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High-temperature thermographic phosphor mixture YAP/YAG:Dy^{3+} and its photoluminescence properties

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ABSTRACT

In this work we report on the investigation of high-temperature thermographic phosphors Dy^{3+}-doped yttrium aluminum garnet and the mixture of yttrium aluminum perovskite / yttrium aluminum garnet (YAP/YAG). The phosphors were synthesized by conventional high temperature solid-state method using lithium fluoride (LiF) as a flux. The latter serves also as a source of co-doping Li^+ and F^- ions affecting the luminescent properties. The photoluminescence intensity of YAP/YAG:Dy (75/25%) mixture was doubled at room temperature compared to YAG:Dy and the intensity ratio of the lines in the regions 450–460 and 480–500 nm was increased from 0.45 to 0.63 at 1293 K, favoring temperature measurements. Therefore, the mixture of $YAlO_3/Y_3Al_5O_{12}$:Dy is promising material for high temperature phosphor thermometry.

1. Introduction

Over the couple of decades there has been increasing need for advanced temperature measurement methods such as phosphor thermometry. Phosphor thermometry is based on the correlation between the photoluminescence (PL) properties of phosphors and temperature. Thermographic phosphors could be employed for temperature measurement in gas turbines [1,2] and engines [3] as well as for temperature analyses on gaseous flows [4–8]. This technique promises temperature detection of up to 1400 °C and more exhibiting low measurement errors. Phosphor thermometry may also be applied under very large background radiation as it utilizes active triggering of the luminescent signal via a light source such as a laser or LEDs. It was currently shown that signals buried in a 2000 time larger background signal may be easily be detected with a rather simple dual-channel lock in setup and, accordingly, surface temperature may be deduced to at least up to 1000 K within an error of lower than 10 K [9]. Each application requests a material with certain optical and structural properties. In general, no phosphor fulfills the requirements for all applications. Thus, improvement of one or more properties is desirable in the quest for efficient thermographic phosphors [10,11], with high chemical stability, radiation hardness, high luminescent yield and in some cases short lifetime of PL [12,13]. Besides, phosphors should be inexpensive and easy to produce. Commonly used as host material in phosphor thermometry is the yttrium – aluminum Y_2O_3–Al_2O_3 system, which exists in three phases: yttrium aluminum monoclinic $Y_4Al_2O_9$ (YAM), yttrium aluminum perovskite $YAlO_3$ (YAP) and yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG). Generally, yttrium orthoaluminate YAlO3 (YAP) is a host material exhibiting good optical, thermal and mechanical properties similar to YAG. It is well-suited for the development of optical materials for different applications. Various rare earth dopants including Ce, Tb, Eu, Nd, Dy and also Cr and Bi have been incorporated into YAG and YAP to control the phosphor luminescence [14].

YAG doped with rare earth (RE^{3+}) ions [1], especially YAG:Dy [15,16], is one of the most widely used phosphors in phosphor thermometry [17]. The YAP crystals belong to a group of materials serving as host for laser crystals, scintillators, optical recording media and also as a substrate for thin films of high temperature superconductors [18]. Rare earth ion doped yttrium orthoaluminate ($YAlO_3$) phosphors are especially attractive for the development of optoelectronic devices [19,20]. $YAlO_3:Eu^{3+}$ has been reported for successful storage and retrieval of 248-bit temporal optical data by accumulated photon echoes, owing to the long storage time of this material [21]. $YAlO_3$ phosphors co-activated with Eu^{3+} and Ce^{3+} have been widely applied in the development of flat panel field emission displays and plasma display [22]. Baig et al. reported thermoluminescence studies of $YAlO_3:Dy^{3+}$ and its low stability to UV exposure compared to gamma irradiation [23]. Premkumar et al. suggested the possible application of

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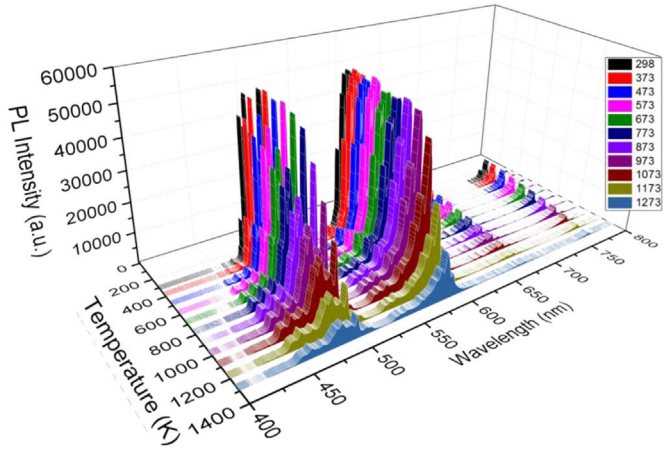

Fig. 1. Emission spectra of the YAG:2% Dy^{3+} phosphor synthesized with LiF flux. The 355 nm excitation wavelength was used for generation of emission spectra.

$YAlO_3$:Dy phosphor in dosimeters. Fading at low doses is possibly due to the formation of shallow and thermally unstable traps [24]. Yuexia et al. summarized that Dy^{3+} doped hexagonal nanocrystalline $YAlO_3$ is a promising material with potential applications in lighting and display technology [25].

