

Assessing the dosimetric properties of $\text{CaSO}_4\text{:Ce,Mn}$ phosphors synthesized by different techniques: From beta irradiation to radiation processing dosimetry

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Crystalline materials that exhibit luminescent properties are valuable for monitoring various physical phenomena and for applications such as ionizing radiation dose assessment. Optically stimulated luminescence (OSL) and thermoluminescence (TL) are two widely adopted radiation dosimetry techniques. This study reports on the synthesis and characterization of novel $\text{CaSO}_4\text{:Ce,Mn}$ phosphors obtained via solid-state diffusion, co-precipitation, and slow evaporation routes. Pellets were prepared by mixing Teflon with phosphor powders, then sintering the mixture at 400 °C for 1 h. The luminescent behavior was characterized using a TL/OSL reader equipped with Schott BG-39 and Hoya U-340 bandpass filters. TL measurements revealed that the synthesis route strongly affects trap distribution, luminescent efficiency, and signal stability, with the slow evaporation and co-precipitation methods yielding the most intense glow curves. Spectral discrimination confirmed the simultaneous contribution of Ce^{3+} and Mn^{2+} centers, enabling targeted analysis of recombination processes. OSL analyses under continuous blue LED stimulation revealed that all samples exhibited typical exponential decay, indicating effectively photoionized traps, with the slow evaporation route yielding the highest OSL intensity. The synthesized pellets displayed a linear response over a broad dose range (0.14 Gy–500 Gy), while samples produced via solid-state diffusion and co-precipitation demonstrated improved signal stability. Beyond the luminescent evaluation under beta irradiation, a preliminary assessment demonstrated the potential of these materials for radiation processing dosimetry. The enhanced OSL and UV TL emissions of $\text{CaSO}_4\text{:Ce,Mn}$ produced via the slow evaporation route demonstrate that Ce^{3+} co-doping improves charge trapping and recombination processes compared with $\text{CaSO}_4\text{:Mn}$ under the same synthesis conditions.

1. Introduction

Ionizing radiation dosimetry is essential for radiation protection, equipment commissioning, and quality assurance. Globally, occupational and environmental dose assessment programs as well as equipment quality control protocols rely on passive solid-state dosimeters. Thermoluminescence (TL) and optically stimulated luminescence (OSL) are the dosimetric techniques that most widely employ these dosimeters (Gasparian et al., 2023; Izewska et al., 2003; ICRP, 2007; Kry et al., 2018; Yukihiro and McKeever, 2011).

These techniques rely on the correlation between the population of trapped charge carriers generated by ionizing radiation and the

absorbed dose. Upon thermal or optical stimulation, the trapped electrons and holes recombine, producing the TL or OSL signal. Consequently, the design of luminescent materials that can effectively trap and release charge carriers is essential to improving both sensitivity and measurement accuracy to radiation dose (McKeever, 2022).

Among the materials investigated for radiation dosimetry, appropriately doped calcium sulfate (CaSO_4) stands out due to its high sensitivity and excellent signal reproducibility, being compatibility with both TL and OSL techniques (Doull et al., 2014; Guckan et al., 2023; Junot et al., 2014, 2016, 2019; Kasa et al., 2007; Gasparian et al., 2022; Yukihiro et al., 2015). This dual-mode capability makes CaSO_4 a highly versatile matrix for a broad spectrum of dosimetric applications, ranging

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from personal monitoring to environmental and clinical radiation assessment.

Over the past few decades, researchers have focused on optimizing the luminescent properties of phosphors by co-doping them with unconventional elements. The most common dopants are rare-earth ions, such as europium (Eu), thulium (Tm), terbium (Tb), samarium (Sm), cerium (Ce), praseodymium (Pr), gadolinium (Gd), and dysprosium (Dy), as well as transition metals like manganese (Mn), titanium (Ti), zinc (Zn), copper (Cu), and silver (Ag), alkaline-earth metals such as magnesium (Mg), and alkali metals like sodium (Na) and lithium (Li). These elements enhance luminescent efficiency and stability (Nunes (2012); Nair et al., 2000; Maghrabi et al., 2000; Kasa et al., 2007; Nunes (2012); Junot et al., 2014, 2016, 2019, 2024; Bastani et al., 2019; Silva et al., 2020, 2021, 2022, 2023, 2024, 2025).

Given the growing demand for new materials in luminescent dosimetry and their potential technological applications, this study is part of an ongoing experimental series developed by our research group. Building upon the foundational work of Silva et al. (2022, 2023), we found that $\text{CaSO}_4\text{:Mn}$ phosphors synthesized via the slow evaporation route exhibited optimized dosimetric properties, including significantly less fading than those produced by other synthesis methods. Further improvements were achieved by co-doping $\text{CaSO}_4\text{:Mn}$ with rare-earth elements such as Tb, which enhanced both the luminescent efficiency and signal stability of the material. For instance, $\text{CaSO}_4\text{:Mn,Tb}$ samples displayed well-defined TL peaks at 205 °C and exhibited reduced fading compared to mono-doped samples. These results suggest that co-doping effectively stabilizes charge recombination centers at deeper energy levels.

Nair et al. (2000) reported that cerium is a relatively inefficient activator for the intrinsic luminescence of CaSO_4 ; however, its presence significantly enhances emission intensity when co-doped with other ions. In this context, Nunes (2012) and Bastani et al. (2019) investigated various $\text{CaSO}_4\text{:Ce,RE}$ phosphors (RE = rare earth elements) synthesized by the slow evaporation and co-precipitation routes, respectively, using co-dopants such as Nd, Eu, Tb, Tm, Pr, Gd, and Ti. Nevertheless, Ce,Mn co-doped samples produced via the slow evaporation method have remained unexplored. Silva et al. (2026a) reported a systematic investigation of $\text{CaSO}_4\text{:RE,Mn}$ (RE = Dy, Tb, Tm, Yb, Eu, Ce) phosphors synthesized via the slow evaporation method, demonstrating that Ce^{3+} consistently provides one of the most intense luminescent responses to ionizing radiation, particularly in OSL and UV TL, surpassing the performance of other highly sensitive $\text{CaSO}_4\text{:RE,Mn}$ compositions (RE = Dy, Tb, Yb, Eu).

