

FULL PAPER

Influence of sintering temperature on the persistent luminescence behavior of $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}^{3+}$ ceramic phosphors

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Fabrication conditions, involving the introduction of intrinsic defects such as oxygen vacancies in the material, play a crucial role in the persistent luminescence (PersL) properties. In this study, $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (YAGG): Pr^{3+} ceramic phosphors were synthesized in the air from 1400 to 1600 °C by using a solid-state reaction method. The influence of sintering temperature on luminescence properties and PersL properties was investigated. YAGG: Pr^{3+} prepared via a low sintering temperature (1400 °C) exhibits the relative strongest 5d-4f photoluminescence and PersL in the UV region of Pr^{3+} among the samples. The Thermoluminescence (TL) measurements revealed that the intensity of two strong TL peaks related to intrinsic trap centers increases with the rise in sintering temperature. A significant reduction in deep traps, associated with the oxygen vacancies in the sample sintered at 1400 °C, can be observed in the normalized TL glow curves. Consequently, the enhancement of UV PersL of Pr^{3+} was observed which may through suppressing the relaxation process from the 5d state to $^1\text{D}_2$ level through the state of intrinsic defects.

Key-words : Ceramic phosphor, Persistent luminescence, Pr^{3+}

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1. Introduction

Persistent luminescence (PersL) is a phenomenon where a phosphor consistently emits light from minutes to days after optical excitation is ceased. The optical excitation is typically from ultraviolet (UV) light or X-ray, while in other cases visible light is also used as an excitation light source.^{1)–6)} The phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} ,⁷⁾ which shows PersL with excellent brightness and lifetime, is one of the most well-known commercially PersL phosphor materials. Since then, a series of PersL phosphors have been developed.^{8)–12)} Despite the rapid commercialization of these excellent materials, the complete details of their PersL characteristics are still unclear. The fabrication condition involving the introduction of intrinsic defect such as oxygen vacancies in the materials also play an important role in the PersL properties.^{13)–15)} $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} phosphors are conventionally fabricated by heating Eu^{3+} in the host under a reducing atmosphere. However, it has been reported that the improvement of PersL properties was observed by preheating in the air.¹³⁾ Therefore, studying the influence of fabrication conditions on the PersL properties is of fundamental interest.

Recently, lots of research has been carried out on the PersL properties of Pr^{3+} doped PersL materials because the 13 multiplets in the Pr^{3+} 4f² configuration and higher 4f¹5d¹ states give various luminescence transitions with multiple colors.^{16)–19)} Pr^{3+} -doped materials give rise to the intense luminescent band in the UV (4f¹5d¹ → $^3\text{H}_4$) and visible ($^3\text{P}_1$ → $^3\text{H}_4$; $^1\text{D}_2$ → $^3\text{H}_4$) region, whose relative luminescence intensities can be regulated in different hosts. We already reported the different PersL colors based on the distinct ratio of three domain transitions of Pr^{3+} in $\text{Lu}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (LuAGG), $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (YAGG) and $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (GAGG). In the YAGG: Pr^{3+} sintered at a vacuum atmosphere, no UV PersL can be observed due to the quenching process of the 5d state via oxygen vacancy state although a pure YAGG: Pr^{3+} intrinsically shows the 5d-4f luminescence. Thus, different sintering conditions may affect the PersL properties in YAGG: Pr^{3+} .

The aim of this work is to investigate the impact of different sintering temperatures in the air on the PersL properties of Pr^{3+} in YAGG. A series of ceramic phosphors sintering in the air from 1400 to 1600 °C were prepared by using a solid-state reaction method. The effect on the 5d-4f transitions of Pr^{3+} was carried out based on the photoluminescence (PL) and PersL measurements. The role of trap centers under different sintering temperatures was also investigated by thermoluminescence (TL) measurements.

