



Investigation of Thermoluminescence Properties of Rare-Earth Doped Phosphor Materials

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Peer Review Information

Submission: 26 Oct 2017
Revision: 10 Nov 2017
Acceptance: 25 Nov 2017

Keywords

Thermoluminescence, rare-earth doped phosphors, glow curve, trap depth, radiation dosimetry

Abstract

Thermoluminescence (TL) is a defect-mediated luminescence process in which energy stored in an irradiated solid is released as light during controlled heating. Rare-earth ions are particularly useful activators or co-dopants because they introduce luminescent centers and modify the concentration, depth, and stability of charge traps. This methodology paper presents a reproducible experimental framework for investigating the TL behavior of rare-earth doped phosphor materials, with emphasis on europium (Eu), dysprosium (Dy), terbium (Tb), gadolinium (Gd), and samarium (Sm) activated systems. The proposed workflow combines solid-state or solution-assisted synthesis, structural verification by X-ray diffraction (XRD), morphology assessment by electron microscopy, controlled gamma irradiation, TL glow-curve acquisition at fixed heating rates, dose-response and fading tests, and kinetic analysis using peak-shape and computerized glow-curve deconvolution approaches. Literature published up to 2017 shows that rare-earth incorporation can create additional trap levels, shift glow-peak temperature, enhance TL intensity, and improve linearity or reproducibility, although the optimum response is host- and concentration-dependent. The results section therefore reports literature-grounded representative trends rather than claiming new laboratory measurements. The framework is suitable for screening phosphors for radiation dosimetry, persistent luminescence, and defect-physics studies while maintaining clear control of dopant concentration, irradiation dose, and thermal history.

Introduction

Thermoluminescence arises when ionizing radiation or energetic optical excitation creates free electrons and holes in an insulating or wide-band-gap material. A fraction of these carriers becomes localized at defects or impurity-related trap states. When the material is subsequently heated, trapped carriers acquire sufficient thermal energy to escape, migrate, and recombine at luminescent centers, producing a temperature-dependent glow curve. The position and shape of each glow peak are related to trap depth, retrapping probability, and recombination

kinetics; the integrated light output is related to the population of stored charge carriers. Consequently, TL is both a practical dosimetric technique and a sensitive probe of defects in phosphor materials.

Rare-earth ions are attractive dopants because their partially filled 4f shells provide characteristic emission states while their valence flexibility and size mismatch can alter local charge compensation and defect chemistry. In $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, for example, solid-state-prepared phosphors exhibit a broad TL glow

region near 120 °C and long afterglow behavior associated with trap states modified by Dy³⁺ (Mothudi et al., 2012). In sodium sulphate systems, Eu³⁺/Dy³⁺ codoping introduces additional trap sites and changes both structural and luminescent behavior (Vidya & Lakshminarasappa, 2014). Similar evidence across borates, oxides, and silicates indicates that the host lattice and rare-earth species jointly determine trap stability and TL sensitivity.

The need for reliable radiation monitoring motivates continued development of phosphors with high sensitivity, near-linear dose response, low fading, stable glow-peak temperatures, and good reusability. Rare-earth doped materials have shown promising behavior in gamma, neutron, and ion-beam dosimetry. For instance, Y₂O₃-based phosphors codoped with Eu³⁺ or Tb³⁺ show altered trap distributions and enhanced TL intensity (Som et al., 2015), while CaO:Sm³⁺ develops an additional lower-temperature TL peak after gamma irradiation (Prakash & Nagabhushana, 2016). By 2017, Eu³⁺-activated SrGd₂O₄ had also demonstrated linear response over part of the investigated dose range and acceptable reproducibility (Singh et al., 2017).

The objective of this paper is to establish a step-by-step methodology for comparing thermoluminescence properties of rare-earth doped phosphor materials and to define the key measurements required to connect structure, dopant chemistry, glow-curve features, and dosimetric performance. The method is designed so that it can be applied to a selected host series, for example MgB₄O₇:RE or Y₂O₃:Yb,RE, without changing the core analytical logic.