In this study, we synthesized a new series of CaSO_4 phosphors nominally co-doped with 0.1 mol% Ce and 0.1 mol% Mn using three distinct synthesis routes. To evaluate the spectral response of the phosphors, TL glow curves were recorded in both the ultraviolet (UV) and visible (VIS) spectral regions. The TL and OSL results were compared with previously reported data for $\text{CaSO}_4\text{:Mn}$ samples prepared by the slow evaporation method (Silva et al., 2023), as well as with OSL investigations reported by Bahl et al. (2017) for $\text{CaSO}_4\text{:Mn}$ phosphors synthesized by the recrystallization method. To the best of our knowledge, this is the first comprehensive investigation to systematically evaluate the influence of synthesis route on the luminescent performance of $\text{CaSO}_4\text{:Ce,Mn}$ under beta and high-dose gamma irradiation. The findings of this study highlight the crucial role that microstructural variations play in optimizing the dosimetric efficiency of this phosphor.

2. Materials and methods

2.1. Synthesis routes

2.1.1. Solid state diffusion method

$\text{CaSO}_4\text{:Ce,Mn}$ phosphors were synthesized via the solid-state diffusion method, following the procedure reported by Rani et al. (2015). The

raw materials used were calcium sulfate dihydrate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, Dinâmica), cerium (III) oxide (Ce_2O_3 , Merck), and manganese (II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, Merck). Initially, Ce_2O_3 and $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were dissolved in distilled water under constant magnetic stirring. The dopants were added at a concentration of 0.1 mol% each. After complete dissolution and homogenization, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ was added to the solution and stirred thoroughly. The mixture was then dried at 180 °C for 2 h, ground, and sintered at 600 °C for 1 h.

2.1.2. Co-precipitation method

Co-precipitation synthesis was carried out according to the method described by Salah et al. (2006). Stoichiometric amounts of calcium acetate ($\text{Ca}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, Neon), Ce_2O_3 , and $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were dissolved in triply-distilled water under constant stirring. Then, the resulting solution was mixed with a stoichiometric amount of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, Dinâmica) in the presence of ethanol to promote the co-precipitation of the doped calcium sulfate. The precipitate was filtered, washed several times with distilled water, and then dried at 100 °C for 2 h. Finally, the resulting powder was annealed at 650 °C for 2 h to complete the crystallization process.

2.1.3. Slow evaporation method

The synthesis procedure used for the slow evaporation method was adapted from the protocols reported by Junot et al. (2016, 2019) and Silva et al. (2020). First, a solution was prepared by dissolving calcium carbonate (CaCO_3 , Merck) in sulfuric acid (H_2SO_4 , Vetec). Then, Ce_2O_3 and $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were added at a concentration of 0.1 mol% each to dope the material base. The resulting mixture was heated to 375 °C using a heating mantle and maintained at that temperature until the acid had completely evaporated. After cooling, the solid product was washed with distilled water, ground, sieved, and finally calcined at 600 °C for 1 h.

2.2. Methods of characterization

The elemental composition of the samples was assessed by energy-dispersive spectroscopy (EDS) coupled to a scanning electron microscope (SEM, JSM-IT700HR), which was also used to examine the surface morphology and particle size. The crystalline structure was analyzed by X-ray diffraction (XRD) using a Rigaku RINT 2000/PC diffractometer with $\text{Cu-K}\alpha$ radiation, operated at 60 kV and 30 mA. Scans were performed in the 2θ range of 20° to 80°, with a step size of 0.04°.

For luminescence characterization, the phosphor powders were mixed with Teflon (PTFE) at a weight ratio of 1:1 (50 wt% phosphor and 50 wt% PTFE), which improved mechanical strength and facilitated handling. The mixture was pressed into pellets (~30 mg, 6 mm diameter and approximately 0.5 mm in thickness) under a uniaxial pressure of 0.5 ton, then sintered at 400 °C for 1 h to enhance mechanical stability. The resulting pellets are white and opaque. The samples were irradiated using a $^{90}\text{Sr}+^{90}\text{Y}$ beta source (4.33 Gy/min, 2.27 MeV) available in the TL/OSL reader, and a ^{60}Co Gammacell 500 source (8.35 kGy/h, 1.25 MeV average) for high-dose studies at the Radiation Technology Center of IPEN-CNEN/SP.

TL and OSL measurements were performed using a Risø TL/OSL reader model DA-20 (DTU, Denmark). Luminescence signals were detected with a bialkali photomultiplier tube (Electron Tubes, 9235QB). For TL analysis, a heating rate of 5 °C/s was applied, with the temperature reaching up to 400 °C. OSL measurements were conducted using blue LEDs ($\lambda = 470$ nm, FWHM ≈ 30 nm) as the stimulation source, with a power density of ~ 90 mW cm^{-2} and a signal acquisition time of 40 s.

The emitted luminescence was detected using Schott BG-39 bandpass filters (330–600 nm, visible range) and Hoya U-340 filters (270–380 nm, UV range). This setup enabled selective detection of the emission spectra. For the spectral measurements, the photomultiplier tube was replaced by a high-resolution Ocean Optics QE65000 spectrometer coupled to the TL reader through an optical fiber. The TL emission

spectra were acquired under the same heating rate (5 °C/s), with an integration time of 1 s per spectrum. The detected spectral range (200–1000 nm) is defined by the UV–Vis transmittance of the fiber-optic cable, which has a core diameter of 100 μm .

After each TL and OSL evaluation, the pellets were placed on aluminum plates and annealed at 400 °C for 60 min in a 671 IRD/CNEN furnace, ensuring the complete release of trapped charge carriers and enabling sample reuse.

