The Effect of Cerium Concentration on $YBO_3:Ce^{3+}$

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KEYWORDS. YBO_3, Phosphors, Luminescence

BRIEF. The optimal doping concentration of $YBO_3:Ce^{3+}$ was found.

ABSTRACT. Phosphors, powdery substances made of a ceramic material doped with a rare-earth element have been used in applications from solid-state lighting, display technology, to temperature measurement and radiation detection. When these materials are excited, they luminesce. One parameter that can greatly alter the intensity (i.e output) and lifetime of the emission is the doping percentage. Too little dopant results in a low emission intensity, while too much dopant can lead to concentration quenching, lowering the emission intensity of the phosphor. In this investigation we fabricated samples of $YBO_3:Ce^{3+}$ with varying amounts of cerium using the combustion synthesis method. The intensity and lifetime of the emission of each sample was measured and compared. The highest intensity was obtained with a 5% doped sample, while the longest lifetime was obtained with a 1% doped sample. However, 3% and 4% both performed well for each measurement, so either of these concentrations is recommended for use in future applications of this phosphor.

INTRODUCTION.

The meltdown of the Fukushima nuclear reactor in early 2011 highlights the importance of detecting radiation. Large quantities of radiation were released from the reactor and spread all over the world. Various methods were used to detect the extent of the spread of the radiation; however, many of these methods are costly and/or complicated. One promising way to easily and cheaply detect radiation is through the use of phosphors. Phosphors are also capable of and have been used extensively for measuring temperature, which is useful in many fields, including most fields of experimental or applied science [1]. Also, many applications require sensing temperature without direct contact, or operate in harsh or high temperature environments [2]. In both radiation detection and temperature sensing, phosphor-sensing technology relies on optimal doping to provide the most sensitive measurements.

A phosphor is a material that has been designed to luminesce. Phosphors are made of two parts: the host matrix and the dopant. The dopant is the part of the phosphor that luminesces when energy has been absorbed. The host matrix serves to hold the dopant and stabilize it, but the host matrix also controls some of the physical properties of the phosphor. Phosphors are typically excited by a light source, such as a laser. Each type of phosphor is unique based on its specific host matrix and dopant combination, so the exact properties depend on the phosphor used. The fluorescence of phosphors doped with the same material are most similar to each other in terms of luminescent spectrum and lifetime, because the dopant determines the majority of the characteristics of the phosphor.

In temperature sensing, the lifetime of the emission in a phosphor, when excited with a pulsed source, decreases with temperature. Consequently, after the decay time of the emission is measured at various calibration temperatures, the temperature can be deduced from the measured decay of the emission and matched with the calibration curve.

Using phosphors as radiation sensors requires knowing the nominal emission or lifetime in the unirradiated sample. Upon exposure to particle radiation, displacement damage will create quenching centers. These quenching centers will alter the intensity and the lifetime, both of which can be measured to indicate radiation-induced damage.

One of the key factors that determines the effectiveness of any phosphor is the concentration of the dopant in the host matrix. A low dopant concentration results in low luminescence. As the concentration of luminescent centers increases, the luminescence also increases. However, excessive doping can cause concentration quenching, which is when the dopant particles may exchange energy, and the excitation is able to find a quenching center faster, resulting in a lower intensity. The optimal doping percentage of a phosphor occurs when the emission intensity is greatest.

Some phosphors have been heavily studied and thus their properties, including the optimal doping percentage, are well known. One boron-based phosphor paired with a common dopant, $YBO_3:Ce^{3+}$ [3], is studied here because the information in the literature is conflicting. For example, Smirnova *et al.* [4] found a 0.5% concentration to be optimal, but Chen *et al.* [5] found 1% to be optimal. This discrepancy is because of different synthesis methods as well as different definitions of optimal. $YBO_3:Ce^{3+}$ has a high potential to be useful as a radiation sensor, but because of the small amount of published research about this phosphor, more research needs to be conducted on $YBO_3:Ce^{3+}$ in order to know enough about the material to use it as a possible radiation detector. The goal of this research project is to find the optimal doping percentage of $YBO_3:Ce^{3+}$ in order to optimize its emission and determine its viability as a radiation sensor.