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2. Experimental sections

2.1 Sample preparation and characterization

A series of $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}^{3+}$ (0.1 %) ceramic phosphors were synthesized in the air under 1400, 1500, and 1600 °C by using a solid-state reaction method. The chemicals Y_2O_3 (99.99 %), Al_2O_3 (99.99 %), Ga_2O_3 (99.99 %), and Pr_6O_{11} (99.99 %) were used as the starting materials. The powders were mixed by ball milling (Fritsch, Premium Line P-7) with ethanol. The obtained slurry was dried in an oven for 20 h to remove the ethanol and pulverized. The powders were pressed into pellets ($\Phi = 13$ mm) and then sintered at 1400, 1500, and 1600 °C for 12 h in the air. The crystalline phases of ceramic samples were identified as garnet crystals using X-ray diffraction equipment (Ultima IV, Rigaku). All the samples are identified as a single phase of the garnet structure (Fig. S1).

2.2 Optical measurements

Photoluminescence excitation (PLE) spectra and PL spectra of the samples were measured by a spectrophotometer (RF5300, Shimadzu). A 254 nm UV lamp (SLUV-4, As One) was used as the excitation source for TL measurements. Each ceramic sample was set in a thermal stage to control temperatures and firstly heated up to 650 K to empty the trap and cooled down to 80 K. The sample was illuminated by UV light at 80 K for 5 min and kept for 5 min, then heated up to 650 K at a rate of 10 K min⁻¹ after ceasing the light source. The TL signals were recorded by a photomultiplier tube (R11041, Hamamatsu Photonics & Co. Ltd.). The PersL spectra of the samples were measured at room temperature by the CCD spectrometer (QE65Pro, Ocean Optics). The PersL decay curves of the samples were obtained at room temperature with the same photomultiplier tube as in the TL measurements.

3. Results and discussion

The PLE spectra of $\text{YAGG}:\text{Pr}^{3+}$ (1400–1600) were measured by monitoring $4f^15d^1 \rightarrow {}^3\text{H}_4$ emission at 310 nm (a) and monitoring ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ emission at 608 nm (b) as shown in Fig. 1. Two broad bands located in the UV spectral region with maximum peaks at 239 and 280 nm correspond to the transition from the ${}^3\text{H}_4$ ground state to the $4f^15d^1$ level of Pr^{3+} [Fig. 1(a)]. These PLE spectra show the sintering temperature dependence of excitation intensity of $4f^15d^1 \leftarrow {}^3\text{H}_4$ transitions, which is relatively weak in the 1400 sample. It is probably attributed to the low concentration ratio of the $\text{Pr}^{3+}/\text{Pr}^{4+}$ since the higher sintering temperatures might promote the reduction of Pr^{4+} to Pr^{3+} . The PLE spectra monitoring the luminescence from the ${}^1\text{D}_2$ level [Fig. 1(b)] show intense $4f^15d^1 \leftarrow {}^3\text{H}_4$ transitions and several weak narrow excitation peaks located in the spectral range of 400–500 and 560–630 nm, which are assigned to the ${}^3\text{P}_J \leftarrow {}^3\text{H}_4$, ${}^1\text{D}_2 \leftarrow {}^3\text{H}_4$ transitions, respectively. This observation indicates several relaxation processes from the $4f^15d^1$ and ${}^3\text{P}_J$ levels to the ${}^1\text{D}_2$ level.

Figure 2 exhibits the PL spectra (normalized ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transition at 608 nm) of the $\text{YAGG}:\text{Pr}^{3+}$ samples under

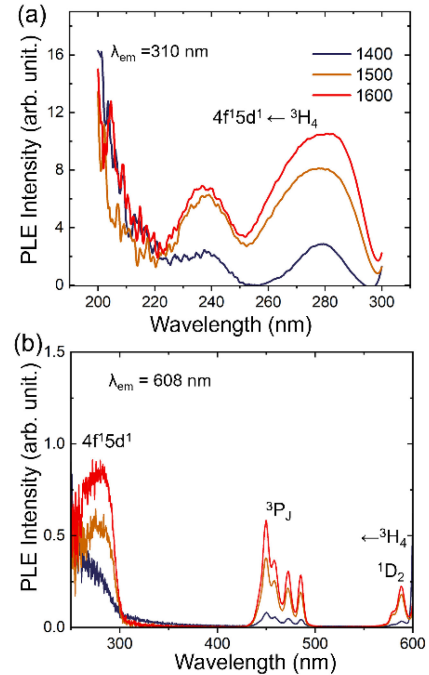


Fig. 1. PLE spectra monitoring different wavelength @310 nm ($4f^15d^1 \rightarrow {}^3\text{H}_4$ transition) (a) and @608 nm (${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transition) (b) of $\text{YAGG}:\text{Pr}^{3+}$ ceramic phosphors under different sintering temperatures (1400, 1500, and 1600 °C).

