



Comparative Thermoluminescence and Trap-Kinetic Analysis of Rare-Earth-Codoped Aluminate Phosphors

¹Ulloriaq Qudratullah

¹Department of Electrical and Computer Engineering, Lagoon Polytechnic of Technology, Maldives

¹ulloriaq.qudratullah@lpt-mv.net

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Abstract

Rare-earth-codoped aluminate phosphors are attractive for thermally stimulated luminescence studies because their emission behavior depends strongly on the distribution and stability of defect-related trapping states. This paper develops a comparative methodology for examining Eu-activated alkaline-earth aluminates modified with codopants such as Dy, Nd, and Tm. The study is designed to determine how codopant selection influences charge storage, trap depth distribution, glow-peak structure, thermal release behavior, and signal stability. Eu-only and Eu/R-codoped phosphors are prepared under controlled and identical processing conditions so that changes in thermoluminescence response can be attributed primarily to codopant effects. After structural and optical verification, the samples are subjected to standardized irradiation and controlled TL readout over a defined temperature range. Comparative evaluation includes glow-peak temperature, integrated light output, dose-response behavior, heating-rate dependence, retained signal after storage, and repeatability. Peak-shape methods are used for initial estimation of trapping parameters, while overlapping glow components are separated using computerized curve fitting when required. Literature evidence for CaAl_2O_4 - and SrAl_2O_4 -based systems indicates that codopants can redistribute shallow and deep traps, alter persistent emission, and change the thermal stability of stored charge. The proposed methodology therefore emphasizes comparative trap distribution and thermal release characteristics rather than simple intensity enhancement. This framework provides a practical basis for distinguishing aluminate compositions suited to persistent luminescence, radiation-sensitive measurements, and defect-state investigations.

Introduction

Thermoluminescence is the emission of light from a previously excited solid when the material is heated according to a controlled temperature program. Irradiation creates

electron-hole pairs; a fraction of these carriers is immobilized at defects or impurity-related trapping states. During subsequent heating, thermal energy releases the trapped carriers, allowing them to recombine at luminescence

centers and emit photons. The intensity-temperature profile is known as a TL glow curve. Its peak temperature, width, symmetry, and integrated area can be used to infer trap stability, activation energy, kinetic order, and the amount of stored excitation energy. The theoretical treatment of glow curves and the use of peak-shape parameters for extracting activation energies and frequency factors were established by Chen (1969) and later summarized in the broader TL framework by Bos (2007).

Rare-earth ions are particularly useful in phosphor hosts because their electronic structures provide efficient luminescence centers and, in some compositions, modify the defect landscape responsible for charge trapping. Europium is widely used as an activator, while trivalent rare-earth codopants such as Dy³⁺, Nd³⁺, and Tm³⁺ can alter trap depth distributions and persistent luminescence. Aitasalo et al. (2004) showed that changing the R³⁺ codopant in CaAl₂O₄:Eu²⁺ significantly changes TL intensity and glow-peak position. In a later study, Aitasalo et al. (2006) demonstrated that apparently simple CaAl₂O₄:Eu²⁺,R³⁺ glow curves may contain several traps and that Nd³⁺ and Tm³⁺ are especially effective in enhancing high-temperature TL components associated with long persistent luminescence.

Strontium aluminate hosts have received similar attention. UV-irradiated SrAl₂O₄:Eu²⁺,Dy³⁺ exhibits persistent luminescence and a measurable dose-related response, supporting the interpretation that stored charge and thermal detrapping are central to its optical behavior (Arellano-Tanori et al., 2008). Pereyda-Pierre et al. (2011) reported multiple TL components near 70, 125, and 245 °C in SrAl₂O₄:Eu²⁺,Dy³⁺, whereas Mothudi et al. (2012) observed broad glow curves centered near 120 °C for solid-state-synthesized material and linked the long afterglow to Dy-related trapping. These findings show that TL can serve both as a characterization technique and as a quantitative probe of radiation-stimulated charge storage.

The objective of the present methodology is therefore to establish a reproducible experimental route for investigating how rare-earth activators and codopants influence thermoluminescence in phosphor materials. The study focuses on glow-curve structure, dose response, heating-rate dependence, fading, repeatability, and trap-parameter extraction. The methodology is deliberately designed so that measured results can later be compared with published benchmark systems while avoiding unsupported numerical claims before experimental data are available.