MATERIALS AND METHODS.

Fabrication.

Samples of $YBO_3:Ce^{3+}$ with cerium concentrations from 0.5% to 15% were prepared by the combustion synthesis method very similar to the one described in Thakare *et al.* [3]. Pure samples of $Y(NO_3)_3$ and $NH_4B_5O_8$, along with a 0.1993 molar solution in water of $Ce(NO_3)_3$, were used as the precursor materials. $C_2H_5O_2N$ was used as the fuel for the reaction. Because boron does not readily react, NH_4NO_3 was used as a catalyst to react with the $C_2H_5O_2N$ in order to force the boron into the desired configuration. A 3:1 ratio of NH_4NO_3 to boron was used for this reaction. The final ratio between reagents for the primary reaction was $10(Y_{(x-1)}(NO_3)_3)$ $(Ce_{(x)}(NO_3)_3)$: $2(NH_4B_5O_8)$: $16(C_2H_5O_2N)$, and $9(NH_4NO_3)$: $2(C_2H_5O_2N)$ for the secondary reaction. The reagents were measured to within 0.0001g of the stoichiometric amounts and mixed in a crucible. The solution became a milky, viscous, gel, which was then placed into a 600°C furnace to combust the solution. The resulting material was pure YBO_3:Ce along with excess carbon and other fouling around the edges of the crucible. To obtain only the YBO_3:Ce, the material was calcined at 900°C to remove all the impurities. The resulting YBO_3:Ce was ground into a fine powder to be analyzed.

Emission Intensity Measurements.

The intensity measurements were obtained by exciting the samples, and then measuring the intensity of the resulting emission. The excitation source was a xenon lamp transmitted through a monochromator. The monochromator was set to output 365 nm, which is the peak excitation wavelength of YBO_3:Ce according to previously obtained excitation measurements. This light was transmitted to the sample via a fiber optic cable. The subsequent emission by the excited phosphor was directed into a fiber optic and transmitted to a spectrometer, which detected and resolved the incoming wavelengths and intensities of each sample. This setup is shown in Figure S1. The measurements were all normalized to the integral of the reflection of the excitation peak to account for variability in the equipment and measurement process.

Emission Lifetime Measurements.

The lifetime measurements of the samples were obtained by exciting the phosphor followed by measuring the decay of the subsequent emission. The phosphor was excited with a nitrogen laser, with a pulse length of 2 or 3 nanosec

onds. The resulting emission was measured using a photomultiplier tube module, which multiplies any incoming photons into a much higher output voltage. The module included a potentiometer to adjust the gain of the photomultiplier tube. The voltage was collected and visualized using an oscilloscope. This setup is shown in Figure S2. The output data were fit to various exponential models to find the best fit and thus obtain the decay time.

RESULTS.

Emission Intensity.

The two main peaks of the emission, 388nm and 414nm, have very similar trends as the cerium concentration changes with the intensity of the 414nm peak being slightly higher (Figure 1). The intensity of the two peaks of the emission with low concentration percentages of 0.5% and 0.75% was relatively small. However, as the concentration increases to 1%, 2%, and 3%, the intensity increases. The intensity dips at 4%, but then rises again to the most intense peak of 5%. After 5%, the intensity declines to a 6% cerium concentration, and then continues to decrease in intensity to 10%. After 10%, the intensity levels off to a low level comparable to where the intensity was at 0.5%. Based on these data, the optimal cerium concentration for cerium doped YBO_3 is 5%. However, 4% and 3% are in the same range as 5% and would work equally well. The intensity measurement of each sample was taken four to six times, normalized to the reflection of the excitation peak to get comparable values, and averaged together. The coefficients of variation (mean/stdev *100%) ranged from 1.116% to 13.119%. This shows that the data are quite consistent. Also, the coefficients of variation for 3%, 4%, and 5% ranged from 3.596% to 7.481%, showing that the data collected were very consistent.

