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Effect of B^{3+} - N^{3-} on YAG:Dy Thermographic Phosphor Luminescence

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The use of thermographic phosphors for high-temperature (> 1000 K) thermometry currently is limited by loss of signal due to thermal quenching. This work demonstrates a new phosphor generated by substituting tetrahedral site Al^{3+} - O^{2-} in YAG:Dy with B^{3+} - N^{3-} to produce YABNG:Dy. Conventional YAG:Dy and YABNG:Dy phosphors were synthesized using identical sol-gel synthesis techniques. X-ray diffraction measurements showed that both had nearly pure crystalline phases, with a minor secondary yttrium-aluminum-monoclinic (YAM) phase present in the YABNG:Dy. The YABNG:Dy sample had a larger and more spherical primary grain than the YAG:Dy in scanning electron microscopy images. Tests of the thermal response showed that the YABNG:Dy had much stronger phosphorescence emissions than YAG:Dy, likely due to the morphological differences. Furthermore, the onset of thermal quenching was delayed by approximately 100 K for YABNG:Dy compared to YAG:Dy, and the rate of signal decrease with temperature was reduced. This resulted in greater signal-to-noise ratios and less uncertainty in the temperature measurements, particularly at high temperatures. OCIS Codes: (120.6780) Temperature, (160.2540) Fluorescent and luminescent materials, (300.6280) Spectroscopy, fluorescence and luminescence <http://dx.doi.org/10.1364/OL.99.099999>

Laser induced phosphorescence (LIP) from thermographic phosphors (TPs) is a non-contact thermometry technique that has several favorable attributes, including high accuracy, no effects from Doppler or pressure broadening of spectral lines, insensitivity to surrounding gas composition, and relatively simple setup [1]. A TP consists of a crystalline host matrix that is doped with a rare-earth or transition metal activator. After UV excitation, dopant electrons are promoted to a higher electronic state, with a distribution over vibrational states that depends on the phosphor temperature. Interaction of the excited electrons with the host matrix results in a complex combination of radiative (phosphorescent) and non-radiative transitions that manifest as temperature-dependent changes in the temporal decay and/or spectral shape of the phosphorescence. LIP thermometry has been applied in a variety of problems, including gas turbine combustor surfaces [2], burning fuel droplets [3], and heated gas flows [4].

An issue with LIP thermometry at high-temperatures (e.g. those found in combustion systems) is that the phosphorescence signal decreases significantly due to thermal quenching. Exacerbating the problem is an increase in background radiation at high temperatures, which increases the measurement noise. The combined effects reduce the accuracy and maximum detectable temperature [5].

Two-dimensional LIP thermometry may be performed based on the phosphorescence temporal decay (using high-speed cameras) [6] or the temperature-dependent ratio of two emissions lines [7]. YAG:Dy ($Y_{3-x}Dy_xAl_5O_{12}$) is a commonly used TP for 2D high-temperature applications [1, 5]. Measurements generally are made based on the ratio of emissions from the $^4I_{15/2} \rightarrow ^6H_{15/2}$ and

$^4F_{9/2} \rightarrow ^6H_{15/2}$ transitions at 456 nm and 497 nm, respectively. While mean 2D measurements with accuracy better than 1% have been reported at 900 K [2], uncertainties in the range of 3% typically are reported at 1500 K in single shot measurements [7].

The host matrix has a major effect on the luminescence behavior of a thermographic phosphor. For example, Hansel et al. [8] substituted 50% of the aluminum in YAG:Ce ($Y_{3-x}Ce_xAl_5O_{12}$) with gallium to produce a low temperature TP, YAGG:Ce ($Y_{3-x}Ce_xAl_{2.5}Ga_{2.5}O_{12-y}$), using solution-combustion synthesis. They found that the luminescent lifetime of YAGG:Ce quenched at a lower temperature than for YAG:Ce, which extended the possible measurement range. Wang et al. [9] substituted the tetrahedral site Al^{3+} - O^{2-} in YAG:Ce with B^{3+} - N^{3-} to produce YABNG:Ce ($Y_{3-x}Ce_xAl_{5-y}B_yN_yO_{12-y}$) using solid state synthesis. The emissions intensity was enhanced over the temperature range of 293 K to 573 K and the thermal quenching was delayed from 323 K to 523 K. However, the mechanism causing the observed delays in thermal quenching currently is not well understood. To our knowledge, similar substitution has not been investigated for YAG:Dy. While the luminescence mechanism of Ce^{3+} and Dy^{3+} are different, in that Ce^{3+} fluorescence is fully allowed while Dy^{3+} involves spin and parity forbidden transitions within the 4f shell, the previous results indicate that B^{3+} - N^{3-} substitution into YAG:Dy has the potential to improve the emissions intensity and delay thermal quenching. This work therefore investigates the thermal response of YAG:Dy and YABNG:Dy ($Y_{3-x}Dy_xAl_{5-y}B_yN_yO_{12-y}$) for high-temperature LIP thermometry.