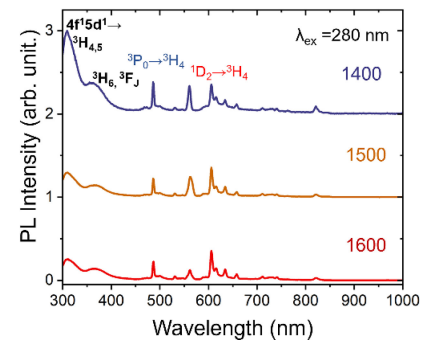


Fig. 2. Comparison of PL spectra of $\text{YAGG}:\text{Pr}^{3+}$ samples (normalized at 608 nm).

280 nm excitation. Two strong and broad emission bands distributed in the UV spectral region are assigned to the parity allowed $4f^15d^1 \rightarrow {}^3\text{H}_J$, ${}^3\text{F}_J$ transitions of Pr^{3+} ion. Several relatively 4f-4f transition emission peaks are displayed in the visible region. Dominant 4f-4f transition peaks of Pr^{3+} such as 487 and 608 nm are attributed to ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ and ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ transitions. It is noted that the 1400 sample exhibits relatively strongest luminescence intensity of 5d-4f transitions in the UV region when compared to other samples. According to the reported results, under the 280 nm excitation, ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ emission is originated from the 5d states by non-radiative process via intrinsic defect state in $\text{YAGG}:\text{Pr}^{3+}$.¹²⁾ Therefore, the UV luminescence enhancement in the 1400 sample may result from the low concentration of intrinsic defects such as oxygen vacancies at a low sintering temperature.