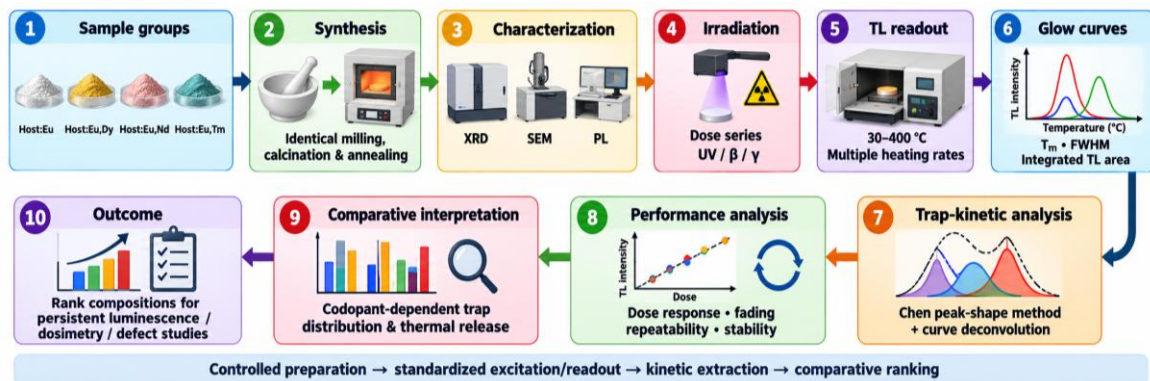


Figure 1. Proposed thermoluminescence mechanism in a rare-earth-doped phosphor (original schematic).

Literature Review

The development of rare-earth-doped persistent phosphors has repeatedly shown that the activator determines the radiative center while intrinsic defects and codopants control charge storage. In CaAl₂O₄:Eu²⁺, Aitasalo et al. (2004) found three low-temperature TL bands and showed that rare-earth codoping can either suppress or enhance specific traps. La³⁺, Y³⁺, and Lu³⁺ reduced the TL response, whereas Nd³⁺ and Tm³⁺ enhanced traps closer to room

temperature. This comparative approach is important because it demonstrates that a change in codopant does not merely change emission intensity; it can restructure the population and stability of traps.

Aitasalo et al. (2006) extended this work above room temperature and applied preheating and initial-rise methods to estimate trap depths. Their analysis revealed that a glow curve peaking near 80 °C could contain several overlapping trapping processes. This

observation is methodologically significant: a single visible maximum should not automatically be treated as a single first-order peak. Accordingly, the present study incorporates both peak-shape analysis and computerized glow-curve deconvolution when peaks overlap. Afouxenidis et al. (2012) showed that complex TL/OSL curves can be deconvoluted into components with accessible numerical tools, providing a practical route for estimating kinetic parameters and comparing fitted and experimental curves.

For SrAl₂O₄:Eu²⁺,Dy³⁺, Arellano-Tanori et al. (2008) reported a useful UV dose response and interpreted persistent luminescence in terms of charge trapping and radiative recombination involving Eu-related emission centers. Pereyda-Pierre et al. (2011) subsequently resolved several glow-curve components and found that shallow traps contributing to a low-temperature peak strongly influence room-temperature afterglow. Mothudi et al. (2012) showed that changes in annealing conditions affected the phosphor structure and TL response, while retaining a broad peak around 120 °C. These

studies support the inclusion of synthesis conditions, annealing history, excitation conditions, and storage time as controlled variables rather than treating the phosphor composition alone as the independent factor.

The orthorhombic Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ system provides a further example of codopant-dependent trap behavior. Emen et al. (2013) reported a dominant TL peak around 80 °C and calculated trap depths over a relatively broad range using computerized glow-curve deconvolution. The authors also observed a higher total TL intensity in Eu/Dy codoped material than in Eu-only material. Such results justify a paired comparison between singly doped and codoped samples in the present design. Finally, Pathak and Kurchania (2015) demonstrated that combustion-synthesized SrAl₂O₄:Eu could be evaluated under Co-60 gamma rays and megavoltage photon beams, and they used Chen's glow-curve-shape method to obtain trapping parameters. Their work confirms that a single phosphor platform can be tested across dose and energy conditions while preserving a common analysis framework.