YAG:Dy and YABNG:Dy samples were prepared by wet-chemical sol-gel synthesis. Extensive parameter studies were performed to optimize the phosphor

Fig. 1 XRD pattern of YAG:Dy and YABNG:Dy (G: YAG, *: YAM)

composition, as well as the various temperatures and times in the synthesis procedure. The optimized phosphors discussed here had $x = 0.03$ (1% dopant concentration) and $y = 0.3$ (6% boron substitution).

Appropriate amounts of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich, 99.997%), yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.8%), dysprosium nitrate hydrate ($\text{Dy}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, Sigma Aldrich, 99.9%), and boron nitride (BN, Sigma Aldrich, 98%) were dissolved in 15 mL deionized water. Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Sigma Aldrich, ACS reagent $\geq 99\%$) was then added into the solution to promote gel polymerization. The solution was stirred at 338 K and 358 K for 2 hrs and 3 hrs, respectively to form a gel. A xerogel then was formed by drying the gel at 383 K for 12 hrs. This xerogel underwent intermediate grinding step using a porcelain mortar and pestle. The resultant powders were calcined in air at 673 K for 2 hrs. After calcination, the powders were ground again, and then sintered in air at 1673 K for 6 hrs. The resultant phosphor powders were ground for a third time. Calcination and sintering in a nitrogen environment also was tested, with no change in the resultant phosphor performance.

The crystal structure of the phosphors was examined using X-Ray Diffraction (XRD), the composition using Electron Microprobe Analysis (EMPA), and the morphology using Scanning Electron Microscopy (SEM). The thermal response of the phosphors was then tested using a calibration setup described below.

XRD was performed using a Philips PW1050 X-Ray powder diffractometer equipped with a $\text{Cu-K}\alpha$ radiation source (40 kV, 40 mA), at room temperature. Figure 1 shows the XRD pattern for the YAG:Dy and YABNG:Dy phosphor. All diffraction peaks of the YAG:Dy corresponded to the cubic yttrium aluminum garnet phase (YAG, JCPDS No. 72-1315), which confirms the absence of impurities. However, a secondary phase was identified in the YABNG:Dy XRD pattern, corresponding to yttrium aluminum monoclinic (YAM, JCPDS No. 14-0475). The intensity of the YAM peak relative to the strongest YAG peak was less than 2% and is not expected to greatly influence the phosphor performance.

It is noted that higher BN levels in the reagents ($y > 0.3$) resulted in a significant yttrium orthoborate phase

Table 1. EMPA mass fractions in YABNG:Dy sample

Element	Theoretical (%)	Experimental (%)
Yttrium (Y)	44.7	44.6 ± 0.2
Aluminum (Al)	21.5	21.3 ± 0.1
Boron (B)	0.60	0.6 ± 0.2
Dysprosium (Dy)	0.80	0.81 ± 0.05
Oxygen (O)	31.7	32.5 ± 0.2
Nitrogen (N)	0.7	n/a

(a)

(b)

Fig. 2 SEM images: (a) YAG:Dy, (b) YABNG:Dy

(YBO_3 , JCPDS No. 83-1205) in the XRD patterns, indicating an additional crystal phase. For example, at $y = 0.5$, the relative intensity of this peak was greater than 3%. With this YBO_3 phase present, the phosphorescence intensity decreased slightly relative to $y = 0.3$. A BN level corresponding to $y = 0.3$ therefore was used for the phosphor presented here. The observed decrease in phosphorescence intensity in the presence of the YBO_3 is consistent with the YAG:Ce results of Wang et al [9]. It is noted that Ref. [9] found optimal performance at $y = 0.5$, which may be due to differences in the synthesis methods.

EMPA was performed using a Cameca SX50 Electron Microprobe to determine the final composition of the YABNG:Dy phosphor. Table 1 shows the measured mass fractions of yttrium, aluminum, boron, oxygen, and dysprosium, along with the theoretical values based on the reactant composition. For nitrogen, the measurement uncertainty was too large to provide meaningful results (several times the measured value), and this value therefore is not included. The mass fractions agreed well with the theoretical values, indicating proper inclusion of the BN into the host matrix. The slightly high oxygen levels may be due to calcination and sintering in air.