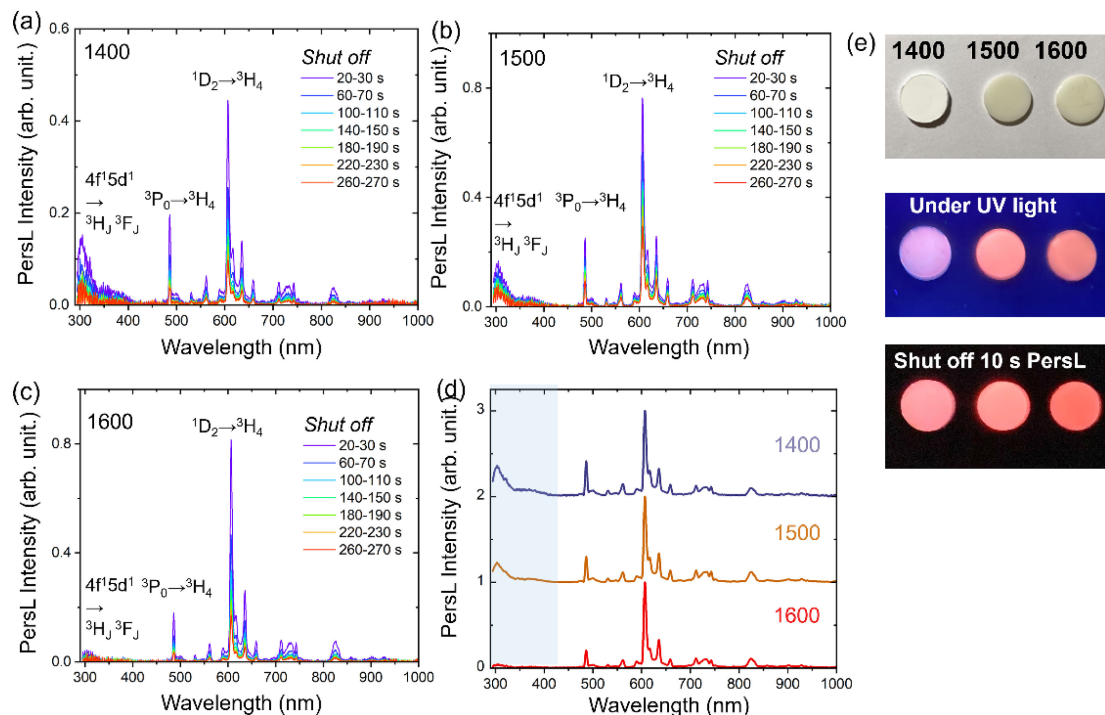


Fig. 3. PersL spectra of $\text{YAGG}:\text{Pr}^{3+}$ ceramic phosphors sintered at 1400 °C (a), 1500 °C (b), 1600 °C (c) after 5 min UV charging. (d) Normalized PersL spectra at 20 s after ceasing the excitation light. (e) Photographs of the as-made three ceramic samples, under UV light, and 10 s after 5 min UV charging.

After ceasing the UV excitation, the corresponding PersL spectra of the three $\text{YAGG}:\text{Pr}^{3+}$ ceramic phosphors at room temperature were recorded as shown in **Figs. 3(a)–3(c)**. Strong PersL of Pr^{3+} at 608 nm attributed to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition can be observed in all the samples. It is noted that the relative intensity of PersL in the UV region attributed to Pr^{3+} 5d-4f transitions displays an increasing tendency with the decline of sintering temperature. The 1400 sample shows the strongest relative 5d-4f PersL among the three samples as shown in the comparison of PersL spectra normalized at 608 nm 10 s after UV excitation for 5 min [**Fig. 3(d)**]. However, almost no UV PersL can be observed in the 1600 sample. We investigated the similar results of no UV PersL in $\text{YAGG}:\text{Pr}^{3+}$ transparent ceramic sintering under the vacuum atmosphere.¹²⁾ Similar to the results of PL spectra, the enhancement of UV PersL of the sample sintered at low temperatures is due to the low concentration of oxygen vacancies. **Figure 3(e)** shows the photographs of the as-made three ceramic samples (upper), under UV illumination (middle), and after ceasing the UV illumination (lower). Under UV illumination, the 1500 and 1600 samples appear distinctly orange-red compared with that of the 1400 sample. These color observations accord with the spectra displayed in **Fig. 2**. Besides, the orange-red PersL color can be seen in all three samples.

The TL glow curves in **Fig. 4** exhibit two intense peaks located at around 385 and 525 K in the three samples. The very similar TL glow curve with two peaks in the $\text{YAGG}:\text{Pr}^{3+}$ samples, whether sintered under a vacuum atmosphere or in the air, suggests the presence of similar

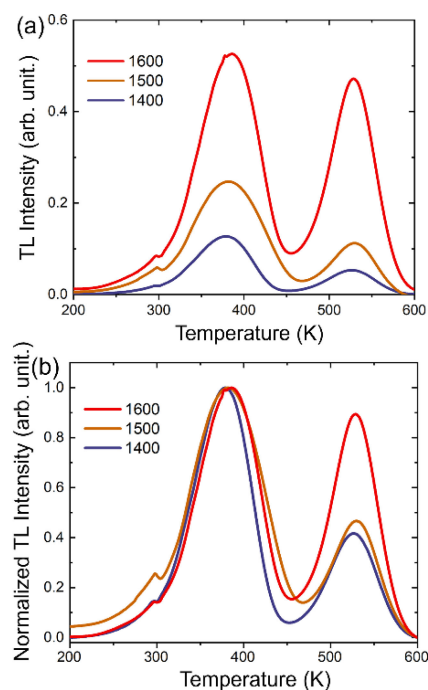


Fig. 4. TL glow curves of $\text{YAGG}:\text{Pr}^{3+}$ (1400 °C, 1500 °C, 1600 °C) ceramic phosphors with a heating rate of 10 K min^{-1} after 5 min UV charging at 80 K.

types of traps in the samples.¹²⁾ The origin of these two peaks is related to oxygen vacancies which were previously investigated by electron spin resonance measurement.¹²⁾ In this study, as the sintering temperature