3. Results and discussions

3.1. Elemental, morphological, and structural characterization

As a preliminary step, the synthesized $\text{CaSO}_4\text{:Ce,Mn}$ powders obtained by the three different methods were characterized in terms of their elemental composition, morphology, and crystalline structure, before the pellet preparation for luminescence analysis. Fig. 1 presents the EDS spectra of the powders, revealing prominent peaks related to

calcium (Ca), sulfur (S), and oxygen (O). These peaks confirm the presence of the main constituents of the CaSO_4 matrix. Despite the low dopant concentrations (≤ 0.1 mol%), signals corresponding to cerium (Ce) and manganese (Mn) were also observed. The EDS mapping further demonstrated the uniform spatial distribution of both dopants, indicating their effective incorporation into the host lattice and highlighting the efficiency of the synthesis methods.

The morphological features of the $\text{CaSO}_4\text{:Ce,Mn}$ powders synthesized by different methods are presented in Fig. 2(a–c), captured at 1000 $\times$ magnification. The SEM images reveal significant differences in particle size, surface texture, and degree of agglomeration, which are all directly influenced by the synthesis method employed. In Fig. 2a, from a sample obtained by the solid-state diffusion method, the micrograph shows irregular, angular particles with a lamellar appearance and heterogeneous size distribution. A moderate degree of agglomeration is observed, along with rough surface textures.

In Fig. 2b, from a sample associated with the slow evaporation method, the SEM micrograph shows grains with smoother surfaces and

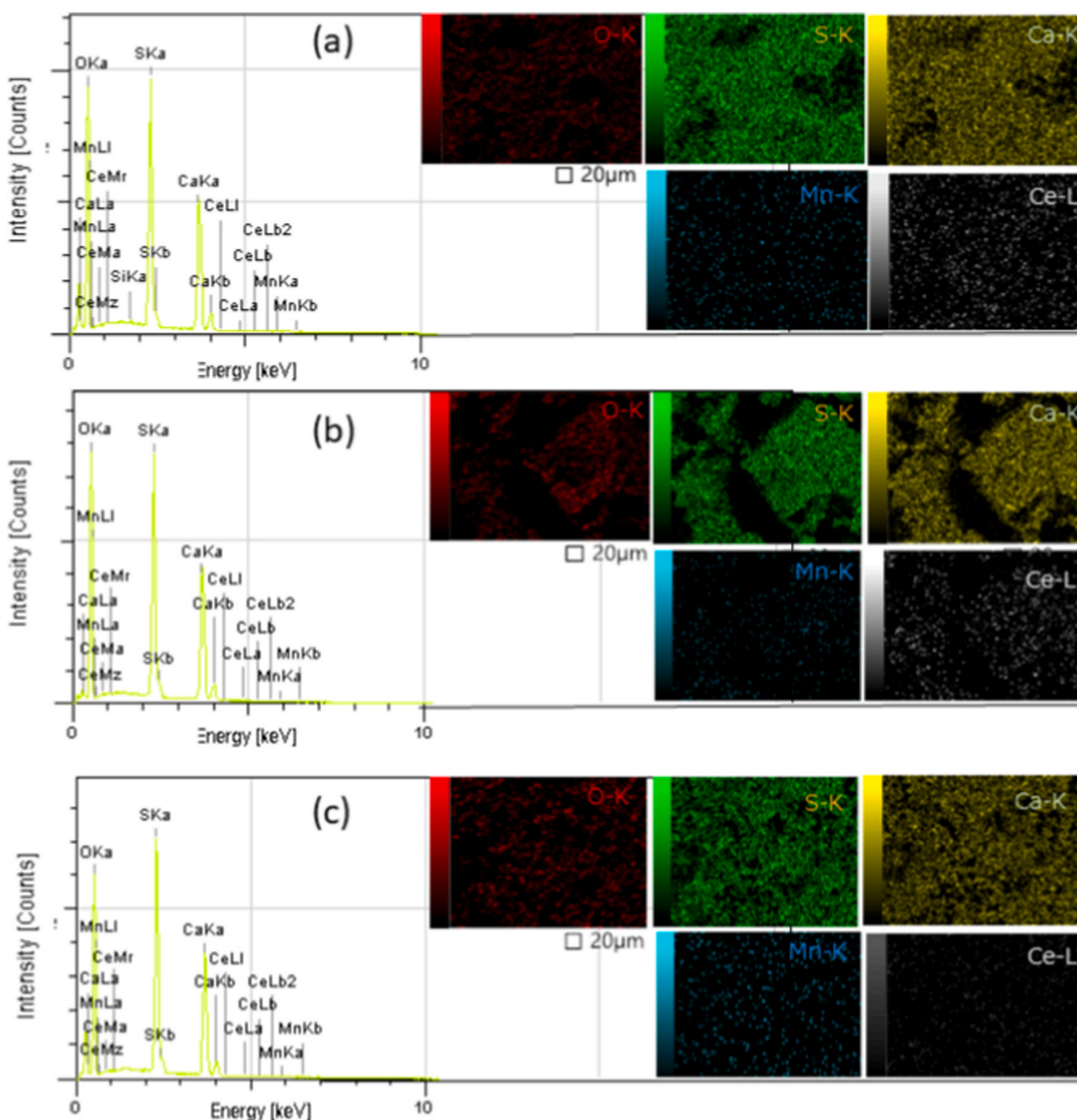


Fig. 1. EDS spectra and elemental mapping of $\text{CaSO}_4\text{:Ce,Mn}$ samples synthesized by different methods: (a) solid-state diffusion, (b) slow evaporation, and (c) co-precipitation.

