

Temperature-dependent luminescence of Ce³⁺ in gallium-substituted garnets

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The luminescent lifetime of cerium-doped yttrium aluminum garnet has been determined as a function of temperature and as a function of gallium content. We have shown that increasing gallium content decreases the decay lifetime and results in luminescence quenching at lower temperatures. The results are quantitatively explained using a configurational coordinate diagram. © 2009 American Institute of Physics. [doi:10.1063/1.3216583]

Thermographic phosphors (TGP) are ceramic materials that have temperature-dependent luminescence and are useful as noncontact temperature sensors. These materials consist of an oxide matrix with a transition metal or rare-earth (RE) dopant.¹ One of the most well-studied phosphors is cerium-doped yttrium aluminum garnet (YAG:Ce). The luminescence of YAG:Ce is temperature-dependent over the range 77–300 °C.² In recent years, researchers have replaced aluminum atoms with trivalent gallium ions (YGG) and studied the how the changes in the lattice structure alter the luminescent properties.³ The emission wavelength blue-shifts as a result of the introduction of gallium into the garnet structure.^{4,5} Some luminescent properties were studied as a function of temperature, however, these studies were conducted at relatively low temperatures (0–300 K).⁶ In order to study the effect of gallium on luminescence quenching in garnets, we have studied the luminescent lifetime of trivalent cerium in several garnet phosphors over a temperature range of 25–125 °C.

Samples were prepared via a simple combustion synthesis method and had the formula $(Y_{2.97}Ce_{0.03})_3(Al_{1-x}Ga_x)_5O_{12}$, where $x=0, 0.25, 0.50,$ and 0.75 . The fuel was urea and the fuel-to-oxide ratio was stoichiometric. All samples were calcined in air for 5 h at 1000 °C.

Room temperature photoluminescence measurements were taken using a 150 W xenon lamp excitation source, a spectrometer, and a photomultiplier tube. A sample emission spectra is shown in Fig. 1. Electrons are excited to the d_2 excited state of the $5d$ levels (see Fig. 3). The splitting of the d_2 and d_1 states in the $5d$ levels is directly related to the bonds from the cerium ion to the surrounding oxygen atoms. The cerium ion in the garnet structure is surrounded by eight oxygens which form a cubelike structure.³ In YAG, the “cube” is highly compressed into a tetragonal distortion. This distortion increases the splitting between the d_2 and d_1 excited states. Emission occurs from the lowest crystal field component of the $5d$ configuration. Since the splitting increases, the lowest component of the $5d$ configuration is now closer in energy to the ground state configuration. The result

is that cerium-doped YAG crystals have long emission wavelengths. In contrast, the luminescent ion in YGG is surrounded by oxygens, which are more cubic in structure. This decompression of the cubic structure results in a smaller splitting of the d_2 and d_1 states of the $5d$ levels. Likewise, the energy gap between the lowest excited state and ground states is much higher compared to YAG. Thus, increasing gallium content in YAG decreases the emission wavelength (see Fig. 3).

The excitation source for the temperature-dependent luminescence experiments was a nitrogen laser with $\lambda_{ex}=337$ nm and an excitation band width of 0.1 nm. The pulse width was 4 ns at a characteristic energy of 300 μ J. The excitation pulse was conveyed via a 1 mm fiber to a 50:50 splitter. This same fiber collected and transmitted the emitted signal back through the splitter to a photomultiplier tube which served as the detector. Each phosphor sample was placed in the bottom of a plastic capsule, which covered the excitation and detector fiber. The capsule/fiber was placed in an oil bath and slowly heated at a rate of 1 °C/min. A k -type bare wire thermocouple, which was placed near the capsule, monitored the temperature of the phosphor. Bandpass filters centered at 540 nm were used to collect the emitted signal. A waveform processing oscilloscope with 350 Hz bandwidth displayed, digitized, and stored the data.

Figure 2 shows the room-temperature decay time with respect to the amount of gallium and the decay lifetime as a function of temperature. The main observations from these data are (1) increasing gallium content decreases the luminescent lifetime and (2) high concentrations (>50%) of gal-

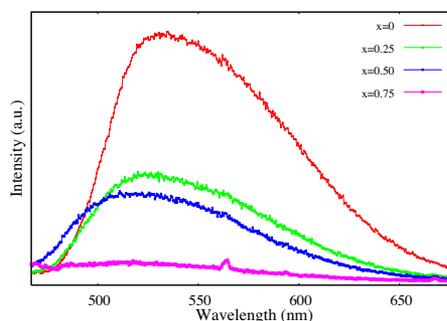


FIG. 1. (Color online) Emission spectra of $Y_{2.97}Ce_{0.03}(Al_{1-x}Ga_x)_5O_{12}$ for $x=0, 0.25, 0.50, 0.75$. $\lambda_{ex}=460$ nm.