SEM images were obtained using a JEOL JSM6610LV scanning electron microscope (10 kV) after sputtering a layer of gold on the powders. The SEM images in Fig. 2 show the morphology of the tested phosphors. The YAG:Dy and YABNG:Dy phosphors were composed of

Fig. 3 Experimental setup for thermal response measurement

grains with diameters around 0.3 μm and 1 μm , respectively. In general, the YABNG:Dy had a larger grain size, a smoother, and a more spherical grain shape than the YAG:Dy. These attributes are expected to increase the emission intensity due to, e.g. lower intrinsic reflection coefficient associated with larger particles [10]. Considering the identical synthesis methods employed, these morphological changes are attributed to the BN acting as a flux. Once again, this is consistent with the observations of BN substitution into YAG:Ce in Ref. [9].

The thermal response of the phosphors was measured using setup shown in Fig. 3. Samples of YAG:Dy and YABNG:Dy powder were pelletized into discs with 15 mm diameter and 0.5 mm thickness. The pellets were then heated in an optically accessible box furnace (Sentrotech ST-1700-445), equipped with a type B thermocouple to measure the interior temperature.

The phosphor pellets were excited by a Nd:YAG laser (Spectra-Physics Quanta Ray) operating at its third harmonic (355 nm) with a pulse duration of about 10 ns, repetition rate of 10 Hz, and pulse energy of 100 mJ. The laser beam was impinged on the phosphor using a dichroic mirror that reflected the laser light but transmitted the phosphorescence signal. The phosphor emissions were filtered by bandpass filters and focused onto a spectrometer (Andor Shamrock SR303i) coupled with a CCD camera (Andor iDus 420). The wavelength resolution of the measurements was 0.1 nm. Day-to-day variability in the signal yield caused by alignment of the optical system was tested and found to be less than 1%.

Measurements were conducted over the temperature range 500-1600 K at 100 K intervals. At each temperature, three independent accumulated spectra, each taken over 100 laser shots was acquired, as well as 10 single shot spectra. The data were corrected for background radiation using accumulated and single-shot measurements at each condition with the laser blocked. The mean emission spectra of YAG:Dy and YABNG:Dy at different temperatures, normalized by the corresponding maxima at each temperature, are shown in Fig. 4. The basic behavior of the phosphors is as reported in the literature for YAG:Dy; the relative intensity of the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transition at 497 nm stayed fairly constant, whereas the intensity of the ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ at 456 nm increased. The temperature therefore can be measured from the ratio of these two emissions lines.

While the basic spectral shapes from the two phosphors are similar, the YABNG:Dy exhibits greater signal-to-

(a)

(b)

Fig. 4 – Normalized emission spectra: (a) YAG:Dy, (b) YABNG:Dy

noise at high temperatures. Figure 5a shows the total integrated spectral intensity from 453.8 - 459.8 nm ($I_{(453.8 - 459.8 \text{ nm})}$) as a function of temperature. Clearly, the YABNG:Dy sample produces more phosphorescence at all tested temperatures, which can be attributed to the morphological differences described above.

Additionally, the onset of thermal quenching is deferred to higher temperatures. This is demonstrated in Fig. 5b, which shows $I_{(453.8 - 459.8 \text{ nm})}$ for YAG:Dy and YABNG:Dy normalized by their respective peak values. The emissions intensity from YABNG:Dy plateaus and begins to decrease at 100 K higher than YAG:Dy. Moreover, the relative rate of signal decrease with temperature for YABNG:Dy was less than for YAG:Dy. This indicates that the presence of BN in the host matrix delays the YAG:Dy thermal quenching mechanism.

The increased signal from YABNG:Dy resulted in improved temperature-measurement accuracy at higher temperatures, particularly for the single-shot measurements. Figures 6a-b show the ratio, R , of the ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ emissions to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ versus temperature determined from the 100 shot accumulated spectra and the 10 single-shot spectra, respectively, for both phosphors. In each case, the integrated emissions intensity in a 6 nm wavelength range around the spectral peaks was used for the calculation. The error bars represent the standard deviation in R from the different trials at the same temperature, i.e. the standard deviation of the three accumulated measurements (Fig. 6a) or the ten single shot measurements (Fig. 6b).

(a)

(b)

Fig. 5 Integrated emissions intensity over 453.8 - 459.8 nm. (a) absolute, (b) normalized

The detection range is defined to be that over which R increases monotonically before the uncertainty was too high to distinguish the temperature. The phosphor sensitivity is defined to be the slope of the R curves over the detection range.