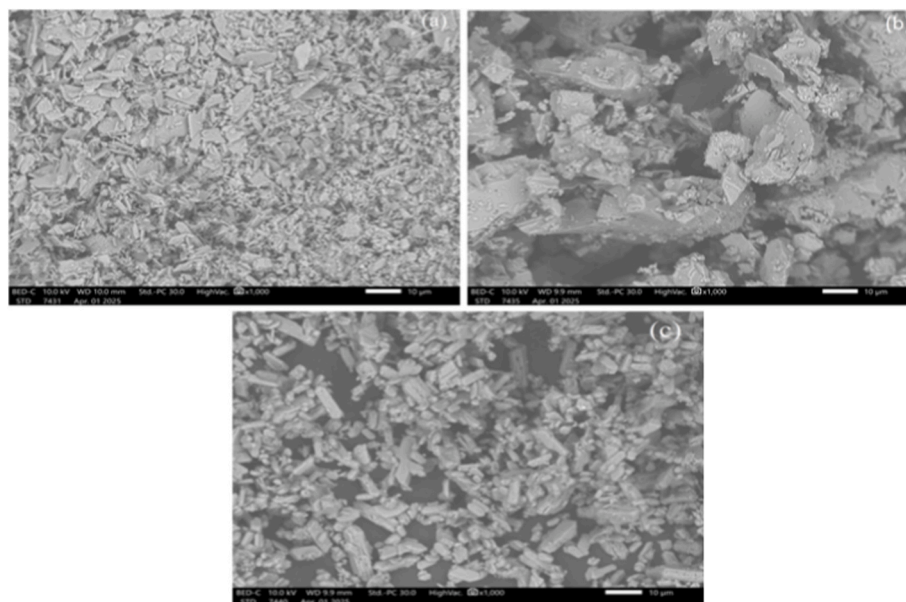


Fig. 2. SEM micrographs of CaSO_4 powders prepared using different methods: (a) Solid-state diffusion, (b) Slow evaporation, and (c) Co-precipitation method.

more rounded or aggregated morphologies. Though some irregularities persist in the samples, this method promotes the formation of larger particle domains and more complex surface textures. In contrast, Fig. 2c depicts the powder synthesized via the co-precipitation method and reveals a more uniform and prismatic morphology, with well-defined edges and a relatively homogeneous size distribution. These morphological differences arise from variations in precursor selection, reaction conditions, and thermal treatment parameters specific to each synthesis method. Such variations can significantly impact the luminescent properties and dosimetric performance of the resulting phosphors.

Complementarily, XRD patterns of the powders (Fig. 3) confirmed the formation of the orthorhombic CaSO_4 phase (JCPDS card no. 01-072-0916) in all samples. The absence of secondary phases related to cerium or manganese oxides suggests that the dopants were successfully incorporated into the CaSO_4 crystal lattice.

3.2. Thermoluminescence and optically stimulated luminescence studies

To investigate the impact of different synthesis methods on the

luminescence properties of $\text{CaSO}_4\text{:Ce,Mn}$, the samples were irradiated with a 5 Gy beta radiation dose and subjected to a constant heating rate of 5°C/s . TL emission curves were recorded and analyzed in both the ultraviolet (UV) and visible (VIS) regions using Hoya U-340 (Fig. 4a) and Schott BG-39 (Fig. 4b) optical filters. These filters enable preferential detection of UV and visible emission components, respectively, allowing comparative evaluation of the dominant recombination pathways, although their transmission bands partially overlap.

In the UV region, the glow curve of the $\text{CaSO}_4\text{:Ce,Mn}$ sample obtained via the slow evaporation route exhibits two distinct peaks at around 150°C and 190°C . The presence of a shoulder extending beyond these peaks indicates additional peaks at higher temperatures ($>350^\circ\text{C}$). In contrast, the samples prepared by solid-state diffusion and co-precipitation show broader peaks that are shifted toward higher temperatures. The differences between the two glow curves indicate variations in trap depth distribution depending on the synthesis route. These results suggest that the synthesis method strongly affects both the nature and population of trapping centers within the material.

Similar behavior was reported by Nunes (2012) for $\text{CaSO}_4\text{:Ce}$ synthesized by slow evaporation. The glow curve of this material, obtained with a heating rate of $2^\circ\text{C}\cdot\text{s}^{-1}$, exhibited a main peak at around 130°C . Meanwhile, Bastani et al. (2019); Maghrabi et al. (2000) and Nair et al. (2000) observed comparable TL profiles featuring a low-temperature peak and additional high-temperature components. In particular, Nair et al. (2000) observed that the TL peak near 400°C in $\text{CaSO}_4\text{:Ce,Mn}$, measured with a quartz-window photomultiplier without neutral density filters, exhibited significantly lower sensitivity than $\text{CaSO}_4\text{:Ce}$, and that the $\sim 120^\circ\text{C}$ peak intensity in $\text{CaSO}_4\text{:Ce,Mn}$ was also lower than that of $\text{CaSO}_4\text{:Mn}$ under the same detection conditions.

In contrast, the monodoped $\text{CaSO}_4\text{:Mn}$ sample presents a single emission curve that is broader and weaker, with maximum intensity near 160°C . The weak response in the UV spectral region is consistent with the low emission efficiency of Mn^{2+} in this spectral range, as its intrinsic ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition occurs predominantly in the visible region.

In the visible region, the relative emission intensities change, with the $\text{CaSO}_4\text{:Mn}$ sample showing the highest TL intensity due to its dominant Mn^{2+} emission (${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition). This confirms the role of Mn^{2+} as the main emissive center. When Ce is incorporated as a codopant, the $\text{CaSO}_4\text{:Ce,Mn}$ sample exhibits emission with a well-defined and nearly symmetrical peak at 137°C . This peak is less intense but narrower, suggesting a more localized distribution of

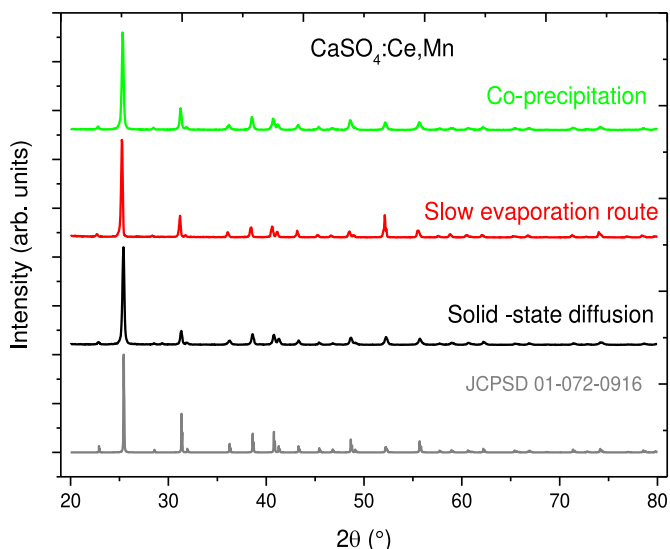


Fig. 3. XRD patterns of $\text{CaSO}_4\text{:Ce,Mn}$ powders produced by different methods.