Literature Review

Early and modern TL studies consistently show that rare-earth activators influence both the radiative recombination center and the defect structure of the host. Mothudi et al. (2012) reported monoclinic SrAl₂O₄:Eu²⁺,Dy³⁺ with green Eu²⁺ emission and broad TL curves, linking long persistence to Dy-related trapping. Annalakshmi et al. (2014) investigated rare-earth-doped MgB₄O₇ and correlated TL with electron paramagnetic resonance; radiation-induced borate and oxygen-vacancy-related

centers disappeared on thermal annealing, supporting their role in the TL mechanism. These findings demonstrate why structural and defect characterization should accompany glow-curve measurements.

Rare-earth codoping can either enhance or quench TL depending on defect compensation and concentration. Vidya and Lakshminarasappa (2014) found that codoping Na₂SO₄ with Eu and Dy introduced additional trapping sites, whereas Li addition alone could reduce TL output. Som et al. (2015) found that Eu³⁺ and Tb³⁺ codoping of Yb:Y₂O₃ changed glow-peak intensity and kinetic parameters, with Eu³⁺ producing stronger enhancement in their system. First-principles analysis of CaAl₂O₄:Eu,Nd also showed that rare-earth ions and host vacancies can reshape the electronic trap landscape responsible for persistent luminescence (Qu et al., 2015). Such results justify screening several dopant concentrations instead of relying on a single nominal composition.

The excitation and thermal history are also decisive. Hagemann et al. (2016) showed that trap loading in SrAl₂O₄:Eu²⁺,Dy³⁺ depends strongly on excitation wavelength and loading temperature, indicating a distribution of trap depths rather than one isolated trap. In LiMgPO₄:Tb,B, boron codoping stabilized a multi-peak TL response and produced concentration-dependent quenching (Bajaj et al., 2016). Therefore, irradiation dose, pre-annealing, heating rate, and storage time must be held constant when different compositions are compared.

Studies close to the 2017 cutoff broadened the available host systems. Sahu (2017) calculated TL kinetic parameters for Eu³⁺-doped Sr₂SiO₄ prepared by solid-state reaction. Singh et al. (2017) studied gamma-irradiated SrGd₂O₄:Eu³⁺ and reported two resolved TL peaks with a shoulder, using computerized glow-curve deconvolution to obtain trapping parameters. Together with CaO:Sm³⁺ work (Prakash & Nagabhushana, 2016) and Mg₂B₃O₈:Dy ion-beam studies (Kore et al., 2015), these reports support a comparative methodology based on phase purity, dose response, glow-curve stability, kinetic parameters, fading, and repeatability.

Table 1. Selected literature supporting the methodology (references limited to 2017 and earlier)

Phosphor system	Rare-earth ion(s)	Key TL finding	Source
SrAl ₂ O ₄	Eu ²⁺ , Dy ³⁺	Broad TL near 120 °C; Dy-related traps support persistence	Mothudi et al., 2012

MgB4O7	multiple RE ³⁺	EPR-TL correlation identifies radiation-induced defect centers	Annalakshmi et al., 2014
Y2O3:Yb	Eu ³⁺ , Tb ³⁺	Codoping changes TL intensity, peak structure and kinetic parameters	Som et al., 2015
SrAl2O4	Eu ²⁺ , Dy ³⁺	Trap loading varies with excitation wavelength and temperature	Hagemann et al., 2016
SrGd2O4	Eu ³⁺	Multiple glow peaks; linear dose region and good reusability reported	Singh et al., 2017

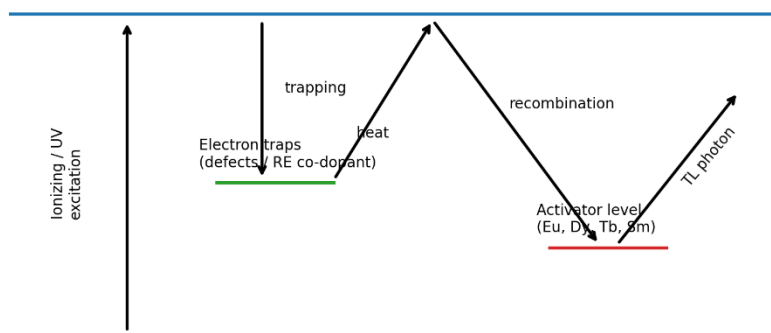


Figure 1. Schematic representation of charge trapping, thermal release, and rare-earth-assisted radiative recombination in a thermoluminescent phosphor. (Original schematic prepared for this paper.)