Table 1. Literature benchmarks used to design the proposed study

Study	Phosphor system	TL feature	Methodological implication
Aitasalo et al., 2004	CaAl ₂ O ₄ :Eu ²⁺ ,R ³⁺	Three bands; strong codopant effect	Compare activator-only and multiple codopants under identical conditions.
Pereyda-Pierre et al., 2011	SrAl ₂ O ₄ :Eu ²⁺ ,Dy ³⁺	Peaks near 70, 125, 245 °C	Use a sufficiently wide readout range and analyze overlapping peaks.
Mothudi et al., 2012	SrAl ₂ O ₄ :Eu ²⁺ ,Dy ³⁺	Broad peak near 120 °C	Control annealing temperature and reducing atmosphere.
Emen et al., 2013	Sr ₄ Al ₁₄ O ₂₅ :Eu ²⁺ ,Dy ³⁺	Dominant peak near 80 °C; multiple trap depths	Use glow-curve deconvolution and compare total integrated intensity.
Pathak & Kurchania, 2015	SrAl ₂ O ₄ :Eu	Dominant high-temperature peak; dose/energy testing	Include dose-response, repeatability, and kinetic analysis.

Methodology

1. Research design and sample selection

A comparative laboratory design is proposed. The primary host will be an alkaline-earth aluminate selected from SrAl₂O₄ or CaAl₂O₄, with Eu as the activator. At minimum, three compositions should be prepared: host:Eu, host:Eu,Dy, and host:Eu,R, where R is Nd or Tm.

A practical starting concentration is 0.5-1.0 mol% Eu with 0.5-1.0 mol% codopant; however, the final concentrations should be held constant across all batches unless concentration itself is being investigated. The comparison should include at least three independently prepared batches per composition so that between-batch reproducibility can be assessed.

2. Synthesis and thermal treatment

Two synthesis routes are suitable. For direct comparison with established persistent aluminates, a conventional solid-state method can be used with high-purity carbonates/oxides, a small borate flux, and a reducing N₂/H₂ atmosphere; the published CaAl₂O₄ and SrAl₂O₄ studies used elevated synthesis temperatures and reducing conditions to stabilize Eu²⁺ (Aitasalo et al., 2004; Mothudi et al., 2012). Alternatively, low-temperature combustion synthesis can be used where fine powders and shorter processing times are required, following the general approach used for SrAl₂O₄:Eu by Pathak and Kurchania (2015). Whichever route is selected, all compositions must undergo the same milling, calcination, annealing, cooling, and storage protocol to prevent processing history from confounding the dopant effect.

3. Structural and optical characterization

Powder X-ray diffraction should be collected over a suitable 2-theta range to verify the intended host phase and identify secondary phases. Crystallite size may be estimated using the Scherrer relation when peak broadening is appropriate for that analysis. Scanning electron microscopy should be used to evaluate particle morphology and agglomeration. Photoluminescence excitation and emission spectra should then confirm the rare-earth emission center and provide the wavelength region relevant to TL detection. For Eu²⁺-activated strontium aluminates, broad visible emission associated with allowed 5d-4f transitions is expected, while the TL experiment probes the trapped-charge population that feeds that emission center during heating (Mothudi et al., 2012).

4. Irradiation and TL glow-curve measurement

Before irradiation, samples should be annealed using a standardized erase cycle to remove residual TL. Equal masses of phosphor should then be irradiated with a calibrated source. A beta or Co-60 gamma source is suitable for general TL characterization; a UV source may be included when persistent-luminescence behavior is also of interest, as demonstrated in SrAl₂O₄:Eu²⁺,Dy³⁺ studies (Arellano-Tanori et

al., 2008; Pereyda-Pierre et al., 2011). A recommended dose series is 0.1, 0.5, 1, 2, 5, and 10 Gy for ionizing radiation, adjusted to the sensitivity and saturation range of the material. Each dose should be measured in triplicate.

TL readout should be performed in nitrogen to reduce oxidation and spurious light, using a linear heating rate initially set at 2-5 °C s⁻¹ from approximately 30 °C to 400 °C. The upper temperature can be reduced if preliminary scans show no high-temperature components. A heating-rate study should repeat measurements at, for example, 1, 2, 5, and 10 °C s⁻¹. For every glow curve, the following quantities should be recorded: peak maximum temperature (T_m), low- and high-temperature half-intensity temperatures (T₁ and T₂), full width at half maximum, integrated TL area, background level, and signal-to-noise ratio.

5. Trap-parameter and glow-curve analysis

Initial kinetic analysis will use Chen's peak-shape method, which relates peak temperature and width parameters to activation energy and frequency factor (Chen, 1969). Because real phosphor glow curves often contain overlapping components, the apparent kinetic order should not be inferred from peak position alone. Where asymmetry or shoulders are present, computerized glow-curve deconvolution will be applied and the fitted curve will be judged by residuals and a goodness-of-fit criterion. The approach is consistent with the deconvolution strategy described by Afouxenidis et al. (2012) and with the multipeak analysis used for Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ by Emen et al. (2013).