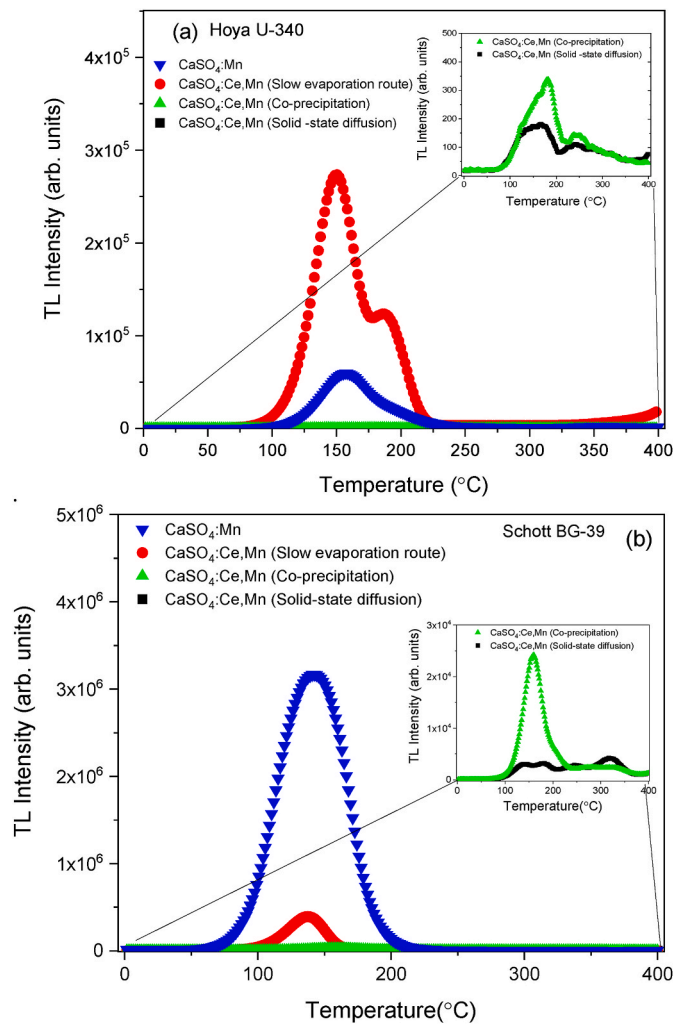


Fig. 4. (a) TL glow curves of $\text{CaSO}_4:\text{Ce,Mn}$ samples prepared by different routes and $\text{CaSO}_4:\text{Mn}$, irradiated with 5 Gy of beta radiation, using a Hoya U-340 filter, and (b) using a Schott BG-39 filter.

trapping levels or reduced overlap between trapping centers. The co-precipitation sample exhibits a weaker and relatively narrow glow peak around 160 °C, as shown in the inset of Fig. 4b. A slight high-temperature tail can also be observed in the co-precipitation curve. However, the solid-state diffusion sample presents a significantly lower overall intensity and a more complex structure with multiple overlapping peaks extending up to about 360 °C. Overall, these differences highlight the distinct thermal stability and trap population associated with each synthesis route.

As shown in Fig. 5, the emission spectrum of $\text{CaSO}_4:\text{Ce,Mn}$ confirms the coexistence of two distinct bands. One band, in the 290–340 nm range, is attributed to the $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$ transitions of Ce^{3+} . The other band, centered around 497 nm, corresponds to the ${}^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} . In comparison, the TL emission of monodoped $\text{CaSO}_4:\text{Mn}$ exhibits a single peak at ~150 °C, confirming the ${}^4T_1 \rightarrow {}^6A_1$ transition and the incorporation of Mn^{2+} into the CaSO_4 lattice (Silva et al., 2023). Earlier TL spectral studies of $\text{CaSO}_4:\text{Ce}$ reported characteristic Ce^{3+} emission bands around 305–325 nm together with glow peaks near 145 °C, confirming the role of Ce-related recombination centers (Maghrabi et al., 2000; Nair et al., 2000). This spectral behavior indicates that no effective energy transfer occurs from Ce^{3+} to Mn^{2+} within the CaSO_4 matrix. Co-doped samples exhibit an enhanced UV emission associated with Ce^{3+} centers, while the visible Mn^{2+} emission is significantly reduced compared to the monodoped phosphor. These

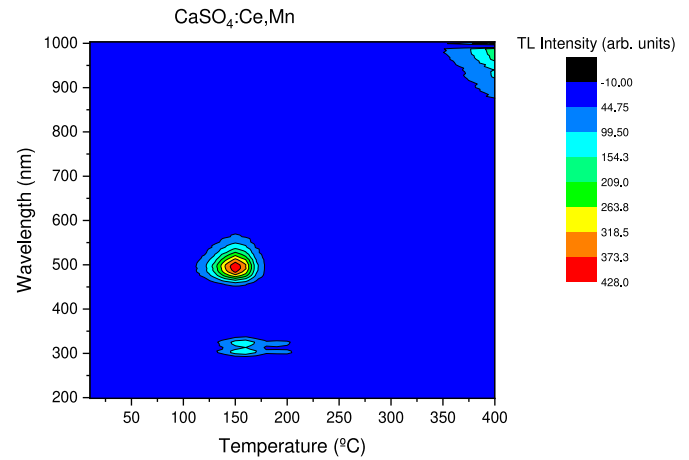


Fig. 5. Contour plot of the TL emission spectrum of $\text{CaSO}_4:\text{Ce,Mn}$ phosphor synthesized via the slow evaporation method.

results suggest that Ce^{3+} and Mn^{2+} act as independent luminescent centers, following competitive recombination pathways rather than energy transfer mechanisms. This interpretation is consistent with the findings of Nair et al. (2000), who also reported the absence of energy transfer from Mn^{2+} to Ce^{3+} during the thermally stimulated luminescence process.