It is essential that luminescent characteristics of the phosphor changes with temperature. In the emission spectrum of $Y_3Al_5O_{12}$:Dy, the intensities of spectral bands differ in their temperature dependence [11,26–28]. The ratio of two photoluminescence (PL) bands of YAG:Dy^{3+} at 458 nm and 497 nm has been utilized for temperature measurements [29]. Dy^{3+} in $YAlO_3$ reveals similar maxima under UV excitation [30]. To the best of our knowledge, the dependencies of spectral lines at 456 nm and 497 nm in YAP:Dy at high temperatures have not been reported in the literature. Moreover, a comparison between YAG:Dy and YAP:Dy has not been undertaken. For a correct comparison of the temperature behavior, it was necessary to synthesize both phosphors under the same conditions. Therefore, a reference sample YAG:2% Dy was synthesized and the temperature dependence of PL in the range of 298–1273 K was measured. As shown in Fig. 1, for YAG:2% Dy with temperature ascending, the intensity of the 456 nm emission peak increases whereas the 497 nm emission peak decreases in intensity.

A detailed analysis of the XRD patterns of $YAlO_3$:Dy in references [23,24] proved a certain amount of garnet phase $Y_3Al_5O_{12}$ in all samples. It seems to be that separation of the phases YAP and YAG needs more efforts. Therefore, our aim is to investigate the PL behavior of the YAP/YAG mixture as a thermographic phosphor suitable for high temperature measurements.

To our best knowledge, the mixture of YAP/YAG:Dy has never been investigated as a thermographic phosphor for high temperature measurements. Thus, the purpose of this paper is to gain deeper insight into physical processes and, in terms of possible application to thermometry, to reach high luminescent intensities of the phosphors. Moreover, we performed a comprehensive study of $Y_3Al_5O_{12}$:2% Dy^{3+} and $YAlO_3$/$Y_3Al_5O_{12}$:2% Dy. The samples were prepared by a conventional high temperature solid-state reaction. The influence of LiF 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 – 1293 K on the PL spectra was analyzed. Finally, the intensity ratio $I_{(450–460\ nm)}/I_{(480–500\ nm)}$ as a function of temperature, which is often used for temperature measurements, was determined.

2. Experimental procedures

2.1. Sample preparation and characterization

Powder phosphors $Y_3Al_5O_{12}$:2% Dy^{3+}(YAG:Dy) and $YAlO_3$/$Y_3Al_5O_{12}$:2% Dy^{3+}(YAP/YAG:Dy) with addition of LiF were fabricated by conventional high temperature solid-state method. LiF was chosen as a flux in order to decrease sintering temperature and to improve the phosphor efficiency.

The raw materials were Y_2O_3, Al_2O_3, (all, 99.99%, Alfa Aesar) Dy_2O_3 (99.9%, Reacton) and LiF (99.99% Alfa Aesar). To synthesize YAG:Dy, Y_2O_3, Al_2O_3 and Dy_2O_3 were weighted according to the stoichiometric ratio of $Y_{2,94}Dy_{0,06}Al_5O_{12}$ and 10 wt% of LiF (99.99% Alfa Aesar) was added to the stoichiometric composition as a flux. The YAP:Dy and mixture of YAP/YAG:Dy was synthesized from Y_2O_3, Al_2O_3 and Dy_2O_3 according to the stoichiometric ratio of $Y_{0,98}Dy_{0,02}AlO_3$. The content of the mixture of YAP/YAG:Dy differs depending on the used amount of LiF-flux. 5, 10 and 15 wt% of LiF (99.99% Alfa Aesar) were added to the stoichiometric compositions. The starting powder was mixed and ground in an agate mortar by hand. Subsequently, it was fired in an alumina crucible at 1673 K for 7 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.

The crystal structure of the phosphors was examined by using X-ray diffraction (Panalytical EMPYREAN XRD Pulver/SAXS Diffractometer) with a Cu-Kα radiation source (λ = 1, 5406 Å) at room temperature. Morphology and elemental analyses of the phosphors were done with the scanning electron microscope (SEM) (JEOL JSM-7610F) equipped with a field emission gun operated at 20 kV. The photoluminescence (PL) and photoluminescence 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

A high temperature single zone tube furnace (Carbolite STF 16/180) was used for spectral emission investigations. For calibration purposes, the laser beam has been directed onto the phosphor samples, which were placed into the alumina crucible and reproducibly positioned inside the furnace. Luminescence was excited by third harmonic of a pulsed Nd: YAG laser (Quant-Ray INDI-40-20) with a pulse duration of 6–9 ns and a repetition rate of 20 Hz. Fig. 2 shows a schematic view of the experimental setup. A 355 nm dichroic mirror guided the laser beam into the furnace while allowing the transmission of the phosphorescence emission. On the detection side the spherical lens collected the luminescence signal and focused the signal on the input slit of the spectrometer. Additionally, a 355 nm long pass edge filter was positioned between the spherical lenses to block the laser light. The

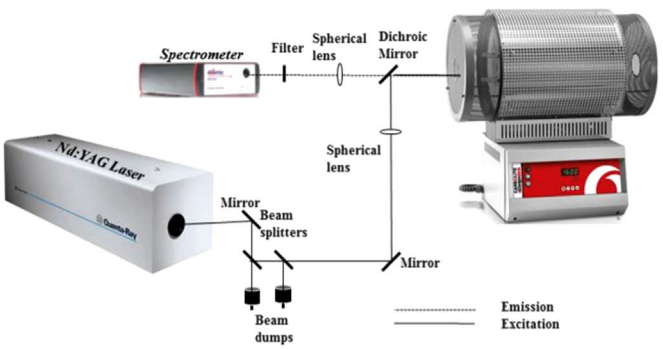

Fig. 2. Schematic view of the experimental setup for high temperature measurements of the emission spectra.