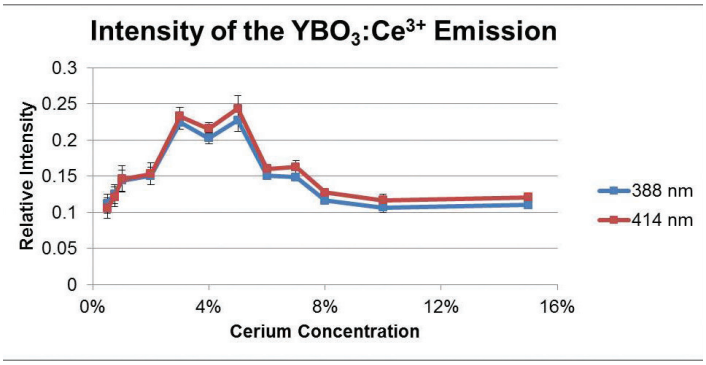


Figure 1. Intensity of $YBO_3:Ce^{3+}$ emission as a function of cerium concentration at both peaks of the emission. The intensity increases with cerium concentration up to 5%. The intensity is at its maximum at 5%, and then decreases as the cerium concentration further increases. Error bars show the standard deviation for each data point.

Emission Lifetime.

The lifetime measurements of the samples show a similar form to that of the intensity measurements with a peak at 1% Ce (Figure 2). However, the lifetime stays fairly constant up to 4%, but sharply declines and stays low as the concentration is further increased. These data suggest the optimal dopant concentration of $YBO_3:Ce^{3+}$ is 1%, based on the peak value. This result contradicts the collected intensity measurements, which peak at 5%. The 5% doped sample had a significantly lower lifetime than that of the peak at 1%. However, for the lifetime measurements, 2%, 3%, and 4%, are in the same range as the peak of 1% and would be viable options. This correlates nicely with the intensity data showing that 3% and 4% are close to the intensity of the peak at 5%. Any of the other concentrations tested either have comparatively low emission intensities or lifetimes.

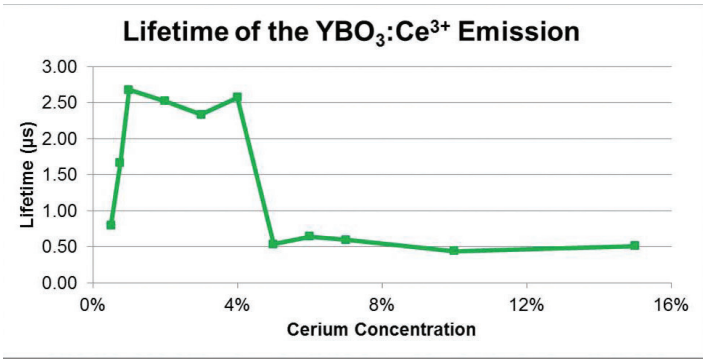


Figure 2: The lifetime of the emission as a function of cerium concentration. As the cerium concentration increases, the lifetime increases up to 1%. The lifetime then stays fairly constant up to 4%. After 4%, the lifetime of the emission decreases greatly.

Table 1. Intensity and lifetime measurements. The greatest intensities are at 5%, while the longest lifetime is with a 1% concentration. The 8% lifetime was somehow lost in the analytical process; after running the script a value was not output for the 8% sample. Bolded values suggest recommended concentrations.

Ce3+ Concentration	388nm Peak Intensity			414nm Peak Intensity			Lifetime µs
	Average	StanDev	Coefficient o	Average	StanDev	Coefficient o	
0.75%	0.112	0.013	11.949	0.106	0.014	13.119	0.798
0.50%	0.125	0.013	10.55	0.121	0.014	11.21	1.661
1%	0.144	0.015	10.203	0.146	0.018	12.521	2.679
2%	0.15	0.012	7.762	0.153	0.015	9.934	2.523
3%	0.224	0.01	4.423	0.233	0.013	5.539	2.336
4%	0.202	0.007	3.596	0.216	0.009	4.039	2.57
5%	0.227	0.015	6.605	0.244	0.018	7.481	0.538
6%	0.15	0.005	3.292	0.16	0.007	4.271	0.645
7%	0.149	0.006	3.912	0.163	0.009	5.353	0.599
8%	0.116	0.001	1.116	0.127	0.002	1.936	~
10%	0.107	0.006	5.821	0.117	0.008	7.04	0.44
15%	0.11	0.003	3.124	0.121	0.006	4.751	0.512

DISCUSSION.

