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Synthesis and photoluminescent properties of the Dy^{3+} doped YSO as a high-temperature thermographic phosphor

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ABSTRACT

Dy^{3+}-doped yttrium orthosilicate (Y_2SiO_5, abbreviated YSO) phosphors were synthesized: (1) by conventional high temperature solid-state method using two types of fluxes: lithium fluoride (LiF) and boron oxide (B_2O_3); (2) by metal alkoxide sol-gel method using isopropoxide assisted co-precipitation with subsequent annealing to explore its possible application in high-temperature thermometry. It was experimentally observed that the use of LiF flux affects the luminescent properties due to improvement of the crystal quality of crystallites and co-doping Li^+ and F^- ions. Herein, a strategy involving the use of different fluxes and concentration of Dy^{3+} ions has been developed to achieve high photoluminescence (PL) intensity and high intensity ratio of different PL peaks. The case of incorporated LiF in the host crystal lattices revealed strong enhancement of luminescence intensity of YSO:Dy (more than three times higher at 293 K) compared to the luminescence intensity of the phosphors synthesized with B_2O_3. Based on the results of high temperature measurements, it can be stated that YSO:Dy is a favorable phosphor for high temperature measurement, with a temperature sensitivity range comparable to YAG:Dy but with a lower PL decay time which is reduced by about 60%. For temperatures up to 1250 K the intensity ratio approach offers better measurement capabilities while the temperature sensitivity above 1250 K is superior for the decay time approach.

1. Introduction

Contactless high-temperature thermometry with luminescent materials has been an important research area over the last couple of decades. Phosphor thermometry is an alternative method of measuring temperature from temperature-dependent aspects of the luminescence such as intensity ratio at different wavelengths and decay time [1]. Thermographic phosphors have been widely investigated and could be employed for temperature measurement in gas turbines [2,3] and engines [4,5] as well as for temperature analyses on gaseous flows [6–10]. Due to the need of getting efficient thermographic phosphors [11–16] with high chemical stability, high luminescence yield and desirable lifetime of luminescence pulses [17–19] new compositions should be identified as thermographic phosphors and an improvement of the optical properties of those phosphors has to be achieved. The commonly used thermographic phosphors for high temperature applications are based on the combination of rare-earth ion centers in ceramic hosts. For instance, YAG doped with rare earth (RE^{3+}) [2,6–8] ions or dual-activated by RE^{3+} and transition ions as Mn^{4+} or Cr^{3+} [20], however especially YAG:Dy, are the most widely used phosphors in phosphor thermometry. Likewise, yttrium orthosilicate (Y_2SiO_5) offers good chemical and thermal stability, a high melting point (~2070 °C) and has recently been used as a thermal barrier coating ceramic. It can be applied as a host crystal for laser materials as well as a host for scintillators and phosphors [21].

Y_2SiO_5 (YSO) has a wide band gap of 7.4 eV and has the capacity to accommodate significant amounts of rare earth ions such as Ce^{3+} [22–24], Tb^{3+} [24,25], Sm^{3+} [26], Eu^{3+} [26,28] and Pr^{3+} [29]. More recently, Bi^{3+} was also used in orthosilicate compounds such as YSO and Lu_2SiO_5 [30]. $Y_2SiO_5:Ce^{3+}$ is an excellent blue emitting rare earth phosphor. Therefore, it is of crucial importance for optoelectronic applications and commonly used in solid-state lasers and solid-state lighting [21,32]. Activation of yttrium silicate with Tb^{3+} generates an efficient green emitting phosphor ($Y_2SiO_5:Tb^{3+}$) having high

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luminescent efficiency under UV light and electron beam excitation [33]. Europium doped silicate (Y_2SiO_5:Eu^{3+}) is a red emitting phosphor and is often used to produce red light in displays [34]. Recently, great attention has been focused on the adjustment and design of emission color of the phosphor compounds, which can be adjusted from yellow to blue by controlling the amount of Ce^{3+} ions [35]. Obtaining highly energy efficient white light because of the contribution of either different activators or one activator in different crystal sites in a single phase is another research direction, which has attracted particular interest [36].

High-temperature lifetime studies of Eu:Y_2SiO_5 (*X*2) and Eu:$Y_2Si_2O_7$ (type *D*) have shown strong luminescence with a temperature sensitivity between approximately 700 °C and 1200 °C [37]. These data are supplemented with additional data for two other rare earths, Tb^{3+} and Dy^{3+}, that were presented for the first time by Chambers and Clarke [38]. All the doped silicates show strong luminescence at high temperatures with sensitivity ranging from 700 °C to at least 1440 °C with a variety of sensitivities; Tb^{3+} shows the strongest temperature dependence [39]. Several environmental barrier coating designs involve composites consisting of a mixture of phases, e.g., Y_2SiO_5 and $Y_2Si_2O_7$ together [40,41], and $Y_2Si_2O_7$ also slowly transforms to Y_2SiO_5 as it loses silica upon exposure to hot water vapor. The high-temperature lifetimes of Eu^{3+} and Tb^{3+} are similar in both Y_2SiO_5 and $Y_2Si_2O_7$, and so with these dopants a mixture of the two silicates should not complicate thermometry measurements. In contrast, Dy^{3+} shows a much shorter high-temperature lifetime in the disilicate than in the monosilicate; however, the intensity also quenches much more quickly such that at 900 °C the longer-lived monosilicate has an intensity advantage by a factor of ten, which increases further at higher temperatures. This high-temperature dominance may allow a possible mixture of Dy:Y_2SiO_5/Dy:$Y_2Si_2O_7$ to be used for thermometry [38].