Fig. 6 shows the continuous wave OSL (CW-OSL) responses of $\text{CaSO}_4:\text{Ce,Mn}$ samples synthesized by solid-state diffusion, slow evaporation, and co-precipitation methods, together with the $\text{CaSO}_4:\text{Mn}$ sample for comparison. The stimulation time was 40 s.

Among the evaluated synthesis methods, slow evaporation route yielded the highest OSL sensitivity, producing samples with integrated signals nearly 20 times greater than those samples from the other two methods. All samples exhibited an exponential decay profile, as the optically active traps are progressively emptied during blue-light stimulation. This behavior indicates that the traps responsible for the OSL signal are effectively photoionized under blue LED excitation.

When the OSL behavior of $\text{CaSO}_4:\text{Mn}$ and $\text{CaSO}_4:\text{Mn,Ce}$ samples synthesized by the slow evaporation route was compared, a substantial enhancement in the OSL signal was observed upon Ce^{3+} incorporation. This result indicates that the luminescent performance of $\text{CaSO}_4:\text{Mn}$

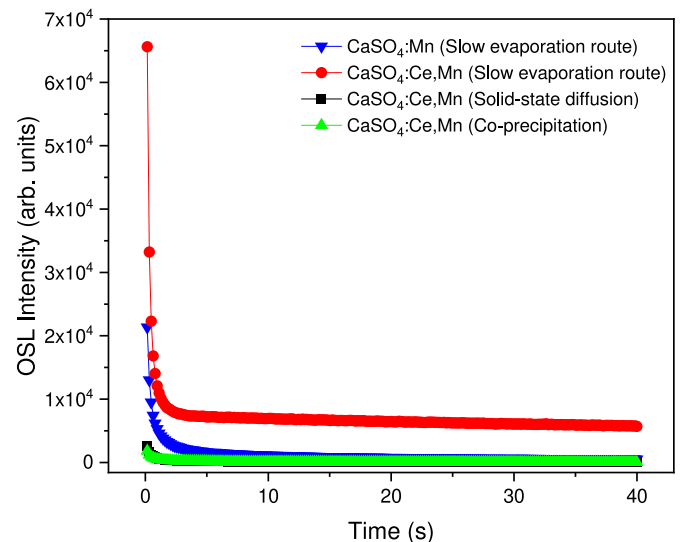


Fig. 6. OSL curves of $\text{CaSO}_4:\text{Ce,Mn}$ pellets produced by different routes and $\text{CaSO}_4:\text{Mn}$, irradiated with 5 Gy of ${}^{90}\text{Sr}+{}^{90}\text{Y}$. Measurements were performed at room temperature (~20 °C) immediately after irradiation.

based phosphors can be effectively optimized through Ce^{3+} activator doping and by controlling of the synthesis conditions appropriately.

As shown in Fig. 7, the integrated TL and OSL responses demonstrate that both the synthesis route and Ce^{3+} incorporation strongly affect the luminescent efficiency of $\text{CaSO}_4\text{:Mn}$. The slow evaporation method yielded the highest overall emission, producing a sixfold increase in the UV TL intensity and a markedly enhanced OSL signal compared with the other routes. In the visible TL region dominated by Mn^{2+} emission, however, $\text{CaSO}_4\text{:Ce,Mn}$ samples exhibited intensities about twenty times lower than those of the monodoped $\text{CaSO}_4\text{:Mn}$ phosphor.

The differences in peak intensity and shape are associated with variations in crystal structure, synthesis route, particle size, and morphology (Nair et al., 2020), which affect both TL and OSL responses. The superior performance of the slow evaporation samples is associated with a more homogeneous matrix and a higher density of effective trapping centers. This behavior is consistent with the Silva et al. (2026b) findings for $\text{CaSO}_4\text{:Mn,Tb}$, which confirm the strong dependence of luminescence efficiency on the synthesis route. The co-precipitation route results in samples that exhibit an intermediate luminescent response, while the solid-state diffusion route in the lowest response.

3.3. Reproducibility, fading, and linearity

Table 1 summarizes the integrated TL and OSL responses, as well as their respective coefficients of variation (CV%) for $\text{CaSO}_4\text{:Ce,Mn}$ samples that were synthesized by solid-state diffusion, co-precipitation, or slow evaporation. Among the evaluated methods, the slow evaporation route produced the most consistent and reproducible results across both optical filters. For TL measurements using the BG-39 filter, the CV% were below 9.2% for all synthesis methods, indicating good reproducibility. OSL measurements exhibited even lower CVs, reaching 3.8%, which confirms the uniform formation of traps and optically active centers. In contrast, the Hoya U-340 TL measurements revealed higher variability for co-precipitation (CV = 18.6%) and solid-state diffusion (CV = 22.7%), suggesting less uniform dopant incorporation and trap distribution. These results reinforce the slow evaporation method as the most reliable synthesis method, likely due to the stable incorporation of Ce^{3+} and Mn^{2+} into the host lattice.

Fig. 8 presents the TL and OSL fading behavior after 30 days of storage at room temperature. The black bars denote the normalized responses immediately following beta irradiation (set to 1.0), while the

red and blue bars indicate the TL and OSL signals after storage, respectively. Samples obtained using the slow evaporation method showed the greatest fading, with reductions of 74.4% for TL and 81.9% for OSL. Solid-state diffusion resulted in lower fading (58.5% for TL and 50.7% for OSL), co-precipitation yielded intermediate losses (59.5% TL, 50.9% OSL). In comparison, the $\text{CaSO}_4\text{:Mn}$ sample prepared by the slow evaporation route showed higher fading rates, with 75% loss in TL intensity (Hoya U-340 filter) and 63.6% fading in OSL after 28 days, as reported by Silva et al. (2023). Overall, the slow-evaporation $\text{CaSO}_4\text{:Ce,Mn}$ sample exhibited significant fading and did not demonstrate improved stability of trapped charges compared to the $\text{CaSO}_4\text{:Mn}$. The results indicate that signal retention is enhanced for the co-precipitation and solid-state diffusion samples, which display the best long-term stability.