The optimal concentration for intensity of the emission was 5%. At this doping level, we also found an increased sensitivity to the concentration in the lifetime measurements. Because a range of doping concentrations will work equally well below 5% and the lifetime increases dramatically with a decrease in doping, we suggest that the optimal concentration for radiation detection is below 5%. Concentrations of 3% and 4% had similar intensities to the 5% doped sample though, and would work well for the application. The 2%, 3%, and 4% concentrations had similar lifetimes to the lifetime of the 1% doped sample, so these would be feasible for use when accounting for the lifetime of the material. Based on both the intensity and lifetime measurements, it is apparent that the optimal concentration to use is between 3% and 4%, as both the lifetime and the intensity at both of these concentrations is close to that of the optimal concentration for each measurement.

These results conflict with published research into this topic due to the double peak in intensity. However, because of the overlap between the excitation and emission, Cerium is known to have both resonant energy transfer and charge quenching. Each mechanism will have a different characteristic quenching, but the results are confounded by the interaction between the mechanisms. Therefore, a double peak is plausible. While this research conflicts with published values for the optimal concentration of cerium in $YBO_3:Ce^{3+}$, the objective of this project was to independently find the optimal concentration, based on a paucity of published research on this topic, none of which take lifetime into account.

One oddity in the results is the omission of the 8% sample from the lifetime of the emission data. The measurement was taken, but was somehow lost in the

analytical process. When run through the script used to normalize the data, no value for 8% was output. A great deal of time was spent trying to find the error, but to no avail. This has a minimal impact on the results however, as it can be safely assumed that the 8% sample has a very short lifetime in accordance with the values around it.

Using the techniques outlined in this study, the optimal concentration of the dopant in a phosphor is not based solely on the lifetime or brightness of emission, but a combination of the two properties. This aids further research into this phosphor as the emission is much easier to detect at the optimal dopant concentration. If the effects of changing other variables of a phosphor are being researched, using the optimal dopant concentration will result in being able to see any changes more easily. This technique can also be applied to other phosphors to obtain the optimal dopant concentration of those and thus obtain all of the outcomes previously discussed, such as ease of further research on the phosphor.

ACKNOWLEDGMENTS. I would like to thank Zach Coppens, Terry Musho, Robert Harl, Sarah Robb, Chris Vanags as well as The School for Science and Math at Vanderbilt and DTRA for funding. The project described was supported by Award Number R25RR024261 from the National Center For Research Resources. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Center For Research Resources or the National Institutes of Health.

SUPPORTING INFORMATION.

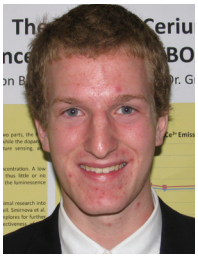
Supplemental Methods.

Figure S1. Experimental setup for intensity measurements

Figure S2. Experimental setup for lifetime measurements

REFERENCES.

1. Allison SW, Gillies GT, *Rev. Sci. Instrum.* 68, 2615 (1997)
2. Alaruri SD, Brewington AJ, *et al.*, *IEEE T Instrum Meas.* 42, 735 (1993).
3. Thakare DS, Omanwar SK, *et al.*, *Opt Mater.* 29, 1731 (2007).
4. R. I. Smirnova, Y. S. Blank, *et al.*, *J Appl Spect.* 15,1169 (1971).
5. J. Chen, H. Guo, *et al.*, *Opt Mater.* 32, 998 (2010).



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