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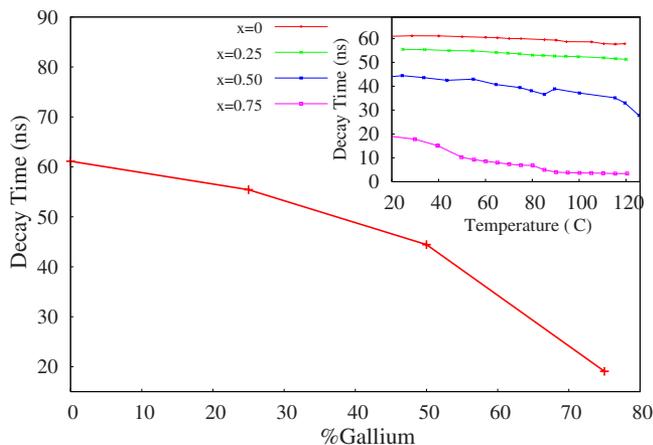


FIG. 2. (Color online) Luminescent lifetime (at 20 °C) as a function of gallium concentration and as a function of temperature (inset). λ_{ex} = 337 nm, λ_{em} = 540 nm.

limum lower the temperature range over which the lifetime is temperature dependent.

These observations can be explained using the using the configurational coordinate diagrams shown in Fig. 3. We will first discuss the luminescent process of YAG Fig. 3(a). Upon excitation, electrons are promoted to the d_2 state of the $5d$ orbitals. The energy of the electron is then transferred nonradiatively to the d_1 state via vibrational energy levels. Radiative emission then occurs from the lowest vibrational level of the d_2 state to the ground state. As the temperature increases, energy can be lost via a nonradiative transfer to a crossover between the d_1 and ground state via the parabola crossover. However, our results and the results of others indicate that this type of nonradiative energy loss is not favorable until at

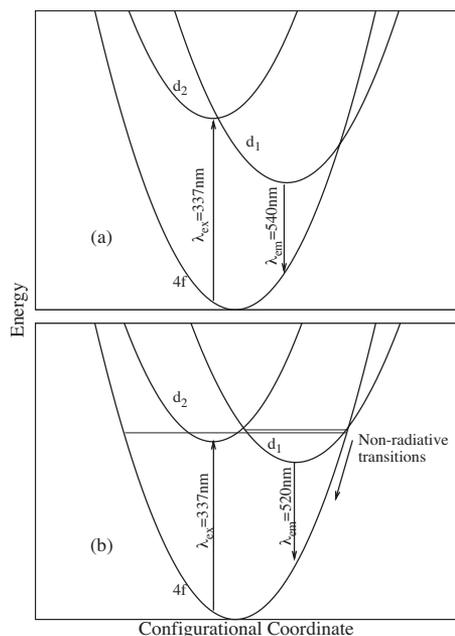


FIG. 3. Configurational coordinate diagram for (a) YAG:Ce and (b) YGG:Ce. Not drawn to scale.

least 150 °C.^{2,7} (Allison *et al.*² has found that the quenching temperature of nanocrystalline YAG:Ce is approximately 77 °C. However, based on x-ray diffraction data and previously obtained electron microscopy images, our samples are mainly composed of large micron-sized particles.)

In YGG [Fig. 3(b)], electrons are also promoted to the d_2 state. Energy is transferred nonradiatively to the d_1 state and then radiative emission occurs from the d_1 state. However, the splitting of the two lowest levels of the $5d$ levels is much less as compared to YAG. In YAG, the d_2 and d_1 levels are split a distance of 7400 cm^{-1} . In contrast, the splitting of the d_1 and d_2 states in YGG is 4300 cm^{-1} .⁸ Consequently, some energy can be transferred nonradiatively to a high vibrational level of the ground state. As the temperature increases, non-radiative transitions are more likely to occur because of the increasing overlap between the vibrational energy levels of the excited states and ground states. From the data presented in this report, luminescence quenching at lower temperatures does not occur unless the sample has at least 75% Ga^{3+} substitution.

Nonradiative transitions also occur as a result of structural defects within the host lattice. These structural defects serve as energy levels, or “traps,” within the band gap of the luminescent ion. Temperature-dependence measurements of the luminescence of YAG:Ce have shown that energy trapped at defect centers can be released thermally, which leads to competition for radiative emission between activator and defect centers.⁶

In the present work, five cerium-doped garnet phosphors were synthesized via combustion synthesis. Trivalent gallium ions were substituted for Al^{3+} in order to determine how the substitution influenced the luminescent lifetime as a function of temperature. The lifetime was measured as a function of temperature over the range of 25–125 °C. We have shown that increasing the gallium content decreases the room-temperature lifetime and increasing gallium content lowers the temperature range over which the lifetime is temperature dependent. Substituting Ga^{3+} ions into YAG decreases the splitting of the d_2 and d_1 excited states of the $5d$ orbitals. This decrease in splitting results in nonradiative transitions occurring via the crossover between the low vibrational levels of the d_2 state and high vibrational levels of the ground state.

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