Dose-response measurements were conducted to evaluate the luminescent behavior of the synthesized materials as a function of the absorbed dose. Fig. 9a shows the TL response of $\text{CaSO}_4\text{:Ce,Mn}$ phosphors produced via slow evaporation, co-precipitation, and solid-state diffusion over a dose range of 0.14 Gy to 100 Gy. The slow evaporation and co-precipitation methods yielded clear linearity TL responses, with correlation coefficients of $R^2 = 0.993$ and $R^2 = 0.996$, respectively. Although the TL emission arises from multiple trapping centers, the high linearity indicates that the dominant dosimetric traps remain proportionally populated within the investigated dose range. This supports the use of full-curve integration as a reliable comparative metric for overall performance. In contrast, the solid-state diffusion sample showed a non-linear TL response ($R^2 = 0.935$), which can be attributed to overlapping glow peaks between 150 °C and 360 °C. This indicates a broad distribution of trapping centers. At higher doses, this results in supralinear behavior and a partial loss of proportionality between TL intensity and absorbed dose. Peak-specific or temperature-window analyses may further refine the trap-dependent dose response, a topic to be explored in future work. Similarly, the OSL dose-response curves (Fig. 9b) of the samples also displayed linear behavior up to 500 Gy. The respective correlation coefficients were $R^2 = 0.992$, $R^2 = 0.993$, and $R^2 = 0.990$ for the samples produced by the slow evaporation method, solid-state diffusion, and co-precipitation, respectively. These results indicate that the synthesized phosphors provide a consistent dose response within the experimental readout conditions adopted in this study.

3.4. Preliminary evaluation for radiation processing dosimetry

Fig. 10 presents the TL glow curves of $\text{CaSO}_4\text{:Ce,Mn}$ samples that were synthesized via slow evaporation, co-precipitation, or solid-state diffusion. The samples were irradiated with high-energy photons from ^{60}Co at a dose of 50 Gy. During TL readout, a Schott BG-39 optical filter was used. It is important to note that this dose is considerably lower than those typically used in radiation processing dosimetry. This condition is associated with the high TL sensitivity of the samples produced via slow evaporation, which exhibited strong TL emission dominated by a sharp peak near 140 °C. The peak intensities is significantly higher than that of other synthesis methods, suggesting a higher concentration of trapping centers. To ensure comparable measurements among samples with markedly different sensitivities and to prevent photomultiplier saturation, the TL readouts were performed using a collimator with a 2-mm central aperture. Therefore, the observed constraints are related to the instrumental configuration rather than to intrinsic limitations of the material. While this pronounced sensitivity is promising for low-dose radiation processing dosimetry, where important applications include radiation-based sterile insect technique and blood bag sterilization, it requires an appropriate adjustment of the detection setup when samples irradiated with higher doses are studied. In the present study, the pellet mass was kept constant for all samples. For future high-dose investigations, mitigation strategies such as reducing the pellet mass may be adopted to prevent exceeding the reader's maximum count capacity. Conversely, the co-precipitation method yielded substantially lower TL

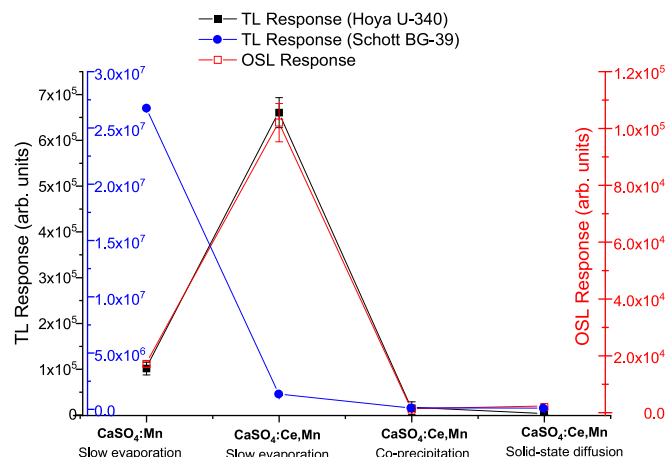


Fig. 7. TL and OSL responses obtained by integrating the areas under the emission curves of $\text{CaSO}_4\text{:Ce,Mn}$ samples synthesized by different routes, along with the monodoped $\text{CaSO}_4\text{:Mn}$ samples, using Schott BG-39 and Hoya U-340 optical filters. Measurements were carried out at room temperature immediately after irradiation.

Table 1

Integrals of the TL emission and OSL decay curves of the produced compounds, respective uncertainties (deviation), and the percentage variation coefficients of the readings (CV%).

Synthesis method	TL				OSL	
	BG-39		Hoya U-340		Hoya U-340	
	Response (arb. units)	C.V (%)	Response (arb. units)	C.V (%)	Response (arb. units)	C.V (%)
Solid-state diffusion	$(4.70 \pm 0.43) \times 10^5$	9.2	$(2.06 \pm 0.47) \times 10^4$	22.8	$(4.52 \pm 0.17) \times 10^4$	3.8
Co-precipitation	$(1.08 \pm 0.03) \times 10^6$	3.4	$(2.72 \pm 0.50) \times 10^4$	18.6	$(3.38 \pm 0.06) \times 10^4$	1.9
Slow evaporation	$(9.40 \pm 0.17) \times 10^6$	1.9	$(9.97 \pm 0.35) \times 10^6$	3.6	$(1.25 \pm 0.04) \times 10^6$	3.3