Dose response will be analyzed by plotting integrated TL intensity against absorbed dose and fitting linear and, when necessary, supralinear models. Repeatability will be reported as coefficient of variation across repeated readouts. Fading will be measured by storing irradiated aliquots in darkness for intervals such as 0 h, 1 h, 24 h, 72 h, and 7 days before readout. The percentage signal retained relative to the immediate measurement will quantify trap stability. Statistical comparisons among dopant groups may be performed by one-way or two-way ANOVA, depending on whether both dopant type and dose are modeled as factors, with significance set at $p < 0.05$.

Table 2. Proposed experimental variables and measurements

Stage	Controlled/independent variable	Recorded response
Composition	Eu-only vs Eu + Dy/Nd/Tm; constant host and batch protocol	Phase purity, PL spectrum, TL intensity and peak structure

Irradiation	Dose; radiation type/energy; excitation time	Integrated TL signal and dose-response linearity
Readout	Heating rate and maximum temperature	T _m , T ₁ , T ₂ , FWHM, glow-curve shape
Kinetic analysis	Peak-shape vs deconvolution model	Activation energy, frequency factor, kinetic order
Stability	Storage time after irradiation	Fading, retained signal, repeatability

Results

Because this paper defines a methodology rather than reporting a completed experiment, this section states the measurable outcomes expected from the protocol and compares them with pre-2016 literature; it does not invent experimental values. The first expected result is a set of reproducible glow curves whose number, position, and intensity depend on both host and rare-earth codopant. In CaAl₂O₄:Eu²⁺,R³⁺, the literature shows that codopant identity can change both low-temperature and near-room-temperature trap populations (Aitasalo et al., 2004), while the corresponding above-room-temperature study indicates that a seemingly single peak may contain several traps (Aitasalo et al., 2006). Therefore, samples that display one broad maximum should still be evaluated for hidden components.

For SrAl₂O₄:Eu²⁺,Dy³⁺, a multicomponent glow curve is plausible. Pereyda-Pierre et al. (2011) reported components near 70, 125, and 245 °C, whereas Mothudi et al. (2012) observed a broad peak centered near 120 °C after solid-state synthesis and annealing. The difference illustrates why synthesis history, irradiation mode, and readout settings must be reported in detail. In the proposed study, a lower-temperature peak would be interpreted as a shallower, less thermally stable trap that may support room-temperature afterglow but fade more rapidly. Higher-temperature peaks would indicate deeper traps and greater thermal stability, although overly deep traps may not contribute efficiently to persistent luminescence at ambient temperature.

The second expected result is a composition-dependent change in integrated TL intensity. Emen et al. (2013) found stronger total TL intensity for Eu/Dy codoped Sr₄Al₁₄O₂₅ than for Eu-only material, supporting the hypothesis that Dy-related defects or Dy-modified intrinsic defects increase the population of useful trapping states. The third expected result is an approximately proportional dose-response region followed, depending on trap filling and recombination competition, by sublinear or

supralinear behavior. Arellano-Tanori et al. (2008) observed a useful initial dose-related persistent-luminescence response under UV exposure, while Pathak and Kurchania (2015) demonstrated measurable TL behavior of SrAl₂O₄:Eu under different photon irradiation conditions.

Kinetic analysis should yield activation energies and frequency factors that vary by resolved glow component rather than a single universal value for the phosphor. Chen's method provides an efficient first estimate from peak geometry (Chen, 1969), but deconvolution is expected to be more informative when multiple traps overlap (Afouxenidis et al., 2012). A successful experimental outcome would therefore be defined not simply by high TL intensity, but by a combination of phase purity, reproducible glow-curve shape, a usable dose-response interval, low fading, and physically plausible kinetic parameters. These criteria allow candidate phosphors to be ranked for dosimetry, defect characterization, and persistent-luminescence applications.

