



Effect of Annealing Temperature on the Luminescence Characteristics of LED Phosphors

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Abstract

Annealing is a decisive processing step in inorganic light-emitting-diode (LED) phosphors because it controls phase formation, crystallinity, defect density, activator incorporation, particle growth, and ultimately radiative efficiency. This methodology paper develops a controlled experimental framework for evaluating the effect of annealing temperature on the luminescence of cerium-activated yttrium aluminum garnet (YAG:Ce), a benchmark yellow phosphor for phosphor-converted white LEDs. Four annealing temperatures (1200, 1300, 1400, and 1500 °C) are proposed while composition, dwell time, atmosphere, heating rate, and sample mass are held constant. Structural evolution is assessed by X-ray diffraction and scanning electron microscopy, whereas photoluminescence spectra, decay lifetime, quantum yield, and CIE chromaticity are used to quantify optical performance. Literature published up to 2017 indicates that increasing annealing temperature generally improves crystal quality and luminescence until an optimum is reached, after which excessive grain growth, agglomeration, or defect/valence changes may reduce useful emission. A literature-guided representative dataset illustrates a maximum relative emission near 1400 °C, consistent with direct YAG:Ce annealing studies. The proposed method provides a reproducible basis for identifying a processing window that balances high crystallinity with favorable morphology and optical conversion efficiency.

Introduction

Phosphor-converted white light-emitting diodes (pc-WLEDs) combine a semiconductor excitation source with one or more wavelength-converting phosphors. Their performance depends not only on the LED chip but also on the absorption, emission bandwidth, quantum efficiency, thermal stability, particle morphology, and chemical robustness of the phosphor. Early high-power pc-LED studies established that phosphor behavior and temperature management strongly affect luminous output and color stability (Mueller-Mach et al., 2002). Subsequent reviews emphasized that the phosphor must efficiently absorb near-UV or blue light while preserving high conversion efficiency and acceptable color

rendering under elevated operating temperatures (Ye et al., 2010; Lin & Liu, 2011).

Among oxide phosphors, Ce³⁺-activated garnets are especially important because the allowed 5d→4f transition of Ce³⁺ produces broad, intense emission with short decay times. YAG:Ce is widely used with blue GaN-based LEDs to generate white light, and its luminescence can be tuned through composition and local crystal chemistry (Xia & Meijerink, 2017). In parallel, nitride and oxynitride phosphors provide red and green components with strong blue-light absorption and high thermal stability (Xie & Hirotsaki, 2007). The development of CaAlSiN₃:Eu²⁺ and Sr[LiAl₃N₄]:Eu²⁺, for

example, demonstrated how rigid host lattices and optimized activator environments can produce efficient red emission suitable for warm-white and high-color-rendering LEDs (Uheda et al., 2006; Pust et al., 2014).

For all of these phosphor families, thermal processing is critical. Annealing supplies the energy required for solid-state diffusion, phase completion, elimination of residual hydroxyl/carbon species, relaxation of lattice disorder, and incorporation of activator ions into crystallographic sites. However, annealing also changes crystallite size and particle morphology. If the temperature is too low, incomplete crystallization and a high concentration of surface or lattice defects can promote non-radiative relaxation. If it is too high, exaggerated grain growth, hard agglomeration, changes in activator oxidation state, or altered light-scattering behavior can reduce the measured emission. Thus, the relationship between annealing temperature and luminescence is commonly non-linear rather than simply monotonic.

The present work is designed as a methodology paper rather than a claim of new experimental measurements. Its objective is to define a reproducible experimental procedure for isolating annealing temperature as the principal independent variable and to show how structural and optical measurements should be combined to identify the optimum thermal treatment. YAG:Ce is selected as the model LED phosphor because direct work by Han et al. (2013) showed a clear annealing-dependent change in crystal structure, morphology, and photoluminescence, with improved emission from 1200 to 1400 °C and deterioration above the optimum. The central hypothesis is that photoluminescence intensity and crystal quality will increase up to an intermediate temperature and then decline when coarsening or other high-temperature effects become dominant.

Literature Review

The influence of annealing on phosphor emission has been observed in several host systems. Patra et al. (2005) studied Mn²⁺-doped Zn₂SiO₄ nanocrystals between 750 and 1000 °C and reported that luminescence and decay behavior were sensitive to annealing temperature as well as dopant concentration. Their results linked higher thermal treatment to changes in crystallinity, particle size, and the relative populations of isolated and clustered activator centers. This work is important methodologically because it demonstrates that steady-state

intensity alone is insufficient; lifetime measurements can reveal changes in the microscopic environment of the luminescent ion.