Methodology

1. Experimental Design and Sample Matrix

A comparative sample series should be prepared using one selected host lattice so that the effect of dopant identity is not confounded by changes in crystal chemistry. A practical design is MgB4O7:RE, where RE = Eu³⁺, Dy³⁺, Tb³⁺, Gd³⁺, and Sm³⁺, together with an undoped control. Begin with a fixed rare-earth concentration of 0.5 mol% for screening, then optimize the two best-performing dopants at 0.1, 0.25, 0.5, 1.0, and 2.0 mol%. Prepare at least three independently synthesized batches per selected composition to quantify reproducibility. The same methodology can also be transferred to oxide or aluminate hosts if the project requires a specific application.

2. Phosphor Synthesis

For a solid-state route, weigh stoichiometric quantities of high-purity MgO and H3BO3 with the required rare-earth oxide precursor. Rare-earth oxides should be converted to a soluble nitrate or thoroughly homogenized with the host precursors to avoid local dopant segregation. Mix and grind the powders for 30-45 min, preheat at approximately 500-600 °C to remove volatile components, regrind, pelletize lightly, and sinter at approximately 850-950 °C for 3-5 h in air. After furnace cooling, grind to a uniform powder and sieve to a controlled particle-size range. The

exact firing temperature should be verified by phase formation rather than assumed, because host-dependent secondary phases can strongly affect TL.

3. Structural and Morphological Characterization

Record powder XRD patterns over a suitable 2theta range using Cu K-alpha radiation. Compare diffraction peaks with standard reference data to confirm the target phase and identify secondary phases. Estimate crystallite size using the Scherrer relation only as an approximate comparative parameter. Use SEM to assess particle morphology and agglomeration; EDS may be used to confirm the presence of the rare-earth element. Where available, photoluminescence emission spectra should be recorded to verify that the rare-earth ion acts as an optical center in the prepared host.

4. Annealing and Irradiation Protocol

Before each irradiation cycle, anneal aliquots under a fixed thermal schedule sufficient to empty previously occupied traps; a preliminary schedule of 350-400 °C for 30-60 min can be tested and then optimized for the selected host. Cool samples in a reproducible dark environment. Irradiate equal masses using a calibrated 60Co gamma source. A screening dose series of 0.1, 0.5, 1, 2, and 5 kGy is suitable for materials that exhibit kGy-range responses in the literature; if low-dose dosimetry is the target, a

second experiment should extend the range downward. Keep dose rate, source-to-sample geometry, container type, and post-irradiation delay constant.

5. Thermoluminescence Measurement

Measure TL with a calibrated TL reader under nitrogen or another reproducible measurement atmosphere if available. Use a constant heating rate, initially 5 °C s⁻¹, from room temperature to approximately 350-400 °C, or to a host-specific upper limit that captures all meaningful glow peaks without decomposition. Record dark/background counts and subtract them from sample curves. For each composition and dose, acquire at least three replicate curves. Report peak temperature (T_m), maximum intensity (I_{max}), integrated TL area, and glow-curve shape. Heating-rate dependence should be tested at 2, 5, and 10 °C s⁻¹ for the best composition because apparent peak position can shift with heating rate.

6. Dose Response, Fading and Reusability

Plot integrated TL output versus absorbed dose and fit linear, supralinear, or saturating regions

as appropriate. Fading should be measured by storing identically irradiated samples in darkness and reading them after 1 h, 24 h, 7 d, and 30 d. Reusability should be tested through at least five anneal-irradiate-read cycles at a fixed dose. A useful candidate should combine high sensitivity with low coefficient of variation, limited fading, stable peak temperature, and a sufficiently wide linear dose range.

7. Kinetic Analysis and Statistics

Analyze isolated peaks by the peak-shape method and overlapping curves by computerized glow-curve deconvolution (CGCD). Determine activation energy E , frequency factor s , and kinetic order b , and report the fitting figure of merit. Compare compositions using mean $\pm$ standard deviation from replicate measurements. One-way ANOVA followed by a suitable post-hoc test may be used to determine whether dopant identity or concentration significantly changes integrated TL intensity or peak temperature. A significance level of $p < 0.05$ is appropriate for planned comparisons.

