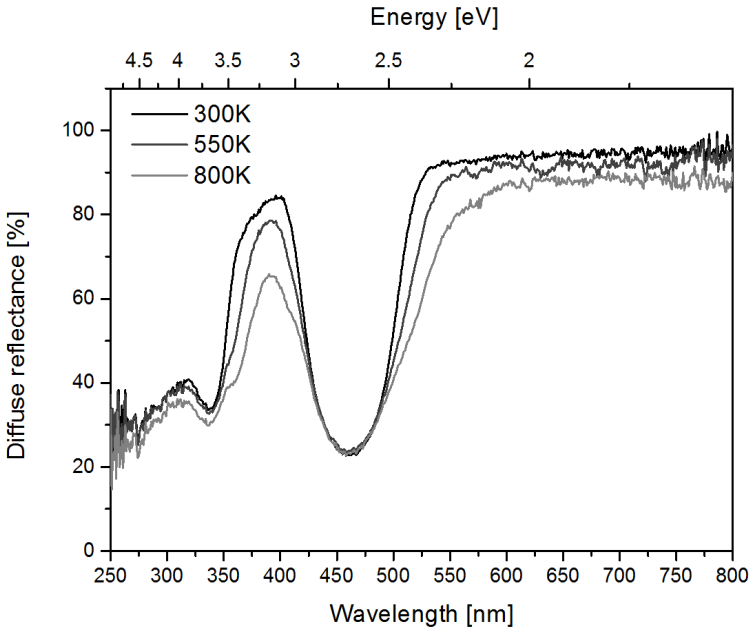

Figure 1. Diffuse reflection spectra of a $Y_3A_{l5}O_{12}:Ce^{3+}$ ceramic at 300, 550, and 800 K (at all temperatures $BaSO_4$ was used as a white standard).

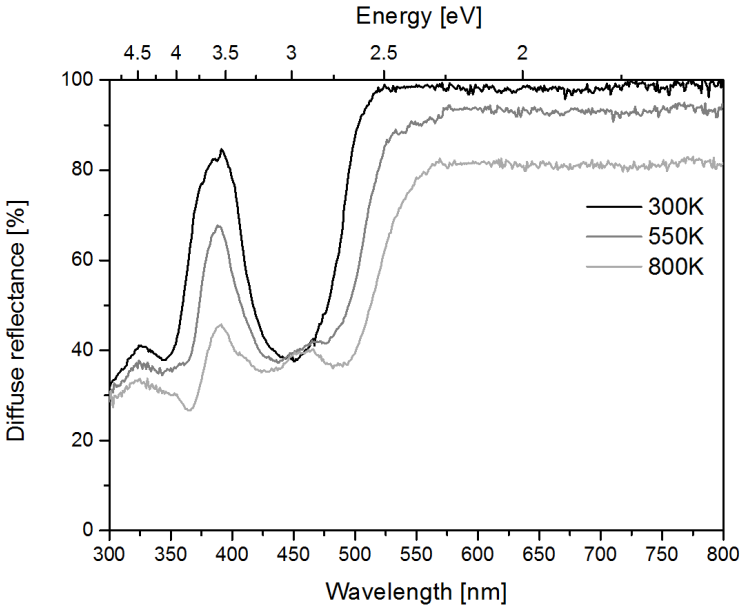

Figure 2. Diffuse reflection spectra of a $Lu_3Al_5O_{12}:Ce^{3+}$ ceramic at 300, 550, and 800 K (at all temperatures $BaSO_4$ was used as a white standard).

significant absorption bands at around 375 nm and 550 nm can be observed for both ceramics. The two allowed absorption bands at 300 K originate from the lowest energy level $^2F_{5/2}$ of the [Xe]4f^1 configuration to the lowest crystal-field component ^2D_J of the [Xe]5d^1 of Ce^{3+} configuration. The second lowest energy level $^2F_{7/2}$ of the [Xe]4f^1 configuration which is separated by approximately 2300 cm^{-1} from the ground state $^2F_{5/2}$ level is almost not thermally populated at room temperature [7]. Therefore, no visible absorption from $^2F_{7/2}$ into the [Xe]5d^1 configuration can be expected at room temperature. With increasing temperature the $^2F_{7/2}$ level gets more and more thermally populated, which results for both garnet ceramics in a novel absorption band.