Conclusion and Discussion

The proposed methodology provides a controlled framework for investigating thermoluminescence in rare-earth-doped phosphor materials while remaining consistent with the state of the literature up to 2015. The central premise is that rare-earth ions have two related but distinct roles: an activator such as Eu can provide the radiative center, whereas codopants and host defects modify the trapping states that determine when and how stored charge is released. Comparative work on CaAl₂O₄:Eu²⁺,R³⁺ and SrAl₂O₄:Eu²⁺,Dy³⁺ confirms that codopant selection, synthesis conditions, irradiation, and thermal history can all reshape the glow curve (Aitasalo et al., 2004, 2006; Pereyda-Pierre et al., 2011; Mothudi et al., 2012). A robust TL study should therefore combine structural verification, optical characterization, standardized irradiation, controlled readout, dose-response analysis, fading measurements, and both peak-shape and deconvolution-based kinetic analysis. The methodology also avoids a common

interpretation error: a single broad maximum is not assumed to represent a single trap. Instead, the glow curve is treated as a possible superposition of trapping processes, consistent with established TL theory and modern deconvolution practice (Chen, 1969; Bos, 2007; Afouxenidis et al., 2012). If implemented experimentally, the protocol should identify which rare-earth combinations produce the most stable and reproducible traps and should clarify whether those traps are best suited to persistent emission, radiation dosimetry, or thermally stimulated defect analysis. Future experimental work can then replace the literature-benchmark Results section with measured glow curves, fitted kinetic parameters, uncertainty estimates, and statistical comparisons.

References

- Chen, R. (1969). On the calculation of activation energies and frequency factors from glow curves. *Journal of Applied Physics*, 40(2), 570-585. DOI: 10.1063/1.1657437.
- Aitasalo, T., Durygin, A., Hölsä, J., Lastusaari, M., Niittykoski, J., & Suchocki, A. (2004). Low temperature thermoluminescence properties of Eu²⁺ and R³⁺ doped CaAl₂O₄. *Journal of Alloys and Compounds*, 380(1-2), 4-8. DOI: 10.1016/j.jallcom.2004.03.007.
- Aitasalo, T., Hölsä, J., Jungner, H., Lastusaari, M., & Niittykoski, J. (2006). Thermoluminescence study of persistent luminescence materials: Eu²⁺- and R³⁺-doped calcium aluminates, CaAl₂O₄:Eu²⁺,R³⁺. *Journal of Physical Chemistry B*, 110(10), 4589-4598. DOI: 10.1021/jp057185m.
- Bos, A. J. J. (2007). Theory of thermoluminescence. *Radiation Measurements*, 41(Suppl. 1), S45-S56. DOI: 10.1016/j.radmeas.2007.01.003.
- Arellano-Tánori, O., Meléndrez, R., Pedroza-Montero, M., Castañeda, B., Chernov, V., Yen, W. M., & Barboza-Flores, M. (2008). Persistent luminescence dosimetric properties of UV-irradiated SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor. *Journal of Luminescence*, 128(1), 173-184. DOI: 10.1016/j.jlumin.2007.07.006.
- Pereyda-Pierre, C., Meléndrez, R., García, R., Pedroza-Montero, M., & Barboza-Flores, M. (2011). Persistent luminescence and thermoluminescence of UV/VIS-irradiated SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor. *Radiation Measurements*, 46(12), 1417-1420. DOI: 10.1016/j.radmeas.2011.07.025.
- Afouxenidis, D., Polymeris, G. S., Tsirliganis, N. C., & Kitis, G. (2012). Computerised curve deconvolution of TL/OSL curves using a popular spreadsheet program. *Radiation Protection Dosimetry*, 149(4), 363-370. DOI: 10.1093/rpd/ncr315.
- Mothudi, B. M., Ntwaeaborwa, O. M., Kumar, A., Sohn, K., & Swart, H. C. (2012). Phosphorescent and thermoluminescent properties of SrAl₂O₄:Eu²⁺,Dy³⁺ phosphors prepared by solid state reaction method. *Physica B: Condensed Matter*, 407(10), 1679-1682. DOI: 10.1016/j.physb.2011.10.033.
- Emen, F. M., Kafadar, V. E., Külçü, N., & Yazici, N. (2013). Thermoluminescence studies and detailed kinetic analysis of Sr₄Al₁₄O₂₅:Eu²⁺,Dy³⁺ phosphor. *Journal of Luminescence*, 144, 133-138. DOI: 10.1016/j.jlumin.2013.06.008.
- Pathak, P. K., & Kurchania, R. (2015). Synthesis and thermoluminescence properties of SrAl₂O₄ (Eu) phosphor irradiated with cobalt-60, 6 MV and 16 MV photon beams. *Radiation Physics and Chemistry*, 117, 48-53. DOI: 10.1016/j.radphyschem.2015.07.009.