For the accumulated spectra, both phosphors had detection ranges from 500 - 1500 K and similar sensitivities. However, the standard deviation was significantly reduced at higher temperatures with YABNG:Dy, e.g. from 4% to 2% at 1500 K.

The difference was more significant in the single shot measurements. The range over which single-shot temperature measurements could be made with YABNG:Dy was 500-1300 K, as opposed to 800-1100 K with YAG:Dy. The uncertainty of the single-shot measurements at 1300 K with YABNG:Dy was approximately 2%. The improvement in precision is attributed to the combined effects of increased emission intensity and delay of thermal quenching.

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References

1. M. Aldén, A. Omrane, M. Richter, and G. Särner, *Prog Energy Combust Sci.* **37**, 4 (2011)
2. J.P. Feist, A.L. Heyes, and A. Seefelt, *P I Mech Eng A-J Pow*, **217** (2003)
3. G. Särner, M. Richter, and M. Aldén, *Opt Lett.* **33**, 12 (2008)

(a)

(b)

Fig. 6 Measured ratio (R) versus temperature curve for YAG:Dy and YABNG:Dy: (a) accumulated, (b) single shot

4. B. Fond, C. Abram, A. L. Heyes, A. M. Kempf, and F. Beyrau, *Opt Exp.* **20**, 20 (2012)
5. J. Brübach, C. Pflitsch, A. Dreizler, and B. Atakan, *Prog Energy Combust Sci.* **39**, 1 (2013)
6. N. Fuhrmann, M. Schneider, C-P Ding, J. Brübach, and A. Dreizler, *Meas Sci Technol* **24**, 9 (2013)
7. L. Goss, A. A. Smith and M.E. Post, *Rev Sci Instrum*, **60**, 12 (1989)
8. R. Hansel, S. Allison, and G. Walker, *J Mater Sci.* **45**, 1 (2010)
9. X. Wang, X. Liu, H. Li, Z. Zhange, Z. Sun, H. Zhang, and Y. Zhao, *Int J Appl Ceram Tec.* **10**, 4 (2013)
10. X. Hu, S. Yan, L. Ma, G. W, and J. Hu, *Powder Technol*, **192**, 1 (2009)

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1. M. Aldén, A. Omrane, M. Richter, and G. Särner, "Thermographic phosphor for thermometry: A survey of combustion applications", *Progress in Energy and Combustion Science* **37**, 4 (2011)
2. J.P. Feist, A.L. Heyes, and A. Seefelt, "Thermographic phosphor thermometry for film cooling studies in gas turbine combustors", *P I Mech Eng A-J Pow*, 217 (2003)
3. G. Särner, M. Richter, and M. Aldén, "Two-dimensional thermometry using temperature-induced line shifts of ZnO:Zn and ZnO:Ga fluorescence", *Optics Letters*, **33**, 12 (2008)
4. B. Fond, C. Abram, A. L. Heyes, A. M. Kempf, and F. Beyrau, "Simultaneous temperature mixture fraction and velocity imaging in turbulent flows using thermographic phosphor tracer particles", *Optics Express*, **20**, 20 (2012)
5. J. Brübach, C. Pflitsch, A. Dreizler, and B. Atakan, "On surface temperature measurements with thermographic phosphors", *Progress in Energy and Combustion Science*, **39**, 1 (2013)
6. N. Fuhrmann, M. Schneider, C-P Ding, J. Brübach, and A. Dreizler, "Two-dimensional surface temperature diagnostics in a full-metal engine using thermographic phosphors", *Measurement Science and Technology*, **24**, 9 (2013)
7. L. Goss, A. A. Smith, and M.E. Post, "Surface thermometry by laser-induced fluorescence", *Review of Scientific Instrument*, **60**, 12 (1989)
8. R. Hansel, S. Allison, and G. Walker, "Temperature-dependent luminescence of gallium-substituted YAG:Ce", *Journal of Materials Science* **45**, 1 (2010)
9. X. Wang, X. Liu, H. Li, Z. Zhange, Z. Sun, H. Zhang, and Y. Zhao, "Effect of boron nitride (BN) on luminescent properties of Y₃Al₅O₁₂:Ce phosphors and their white light-emitting diode characteristic", *Int J Applied Ceramic Technology*, **10**, 4 (2013)
10. X. Hu, S. Yan, L. Ma, G. W, and J. Hu, "Preparation of LaPO₄:Ce,Tb phosphor with different morphologies and their fluorescence properties", *Powder Technology*, **192**, 1 (2009)