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7 **Luminescent thermal history sensing potential in Pr³⁺-activated YAG**
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14 **Abstract** – In this study, it was demonstrated that Pr³⁺-doped YAG powder can record thermal history in the temperature
15 range of template provided by 1100–1600°C. Upon heating, the material undergoes irreversible structural phase
16 transformations (YAM → YAP → single-phase YAG) induced by 2 h of thermal annealing, leading to permanent
17 changes in both the emission intensity and the excited-state lifetime of Pr³⁺ ion. Temperature can be determined using
18 two approaches: by analyzing the intensity ratio of the ³P₀→³H₄ and ¹D₂→³H₄ emission bands, which increases linearly
19 over 1300–1600°C with a sensitivity of 0.001°C⁻¹, and by measuring the luminescence decay time of the ¹D₂→³H₄
20 transition, which decreases linearly over 1100–1600°C with a sensitivity of 0.38 μs·°C⁻¹. The combination of both
21 methods enables durable and quantitative tracking of the material's thermal history, confirming the suitability of
22 YAG:Pr³⁺ powders for high-temperature diagnostics, thermal mapping, and monitoring of industrial processes.

23 **Keywords:** YAG:Pr³⁺, thermal history sensor, luminescence, optical thermometry.

24 **1. Introduction**

25 Temperature is a key thermodynamic parameter in industrial and research applications [1]. At high temperatures, conventional
26 measurement techniques such as thermocouples, resistance sensors, or pyrometers suffer from limitations related to physical
27 contact and restricted material durability [2–4]. Moreover, rare-earth-doped optical fibers are typically unstable above ~1100 °C,
28 limiting their use under extreme conditions [5]. Here, luminescence-based techniques offer a viable alternative. These methods
29 base on the emission of RE³⁺ ions embedded in crystalline hosts such as YAG, which undergo predictable and irreversible
30 structural transformations after 2 h of thermal annealing. These transformations permanently modify the luminescence properties,
31 enabling the material to function as a fluorescent thermal history sensor [6]. Pr³⁺ ions are particularly attractive activators due to
32 their specific energy structure, enabling a broad excitation range and intense visible emission [7,8].

33 In the Y₂O₃–Al₂O₃ system, increasing temperature induces a sequence of phase transitions—from YAM to YAP and finally to
34 single-phase YAG above ~1600 °C [9]. Each phase provides a distinct local crystal field for Pr³⁺ ions, modifying electronic
35 levels, phonon interactions, and thus luminescence properties [10]. Luminescence intensity [11] and lifetime [12] are strongly
36 determined by the local crystal structure, which evolves irreversibly depending on both the temperature and duration of thermal
37 exposure. Therefore, these changes can be exploited to construct a fluorescent thermal history sensor. Crucially, these changes
38 originate from irreversible phase transitions, enabling permanent recording of past thermal exposure and forming the basis of
39 thermal history sensors (THS), which allow reconstruction of the maximum temperature experienced by a material [10,13].
40 Compared to temperature-indicating paints, phosphor powders offer superior chemical stability, quantitative readout, and
41 applicability to complex geometries [13].

42 In the present work, YAG:1%Pr powder was investigated as a potential THS material. The analysis comprised two detection
43 approaches based on the fluorescence intensity ratio (FIR) as well as an analysis of luminescence decay times. The fluorescence
44 intensity ratio (FIR) can be defined either as a comparison of the same emission peak measured at different temperatures [14,15]
45 or, more commonly in optical thermometry, as the ratio of two distinct emission peaks measured at the same temperature. The
46 latter, self-referencing method, provides higher accuracy and greater robustness against fluctuations in excitation power, optical
47 losses, and environmental conditions [11], and therefore constitutes the primary focus of the present study. In the second
48 detection approach, the luminescence decay times of the ¹D₂ → ³H₄ transition were analyzed. This transition is characterized by
49 a significantly longer lifetime and a stronger temperature dependence than the ³P₀ → ³H₄ transition, which makes lifetime-based
50 analysis a sensitive complementary tool for determining the maximum temperature reached during thermal exposure.