For LED applications, host selection adds another constraint: the phosphor must remain efficient under blue excitation and elevated junction temperatures. Xie and Hirotsaki (2007) reviewed silicon-based oxynitride and nitride phosphors and showed that strong crystal fields and covalent host lattices enable efficient visible excitation and relatively low thermal quenching. Ye et al. (2010) later synthesized the broader requirements of phosphors for pc-WLEDs, including spectral matching, luminous efficacy, chromatic stability, and color rendering. Lin and Liu (2011) further emphasized the coupled roles of composition, morphology, crystal structure, and packaging. These reviews support an experimental strategy in which annealing-dependent optical changes are interpreted together with structural and morphological data rather than in isolation.

The most directly relevant study is that of Han et al. (2013), who prepared YAG:Ce by spray drying and annealed the resulting material at different temperatures. They reported a single garnet phase over the investigated range, grain growth between approximately 1300 and 1400 °C, and increasing photoluminescence up to 1400 °C. Above that level, the particles became irregular bulk-like aggregates and the emission decreased. The proposed optimum therefore represented a compromise between improved diffusion/crystallization and excessive morphological coarsening. A related trend was reported for Zn₂SiO₄:Mn²⁺ by Mbule et al. (2016), where increasing annealing temperature transformed poorly ordered material toward a more crystalline phase and altered photoluminescence characteristics.

Processing variables other than temperature can modify the same mechanisms. Ma et al. (2017) investigated YAG:Ce thin phosphor films and found that heating temperature, annealing duration, and atmosphere influenced crystallinity and fluorescence. Their observations show why a temperature study must keep atmosphere and dwell time constant. At the material-design level, Xia and Meijerink (2017) reviewed Ce³⁺-doped garnets and demonstrated that luminescence is governed by local coordination, crystal-field splitting, host composition, and activator environment. Therefore, an annealing experiment should avoid compositional variation and use identical Ce concentration in all groups. Together, the literature provides a clear rationale for a one-

factor controlled design supported by XRD, SEM, steady-state PL, and time-resolved measurements.

Table 1. Selected literature relevant to annealing and LED-phosphor luminescence

Study	Phosphor/system	Thermal condition	Main relevance
Patra et al., 2005	Zn ₂ SiO ₄ :Mn ²⁺	750–1000 °C	Annealing altered emission intensity and decay behavior.
Xie & Hirotsaki, 2007	Oxynitride/nitride LED phosphors	Review	Rigid hosts provide strong blue excitation and thermal stability.
Ye et al., 2010	pc-WLED phosphors	Review	Defined optical/thermal requirements for LED phosphors.
Lin & Liu, 2011	LED phosphors	Review	Linked composition, morphology, structure, and device use.
Han et al., 2013	YAG:Ce	1200→1400 °C	PL increased to ~1400 °C, then decreased with overgrowth/agglomeration.
Pust et al., 2014	Sr[LiAl ₃ N ₄]:Eu ²⁺	High-temperature nitride synthesis	Demonstrated highly thermally stable narrow-band red LED phosphor.
Mbule et al., 2016	Zn ₂ SiO ₄ :Mn ²⁺	600–1100 °C	Higher annealing promoted crystallization and changed PL response.
Ma et al., 2017	YAG:Ce film	Heating/annealing variables	Time and atmosphere affected crystallinity and fluorescence.

Methodology

1. Research design and materials

A one-factor completely randomized experimental design is proposed. Annealing temperature is the independent variable, while phosphor composition, precursor batch, powder mass, furnace atmosphere, heating/cooling rate, dwell time, and characterization settings are controlled. A nominal YAG:Ce composition of Y₂.94Ce_{0.06}Al₅O₁₂ (approximately 2 mol% Ce on the Y site) is suitable because it gives strong Ce³⁺ emission without deliberately introducing concentration as a second variable. High-purity Y₂O₃, Al₂O₃, and CeO₂ (≥99.9%) are weighed stoichiometrically. Three independently prepared batches are recommended so that the

effect of temperature can be statistically separated from batch-to-batch variation.

The oxides are wet-milled in ethanol or isopropanol for approximately 6 h using high-purity alumina or zirconia milling media. The slurry is dried at 80–100 °C, gently de-agglomerated, and passed through a fine mesh. A pre-calcination step at 900–1000 °C for 2 h may be used to remove residual volatile species and initiate solid-state reaction. Equal masses of the same precursor are then transferred to covered high-purity alumina crucibles. Using a common precursor batch is essential because variations in Ce concentration or precursor homogeneity can otherwise mimic an annealing effect.