3.2. Excitation Spectra

The normalized excitation spectra, as depicted in **Figure 3** and **Figure 4**, of the YAG:Ce and LuAG:Ce ceramic were recorded in the same temperature range, viz. between 300 and 800 K, like the reflection spectra discussed above. The spectra show two excitation bands at 300 K which are as-signed to transitions to the two lowest energy levels of the five crystal field levels for a ligand field with D_2 symmetry. The two bands, which are observed around 344 and 460 nm for YAG:Ce and about 350 and 450 nm for LuAG:Ce are assigned to the two lowest crystal-field components. These findings are in excellent agreement with the literature [7]. However, with increasing temperature up to 800 K two novel sidebands appear, which are attributed to the thermal population of the spin-orbit split sublevel $^2F_{7/2}$. This population continuously increases with temperature as expected. This effect can be observed for YAG:Ce, but is much stronger for LuAG:Ce. We assume that this difference is caused by the larger spin-orbit coupling of the Ce^{3+} ground state level in LuAG in comparison to YAG.

4. Conclusions

A dedicated investigation on the temperature dependence of the reflection and excitation spectra of YAG:Ce and LuAG:Ce ceramics was reported for the first time. Temperature dependent reflection spectra show two new absorption bands occurring above 550 K for both ceramics, which is attributed to the thermal population of the $^2F_{7/2}$ spin-orbit split level of the [Xe]4f^1 configuration and the respective transition to the lowest crystal-field levels of the [Xe]5d^1 configuration of Ce^{3+}. In order to validate this striking effect, temperature-dependent excitation spectra were recorded as well.

The changes of the absorption spectrum of YAG:Ce and LuAG:Ce ceramics, will have a strong impact on the application of these ceramics in phosphor converted high power LEDs, if the chip temperature exceeds 200˚C or even higher [2]. In other words, the novel absorption bands will enhance the re-absorption in the LED package

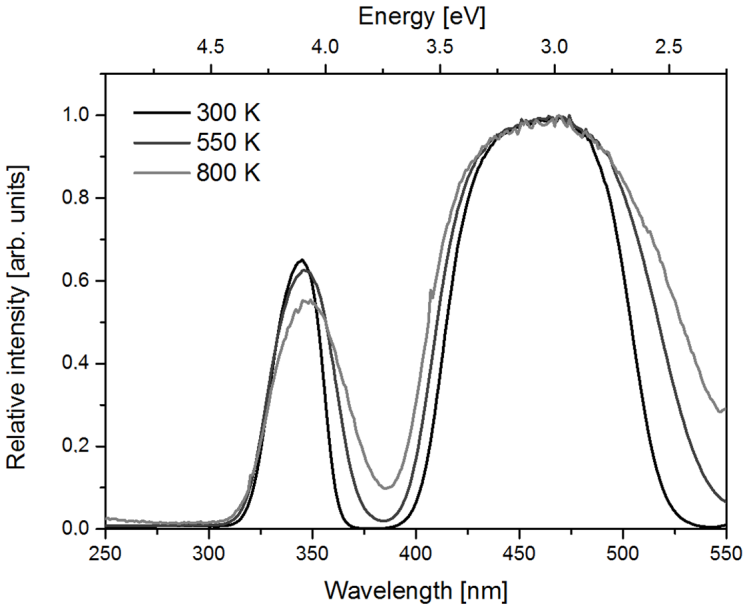

Figure 3. Excitation spectra of $Y_3Al_5O_{12}:Ce^{3+}$ ceramic at 300 K, 550 K and 800 K. Emission monitored at 560 nm.

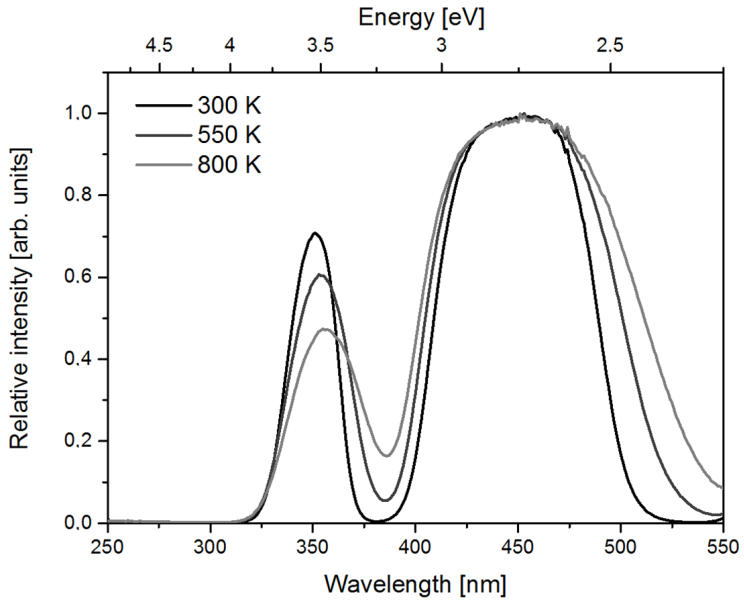

Figure 4. Excitation spectra of $Lu_3Al_5O_{12}:Ce^{3+}$ ceramic at 300 K, 550 K and 800 K. Emission monitored at 560 nm.

and will reduce the package gain once the quantum efficiency is not unity.

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