51 2. Materials and Methods

52 The samples of yttrium-aluminum garnet doped with Pr³⁺ ions (general formula Y_{2.97}Pr_{0.03}Al₅O₁₂) were synthesized using a solid-
53 state reaction assisted by high-energy milling, using high-purity commercial powders of Al₂O₃ (Krahn Ceramics, >99.99%),
54 Y₂O₃ (NYC YT3WP, 99.9%) and Pr₆O₁₁ (Thermo Scientific Chemicals, 99.996%). Stoichiometric amounts of the starting
55 materials were mixed and milled with anhydrous ethanol (Chempur, 99.8%) and tetraethyl orthosilicate (Sigma-Aldrich), added
56 at a concentration of 4.66 μL per gram of total mass. Planetary milling was carried out in a Fritsch Pulverisette 7 Premium Line
57 system using 5 mm Si₃N₄ balls. The milling process consisted of ten cycles of 10 min at 300 rpm, each followed by a 10 min
58 cooling break. An 80 mL silicon nitride jar and 250 milling balls were used. The slurry was dried on a hot plate at 80 °C for 24
59 h to remove ethanol. The powder was then subjected to two stages of thermal treatment in air muffle furnaces. In the first stage,
60 the powder was heated to 600 °C at 5 °C/min (30 min dwell), then to 900 °C at 7 °C/min (30 min dwell). In the second stage, it
61 was heated to 600 °C at 10 °C/min (15 min dwell), then to the target temperature of 1100–1600 °C at 10 °C/min (120 min dwell),
62 followed by controlled cooling to 400 °C at 10 °C/min.

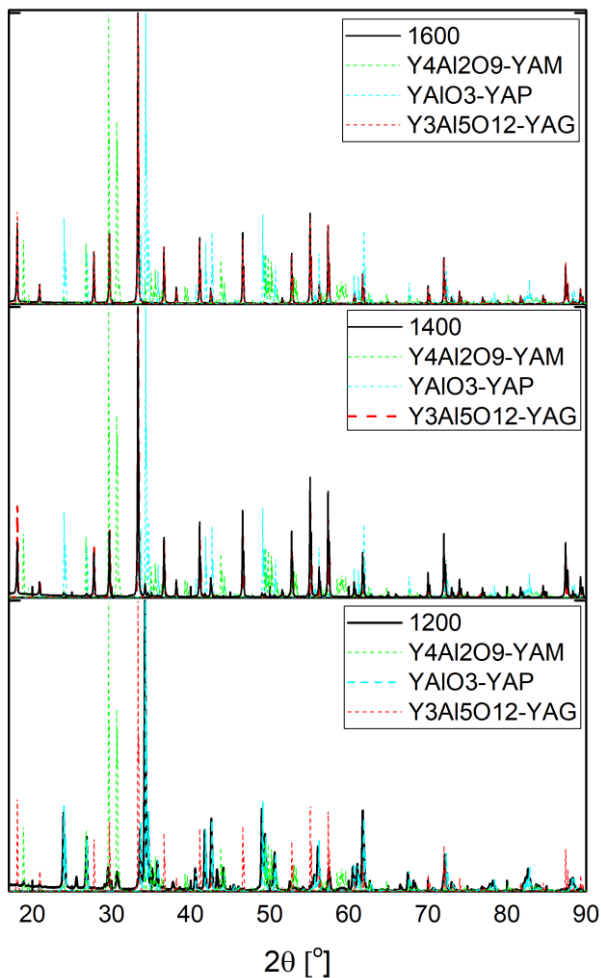
63 After annealing, the obtained powders were manually ground in an alumina mortar to obtain a homogeneous powder fraction
64 suitable for subsequent characterization. The X-ray diffraction patterns were collected in the 2θ range of 5–100° with a step size
65 of 0.01° and a scanning rate of 2.0156° per minute. Cu Kα₁ radiation (λ = 1.5406 Å) with a nickel filter was used. The quantitative
66 phase composition and lattice parameters were evaluated by Rietveld refinement.