It was shown that dissimilarity in room-temperature lifetimes for Eu^{3+} and Tb^{3+} between hosts is due to differences in radiative emission strengths, whereas the similarity of high-temperature lifetimes indicates that the non-radiative process controlling the high temperature decays is similar. The process governing the temperature dependence of the decay times of Dy^{3+} is less clear. Studies measuring the effect of concentration, possible filling of lower emissive levels (e.g., $^6F_{5/2}$), and the lifetime of potential thermalized levels ($^4I_{15/2}$) will be necessary to determine which of several processes is dominant.

The aim of this work was to study the high temperature luminescence properties of Dy^{3+} doped Y_2SiO_5 phosphor. The temperature dependence of the luminescent intensity in the temperature range of 293 – 1500 K for Y_2SiO_5 has not, to our knowledge, been studied so far. For this purpose, the high temperature luminescence of Dy^{3+} doped Y_2SiO_5 was investigated. The samples were prepared by a conventional high temperature solid-state reaction and by sol gel synthesis. The influence of LiF, B_2O_3 as a flux and a possible origin of co-doping elements on the synthesis and the PL properties of phosphors was investigated. The effect of temperature in the range of 293 – 1500 K on the PL spectra and decay time was analyzed. Finally, two different wavelength bands for calculating the intensity ratio as a function of temperature, $I_{(445–465\ nm)}/I_{(480–500\ nm)}$ and $I_{(445–465\ nm)}\ /\ I_{(492–497\ nm)}$, were determined.

2. Experimental procedures

2.1. Sample preparation and characterization

Powder phosphors Y_2SiO_5: xDy^{3+} (YSO:xDy) (x = 1, 2 and 3 mol%) with addition of LiF or B_2O_3 were fabricated by conventional high temperature solid-state method (SSS) and by metal alkoxiedes sol-gel method (SGS) with subsequent annealing. Lithium fluoride (LiF) and boron oxide (B_2O_3) were chosen as fluxes in order to decrease sintering temperature and to improve the phosphor efficiency.

Solid-state synthesis (this procedure has already been detailed in previous studies [12]) was undertaken with stoichiometric amounts of Y_2O_3, (all, 99.99%, Alfa Aesar), SiO_2 and Dy_2O_3 (99.9%, Reacton) which were used as starting materials in the present work. 2.5, 5 and 10 wt% of LiF; 5 wt% of B_2O_3 (99.99% Alfa Aesar) were added additionally to the stoichiometric compositions. The starting powder was mixed and ground in an agate mortar by hand. Subsequently, they were fired in an alumina crucible at 1473 K for 4 h in air to produce the final samples. After firing, samples were cooled to room temperature in the furnace and were ground again to powder for subsequent use.

Sol-gel synthesis was performed by using isopropoxides assisted coprecipitation method by using Dysprosium (III)- and Yttrium (III) isopropoxides as well as TEOS in stoichiometric amount. The mixture was staring for 12 h at 80 °C to form gel. Then the isopropoxides were fired at 1473 K for 4 h in air to produce the final samples.

The crystalline structure of the phosphor powders was analyzed by X-ray diffractometer (PANalytical EMPYREAN XRD Powder/SAXS Diffractometer) with a Cu-Kα radiation source (λ = 1, 5406 Å) at room temperature. The morphology and size of the powder phosphors were observed by using scanning electron microscope (SEM) JEOL JSM-7610F equipped with a field emission gun operated at 20 kV. The photoluminescence emission (PL) and excitation (PLE) spectra of powders at room temperature were measured with a spectrofluorometer Jasco FP-8500. Optical measurements were conducted under identical conditions for all samples with a spectral resolution of 5 nm on both, excitation and emission side.

2.2. Experimental setup for high temperature measurements

The temperature dependent decay time and spectral emission behavior was evaluated up to 1500 K. The YSO phosphor samples were placed into corundum ceramic sample carriers and reproducibly positioned inside a high temperature oven (Supertherm HT 18/10). The measured temperature range was between 300 K and 1500 K, while the temperature inside the oven close to the phosphor sample was monitored by a type B thermocouple. Measurement data was taken in 100 K increments from 300 K to 700 K and every 50 K above 700 K, where a higher temperature sensitive behavior is expected.

The third harmonic of a pulsed Nd:YAG laser (Quantel Q-smart 450) with a pulse duration of 6 ns and a repetition rate of 10 Hz was used to excite luminescence. The average laser pulse energy was kept at 8 mJ per pulse over the whole temperature range to eliminate influences of the laser fluence on the temperature dependent luminescent behavior. A schematic view of the experimental set-up is given in Fig. 1. The laser beam for excitation was guided into the furnace using a 355 nm dichroic mirror, which allowed the transmission of the phosphorescence emission. Two spherical lenses first collected the luminescence signal and then focused it onto the detector. A 355 nm long pass edge filter ensured that no laser light was captured by the detection device.

Two high speed photo diodes (Thorlabs, DET210) served for measuring the decay time in two wavelength ranges, while the photo current was read out temporally resolved by an oscilloscope (PicoScope 6,

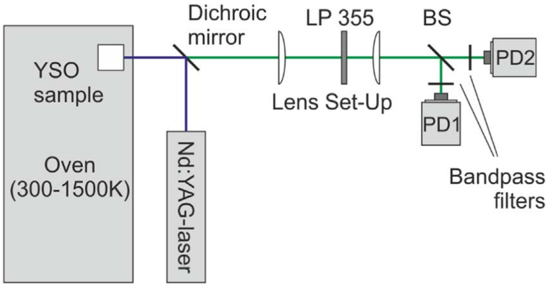

Fig. 1. Schematic view of the experimental setup for high temperature measurements of the phosphorescence decay and emission spectra. For spectral emission analysis, a spectrometer replaced the photodiodes.