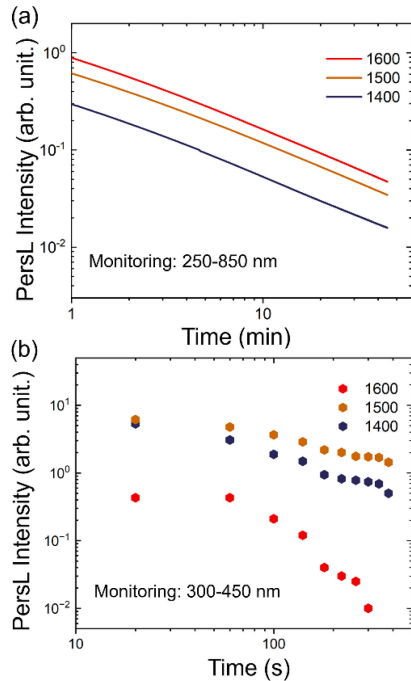


Fig. 5. PersL decay curves of YAGG:Pr³⁺ (1400 °C, 1500 °C, 1600 °C) ceramic phosphors after 5 min UV charging at room temperature monitoring 250–850 nm (a) and 300–450 nm (b).

decreases, the intensity of both two TL glow peaks decreases. This result indicates a reduction in the amount of oxygen vacancies at lower sintering temperatures. Additionally, the normalized TL glow curves demonstrate a significant drop in the relative intensity of the deep trap significantly drops at lower sintering temperatures, suggesting that the lower sintering temperature preferentially compensates for the deep trap. The trap depth can be estimated by the well-known first-order kinetics presented by Randall and Wilkins:^{20),21)}

$$\frac{\beta \varepsilon}{kT_m^2} = s \times \exp\left(-\frac{\varepsilon}{kT_m}\right) \quad (1)$$

where β is the heating rate (K min⁻¹), k is the Boltzmann constant (eV K⁻¹), ε is the trap depth, s is the frequency factor (s⁻¹) and T_m is the TL glow curve peak temperature (K). The frequency factor of YAGG:Pr³⁺ samples can be assumed to be 1.00×10^{13} s⁻¹ according to the reported result since the frequency factor depends on the host material other than the dopants.²²⁾ Then the trap depth values of two TL peaks can be estimated from the TL glow curves at 10 K min⁻¹ heating rate, which are 1.14 and 1.54 eV.

Figure 5(a) displays the PersL decay curves of a series of YAGG:Pr³⁺ ceramic phosphors sintered at different temperatures, monitored from 250 to 850 nm after 5 min UV charging. In the UV and visible region of the Pr³⁺ PersL, the 1600 sample exhibits the highest initial PersL intensity among the three samples. Besides, a similar slope of PersL decay was observed in all three samples. This is because the PersL decay for a short duration can be mainly caused by the shallow trap, which is almost identical

among the three samples based on the TL measurements. However, the UV PersL decay shows a distinct behavior as depicted in Fig. 5(b). The higher initial intensity of UV PersL as well as the slower detrapping rate in the samples at lower sintering temperatures further demonstrate that a low concentration of intrinsic defects of oxygen vacancies could prolong the duration time and initial intensity of UV PersL of Pr³⁺ ions.

4. Conclusions

YAGG:Pr³⁺ ceramic phosphors were synthesized in the air at various sintering temperatures via a solid-state reaction method. The influence of sintering temperature on luminescence properties and PersL properties was investigated through a series of PL, PersL as well TL measurements. The enhancement of Pr³⁺ 5d-4f PL and PersL at low sintering temperatures was confirmed in the PL spectra, PersL spectra, and PersL decay curves. The improved 5d-4f PersL intensity is primarily attributed to the reduction of intrinsic defects such as oxygen vacancies at low sintering temperatures. As indicated by the results of TL glow curves and UV PersL decay curves, the decrease in oxygen vacancies significantly enhances the UV PersL of Pr³⁺ in the samples sintered at low temperatures. This research provides insight into the effect of intrinsic defects introduced by different sintering temperatures on the PL and PersL of YAGG:Pr³⁺. We hope it would be helpful in understanding the influence factor of the PersL and developing novel PersL phosphors of interest for potential applications.

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