67 Emission spectra and excited-state lifetimes were measured at room temperature using an Edinburgh Instruments FS5
68 spectrometer with a 150 W xenon lamp, Czerny–Turner monochromators, optical system optimized for powder measurements,
69 and a temperature-stabilized single-photon-counting PMT (Hamamatsu R928). Spectra were corrected for instrumental response
70 using FLUORACLE. Lifetime measurements were performed in time-resolved mode, and decay curves were fitted using
71 dedicated exponential-fit routines in FLUORACLE to obtain Pr³⁺ emission lifetimes.

72 3. Results and discussion

73 3.1. Structural characterization

74 YAG:1%Pr³⁺ samples were synthesized and thermally treated at temperatures ranging from 1100 to 1600 °C for 2 h.
75 Subsequently, X-ray diffraction (XRD) measurements were performed to analyse the crystalline structure formed at each
76 annealing temperature. The XRD pattern of the sample annealed at 1600 °C, 1400 °C, 1200 °C is presented in Fig. 1.



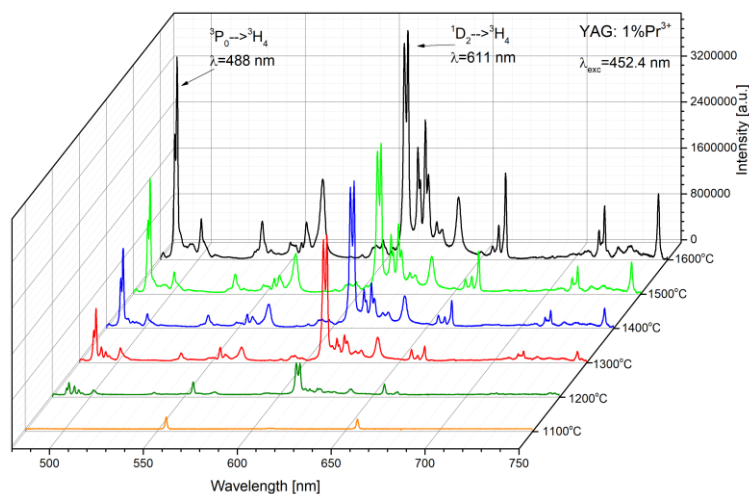
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78 **Fig. 1** . X-ray diffraction pattern of YAG:1%Pr³⁺ annealed at 1200 °C, 1400 °C, 1600 °C, for 2 h, with overlaid reference lines
79 of the best-matching phase standards from crystallographic databases.

80 Phase identification analysis indicates that the sample annealed at 1200 °C for 2 h is multiphase, with a predominance of the
81 intermediate YAP crystalline phase (YAP = 71.4 wt.%, YAM = 6.8 wt.%, YAG = 1.79 wt.%, Al₂O₃ = 19.7 wt.%, Y₂O₃ = 0.33
82 wt.%). With increasing annealing temperature, the content of the target YAG crystalline phase increases. At an annealing
83 temperature of 1400 °C, the YAG phase becomes dominant (YAG = 92.1 wt.%, YAP = 5.01 wt.%, Al₂O₃ = 2.9 wt.%). Upon
84 further increasing the annealing temperature to 1600 °C, a nearly single-phase YAG sample is obtained (YAG = 99.1 wt.%, YAP
85 = 0.3 wt.%, YAM = 0.6 wt.%).