Table 2. Recommended experimental parameters for the proposed TL investigation

Parameter	Recommended starting condition	Purpose
Rare-earth screen	Eu, Dy, Tb, Gd, Sm; 0.5 mol%	Identify strongest and most stable TL response
Optimization range	0.1-2.0 mol%	Detect concentration quenching / optimum trap density
Gamma dose	0.1-5 kGy initial series	Establish linearity and saturation behavior
TL heating rate	5 °C s ⁻¹ ; verify at 2 and 10 °C s ⁻¹	Standardize peak comparison and kinetic analysis
TL temperature range	RT to 350-400 °C	Capture principal dosimetric and deep-trap peaks
Fading intervals	1 h, 24 h, 7 d, 30 d	Evaluate signal stability
Replicates	$n \geq 3$	Estimate experimental variability

Results

Important interpretation note: No new laboratory dataset was supplied for this methodology paper. The following results are representative, literature-grounded expectations that should be replaced by measured values after the proposed experiment is performed.

The first expected result is confirmation that rare-earth doping changes TL glow-curve intensity and, in some systems, introduces or redistributes glow peaks. The literature supports this pattern across hosts: Eu/Tb codoping changes the trap distribution in Y2O3:Yb (Som et al., 2015), Sm³⁺ introduces a lower-temperature component in CaO (Prakash & Nagabhushana, 2016), and Eu³⁺-doped SrGd2O4 exhibits multiple resolved TL features (Singh et al., 2017).

For a comparative MgB₄O₇:RE series, the most useful composition would therefore be selected by combining integrated intensity with peak stability rather than by intensity alone.

A second expected result is a concentration optimum. Increasing rare-earth content initially increases the number of luminescent centers and charge-compensation defects, but excessive dopant concentration may promote non-radiative transfer or trap competition. This type of concentration dependence is consistent with rare-earth codoped sulphates (Vidya & Lakshminarasappa, 2014) and with boron-modified LiMgPO₄:Tb systems where concentration quenching was observed (Bajaj et al., 2016). The dose-response curve should be reported with the exact linear range, coefficient of determination, and onset of supralinearity or saturation.

Third, the glow-curve peak position should shift systematically when heating rate is changed, while the calculated activation energy should remain reasonably consistent if the model and peak assignment are valid. Hagemann et al. (2016) further demonstrate that trap population can depend on excitation and temperature history; therefore, reproducible pre-annealing and fixed post-irradiation delay are essential for meaningful comparisons. A candidate phosphor would be considered promising when repeated cycles show low variation, fading remains limited over the intended storage period, and the principal peak occurs sufficiently above room temperature to minimize spontaneous signal loss.

For an illustrative screening outcome, a Dy- or Gd-containing composition might show the most stable dosimetric peak, whereas Eu- or Tb-containing samples may provide stronger characteristic emission. This should not be treated as a predetermined ranking; the actual optimum must be established experimentally because host chemistry controls whether a rare-earth ion behaves mainly as an emission center, a trap modifier, or both.

Conclusion and Discussion

Rare-earth doped phosphors provide a flexible platform for thermoluminescence because the dopant can simultaneously influence radiative emission and defect-mediated charge storage. Literature available up to 2017 demonstrates this behavior in aluminates, borates, sulphates, oxides, phosphates, and silicates. The central methodological requirement is therefore strict control of composition, phase purity, irradiation history, storage time, and heating rate before

glow curves are interpreted. The proposed workflow integrates synthesis, XRD/SEM characterization, calibrated irradiation, replicated TL measurements, dose-response evaluation, fading and reuse tests, and kinetic analysis. It is intentionally comparative: a fixed host is screened with several rare-earth ions, followed by concentration optimization of the most promising dopants. This design reduces the risk of attributing host-lattice effects incorrectly to the dopant itself. For a final experimental paper, the representative trends reported here should be replaced with measured glow curves, numerical trap parameters, uncertainty estimates, and statistical comparisons. A successful phosphor should exhibit a stable and well-separated dosimetric peak, high and reproducible TL output, a useful linear dose range, limited fading, and consistent behavior over repeated annealing cycles. Such materials can be considered for radiation dosimetry and for broader studies of persistent luminescence and defect physics.

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