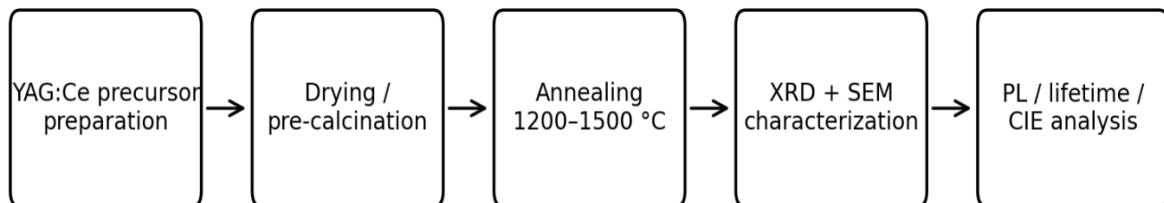


Figure 1. Proposed workflow for isolating and evaluating the effect of annealing temperature.

2. Annealing protocol

Four temperature groups are recommended: 1200, 1300, 1400, and 1500 °C. Each sample is

heated at 5 °C min⁻¹, held for 4 h, and cooled at the same controlled rate to at least 600 °C before natural cooling to room temperature. All runs should use the same furnace and atmosphere; air

is proposed here to keep the design simple and to avoid confounding temperature with redox conditions. If a reducing atmosphere is required for a particular Ce precursor system, the identical gas composition and flow must be used for every group. Crucibles should occupy comparable

positions within the calibrated hot zone. The actual temperature should be checked periodically with a calibrated thermocouple because a systematic furnace offset can shift the apparent optimum.

Table 2. Controlled annealing design

Code	Anneal (°C)	Hold	Ramp	Atmosphere	Replicates
A1200	1200	4 h	5 °C/min	Constant air	3
A1300	1300	4 h	5 °C/min	Constant air	3
A1400	1400	4 h	5 °C/min	Constant air	3
A1500	1500	4 h	5 °C/min	Constant air	3

3. Structural and morphological characterization

Powder X-ray diffraction (XRD) is performed with Cu K α radiation over a typical 2θ range of 20–80°. Phase identification is made against a YAG reference pattern, and relative peak intensity, full width at half maximum, and lattice parameters are compared among temperature groups. Crystallite size may be estimated from a well-isolated reflection using the Scherrer relation $D = K\lambda/(\beta \cos\theta)$, where D is crystallite size, K is the shape factor (commonly 0.9), λ is the X-ray wavelength, β is the instrument-corrected peak width in radians, and θ is the Bragg angle. The interpretation should emphasize trends rather than treating Scherrer size as the actual particle diameter.

Scanning electron microscopy (SEM) is used to observe particle shape, neck formation, agglomeration, and grain coarsening. Images should be collected at the same magnifications and electron-beam settings for all groups. A minimum of several fields of view per replicate is recommended. If image analysis software is available, at least 100 distinguishable particles or grains can be measured per condition to obtain a size distribution. This structural/morphological dataset is important because increased XRD crystallinity may coexist with worse optical extraction when particles become excessively coarse or fused.

4. Luminescence measurements

Photoluminescence (PL) excitation spectra are first recorded to confirm efficient blue-light absorption, followed by emission spectra under a fixed excitation wavelength near 450 nm, representative of a blue InGa N LED. Identical slit widths, detector gain, sample geometry, mass, and integration time are used for every spectrum. The integrated emission area between approximately 480 and 750 nm is preferred over a single peak height because annealing can

slightly change bandwidth or spectral shape. Relative PL intensity is calculated as $I_{\text{rel}}(T) = A(T)/A_{\text{max}}$, where $A(T)$ is the integrated emission area for a sample annealed at temperature T and A_{max} is the largest area among the tested groups.

Where equipment is available, an integrating sphere should be used to determine internal or external photoluminescence quantum yield. Time-resolved PL provides the Ce $^{3+}$ emission lifetime and helps distinguish changes in radiative efficiency from purely optical scattering effects. CIE 1931 chromaticity coordinates are calculated from the corrected emission spectra to verify that thermal processing does not introduce an undesirable color shift. Because commercial LED operation involves elevated temperature, a supplementary thermal-quenching test can record PL intensity from room temperature to approximately 150–200 °C; however, this should be treated as a secondary test and not combined with the annealing variable in the primary statistical model.