86 3.2. Emission spectra

87 The measured emission spectra of YAG:1%Pr³⁺ powders are shown in Fig. 2.

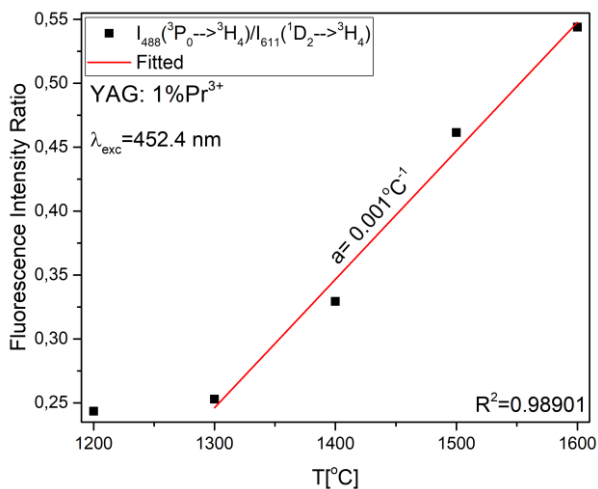


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89 **Fig. 2** Emission spectra of YAG:1% Pr³⁺ samples annealed to different temperatures.

90 As can be seen, the intensity of the emission lines varies with the temperature at which the crystalline phases were formed,
 91 showing an overall increase in peak intensities with increasing formation temperature. The intensities of the two strongest peaks
 92 exhibit distinct trends with annealing temperature: the 488 nm line increases more markedly, while the 611 nm line shows a
 93 comparatively weaker dependence. After thermal annealing at 1100 °C for 2 h, the luminescence is too weak to reliably determine
 94 the intensities of the 488 nm and 611 nm peaks.

95 Accordingly, the intensity ratio of the ³P₀ → ³H₄ (488 nm) and ¹D₂ → ³H₄ (611 nm) transitions was measured as a function of
 96 annealing temperature (Fig. 3).



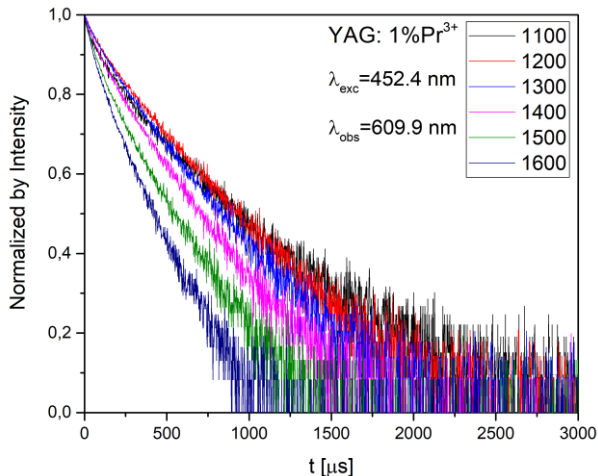
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98 **Fig. 3** Change of peak intensity ratios as a function of temperature in YAG:1%Pr³⁺ powder.

99 A linear increase in the ³P₀ → ³H₄ / ¹D₂ → ³H₄ peak intensity ratio with increasing annealing temperature allowed calibration
 100 from 1300 to 1600 °C. The slope, determined by least-squares fitting, was 0.001 ± 7.49×10⁻⁵ °C⁻¹, defining the powder's
 101 temperature sensitivity.

102 **3.3. Fluorescence decay time**

103 An analysis of the change in excited-state decay times under the influence of temperature in the range of 1100 °C to 1600 °C
 104 was carried out. Figure 4 presents the examination of the ¹D₂→³H₄ transition.

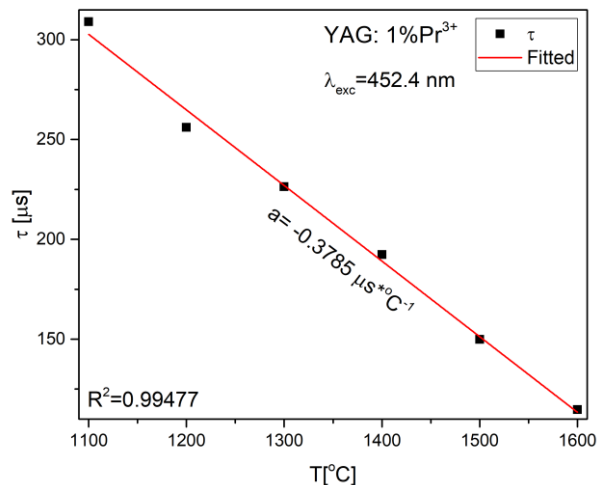


105
 106 **Fig. 4** Luminescence decay curves resulting from the 1D₂→3H₄ transition in YAG:1%Pr powder, recorded after annealing at
 107 different temperatures ranging from 1100 to 1600 °C.

108 Changes in the annealing temperature of the luminescent powder also affect the lifetimes of the excited states. As the annealing
 109 temperature increases, the luminescence decay time becomes shorter. At 1600 °C, a single-phase YAG sample with high
 110 symmetry and a regular crystal structure is obtained. Such a homogeneous environment promotes radiative transitions and
 111 stronger electron–photon interactions, resulting in shorter decay times.

112 At lower annealing temperatures, the powder is multiphase, initially composed mainly of YAM and YAP phases. Upon heating,
 113 these phases irreversibly transform into YAG, creating a more homogeneous environment as the temperature rises. The evolving
 114 crystal structure modifies the crystal field symmetry and the local environment of the active Pr³⁺ ions, thereby altering the
 115 intensity parameters and probabilities of electronic transitions. Consequently, the lifetime of the ¹D₂ level decreases as the
 116 annealing temperature increases.

117 The determined luminescence decay constants as a function of temperature are presented (Fig. 5).



118
 119 **Fig. 5** Measured lifetime of the 1D₂ excited state of Pr³⁺ ions in YAG:1%Pr powder as a function of annealing temperature.

120 A linear decrease in decay time with temperature allowed calibration from 1100 to 1600 °C. Least-squares fitting gave a slope
121 of $-0.3785 \pm 0.0137 \mu\text{s}/^\circ\text{C}$, defining the powder's temperature sensitivity.

123 4. Conclusions

124 In this article, the potential of YAG:1%Pr³⁺ powder as a thermal history sensor is presented. It was demonstrated that the
125 maximum temperature experienced by the investigated material during a 2 h treatment can be determined by analysis of specific
126 emission intensity ratios and luminescence decay times. The results show that by examining the intensity ratio of the ³P₀→³H₄
127 (488 nm) and ¹D₂→³H₄ (611 nm) transitions, temperature detection is possible in the range of 1300–1600 °C with a sensitivity
128 of $0.001 \pm 7.49 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. Furthermore, it was shown that thermal history can also be determined based on the excited-state
129 lifetimes of Pr³⁺ ions. Analysis of the luminescence decay time for the ¹D₂→³H₄ transition ($\lambda_{\text{exc}} = 454.2 \text{ nm}$, $\lambda_{\text{obs}} = 609.9 \text{ nm}$)
130 revealed that temperature detection in the range of 1100–1600 °C is achievable with a sensitivity of $-0.3785 \pm 0.0137 \mu\text{s} \cdot \text{ }^\circ\text{C}^{-1}$.
131 Although the lifetime-based approach enables temperature sensing over a broader temperature range, (1100–1600 °C), the FIR
132 method provides higher sensitivity, as the intensity ratio of the ³P₀→³H₄ (488 nm) and ¹D₂→³H₄ (611 nm) transitions changes
133 more strongly with temperature than the ¹D₂→³H₄ luminescence decay time. It was also observed that as the temperature at which
134 the powder had been held decreases, the material transforms into a multiphase structure (YAM → YAP → YAG). This structural
135 evolution changes the symmetry of the local environment of Pr³⁺ ions, resulting in reduced luminescence intensity and prolonged
136 excited-state lifetimes. These correlations confirm that YAG:1%Pr³⁺ is a promising material for luminescence-based recording
137 and readout of thermal history in high-temperature processes.

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141 Conflicts of interest

142 The authors declare that they have no competing interests to report.

143 Data availability statement

144 Data will be available after request

145 Author contribution statement

146 Conceptualization, O. Bogucki, M. Kaczkan and A. Kozłowska.; Methodology, O. Bogucki.; Validation, O. Bogucki., M. Kaczkan.
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