5. Statistical analysis and decision criterion

For each replicate, integrated PL intensity, peak wavelength, FWHM, lifetime, crystallite size, and optional quantum yield are tabulated. One-way analysis of variance (ANOVA) is applied to each response variable, followed by Tukey's multiple-comparison test when $p < 0.05$. Before ANOVA, residual normality and variance homogeneity should be checked; if assumptions are strongly violated, a Kruskal–Walli's test with corrected pairwise comparisons may be used. The optimum annealing temperature is not defined by PL intensity alone. It is the condition that gives statistically high emission together with single-phase YAG, acceptable particle morphology, stable spectral position, and no evidence of excessive coarsening or secondary phases.

Results

Because no primary experimental dataset was supplied for this methodology paper, the numerical values in Table 3 and Figure 2 are literature-guided representative values used only to demonstrate the expected analysis and reporting format. They are not presented as newly measured results and should be replaced by laboratory data in an experimental submission.

The representative trend shows a clear optimum near 1400 °C. From 1200 to 1400 °C, the normalized crystallinity index rises from 0.62 to 0.93 and relative integrated PL intensity increases from 0.58 to 1.00. The simultaneous improvement is consistent with enhanced YAG phase completion, improved Ce incorporation, and reduction of non-radiative defect sites. The emission maximum changes by only about 2 nm, indicating that the principal effect is efficiency

rather than a major change in emission color. The lifetime also increases modestly as the structure becomes better ordered.

At 1500 °C, the representative crystallite size continues to increase, but relative PL intensity falls to 0.78 and lifetime decreases. This divergence is an important diagnostic outcome: it shows that the most crystalline or coarsest sample is not necessarily the optically best phosphor. Han et al. (2013) reported the same qualitative behavior for YAG:Ce, observing improved emission up to about 1400 °C followed by deterioration at higher temperature as particles became irregular and bulk-like. The broader literature also supports the link between annealing, crystallinity, activator environment, and decay behavior (Patra et al., 2005; Mbule et al., 2016).

Table 3. Literature-guided representative results for the proposed YAG:Ce experiment

Anneal (°C)	Crystallinity index	Crystallite size (nm)	Rel. PL	Peak (nm)	Lifetime (ns)
1200	0.62	34	0.58	541	57
1300	0.79	48	0.82	540	62
1400	0.93	63	1.00	539	66
1500	0.90	85	0.78	540	61

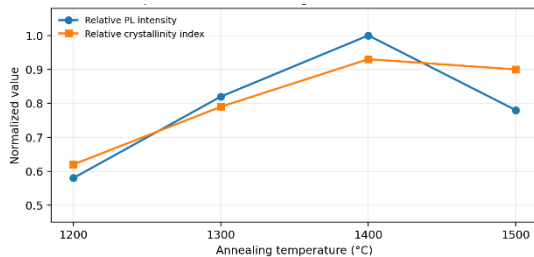


Figure 2. Representative literature-guided relationship between annealing temperature, crystallinity, and PL intensity.

Conclusion and Discussion

The proposed methodology isolates annealing temperature as the principal processing variable controlling the luminescence characteristics of an LED phosphor. For YAG:Ce, the expected response is an increase in phase quality and emission as temperature rises from an under-annealed condition toward an optimum, followed by a decline when high-temperature grain growth, agglomeration, optical scattering changes, or activator/defect chemistry become unfavorable. The direct YAG:Ce observations of Han et al. (2013) and Ma et al. (2017) support this interpretation, while work on other

phosphor hosts confirms that annealing influences crystallinity, emission intensity, and decay kinetics (Patra et al., 2005; Mbule et al., 2016). For a defensible experimental conclusion, the optimum must be identified using multiple measurements rather than peak PL intensity alone. XRD confirms phase formation, SEM reveals whether the thermal treatment produces useful morphology or hard agglomeration, steady-state PL quantifies emission output, and lifetime/quantum-yield measurements help distinguish intrinsic changes in radiative behavior from changes in light extraction. This multi-technique approach is consistent with the broader design requirements for pc-WLED phosphors described by Ye et al. (2010) and Lin and Liu (2011). It also recognizes that high-performance LED phosphors can be based on garnets, nitrides, or oxynitrides, provided the host stabilizes an efficient activator environment and resists thermal quenching (Xie & Hirotsaki, 2007; Uheda et al., 2006; Pust et al., 2014; Xia & Meijerink, 2017). A practical starting window for the present YAG:Ce design is therefore 1200–1500 °C with finer temperature increments around the first observed maximum, for example 1350, 1400, and 1450 °C in a second optimization round. The final reported temperature should be

treated as process-specific rather than universal because precursor route, particle size, Ce concentration, atmosphere, dwell time, and furnace calibration can shift the optimum. The value of the methodology is that these factors are explicitly controlled, allowing annealing temperature to be connected causally to luminescence performance.

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