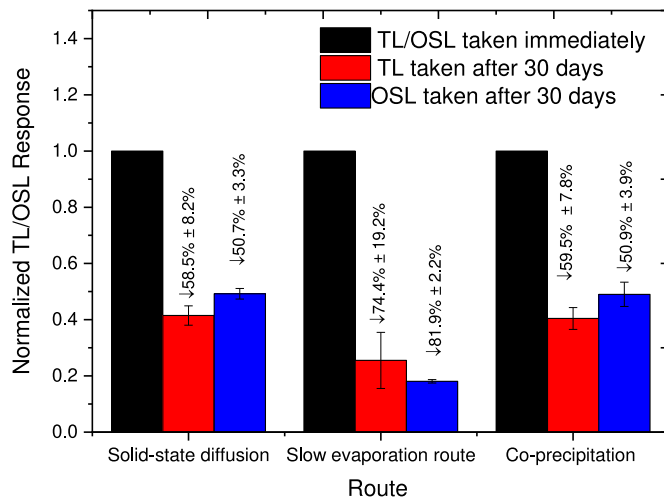


Fig. 8. Normalized TL and OSL responses of $\text{CaSO}_4\text{:Ce,Mn}$ samples measured after irradiation (black bars) and after 30 days (red: TL, blue: OSL). Percentual signal losses are shown for each synthesis method. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

intensity; however, the glow curve profile remained similar to that of the slow evaporation samples, indicating comparable trapping mechanisms but with reduced trap concentration or efficiency. Studies on higher doses and at different dose rates are underway using the samples synthesized via the co-precipitation method.

4. Conclusions

This study systematically assessed the influence of three different synthesis methods on the structural, morphological, and luminescent (TL and OSL) properties of $\text{CaSO}_4\text{:Ce,Mn}$ phosphors. All synthesis methods produced samples with a CaSO_4 crystalline phase and successfully incorporated the dopants into the host lattice. The phosphors synthesized via the slow evaporation route exhibited the most intense and highly reproducible TL/OSL emissions, highlighting their strong potential for ultra-sensitive dosimetry at low radiation doses. In contrast, the co-precipitation and solid-state diffusion methods yielded lower TL/OSL responses but superior long-term signal stability. Their lower luminescent efficiency makes them particularly suitable for applications involving higher radiation doses, including radiation processing. These findings underscore the decisive influence of synthesis parameters on the microstructural tuning of $\text{CaSO}_4\text{:Ce,Mn}$, which directly affects its trapping structure and luminescence behavior. The robust luminescent emission spanning both the UV and visible regions broadens the applicability of this material to diverse and demanding monitoring scenarios. The TL responses were linear in the 0.1–100 Gy range, and OSL responses covered 0.1–500 Gy. Both emissions exhibited high reproducibility. The enhanced OSL and UV TL responses observed for the $\text{CaSO}_4\text{:Ce,Mn}$ phosphor synthesized via the slow evaporation route indicate that, under this specific microstructural condition, Ce^{3+}

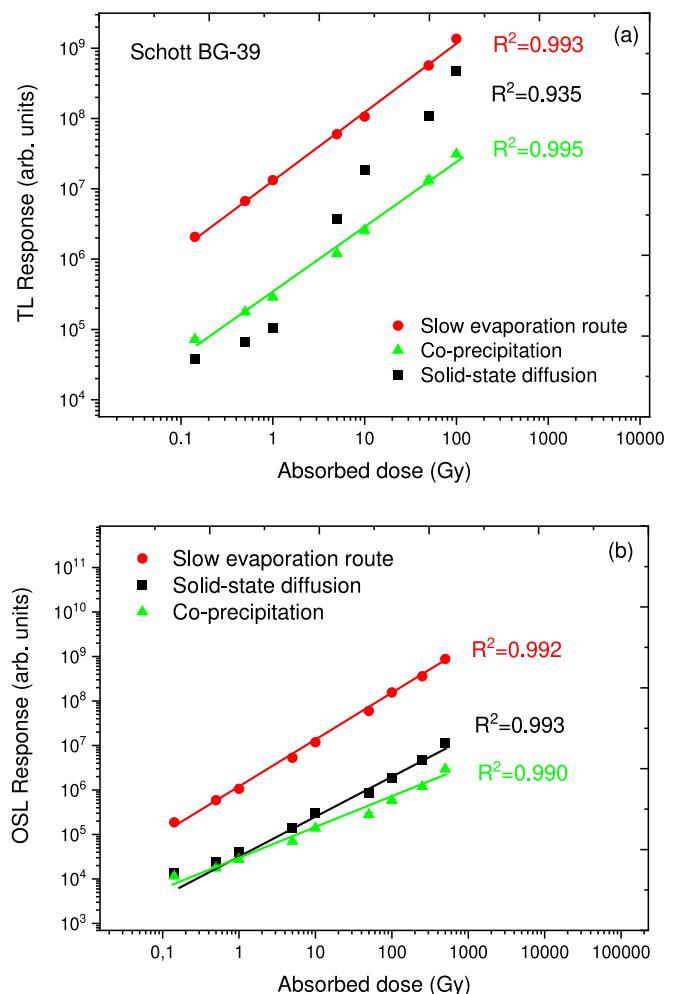


Fig. 9. (a) TL response of $\text{CaSO}_4\text{:Ce,Mn}$ samples synthesized via solid-state diffusion, co-precipitation, and slow evaporation, as a function of beta radiation dose (0.1 Gy – 100 Gy). (b) OSL response of the same samples as a function of absorbed dose after $^{90}\text{Sr}+^{90}\text{Y}$ irradiation (0.1 Gy – 500 Gy).

co-doping contributes to improved trapping and recombination efficiency in the $\text{CaSO}_4\text{:Mn}$. Considering the observed fading, these materials are suitable for dosimetric applications where signal stability is not critical.

CRediT authorship contribution statement

Anderson M.B. Silva: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Patrícia L. Antonio:** Investigation, Formal analysis, Data curation. **Carmen C. Bueno:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Josemary A.C. Gonçalves:** Investigation, Formal analysis. **Divanizia N. Souza:** Writing – review & editing, Validation, Supervision, Funding acquisition, Formal analysis.

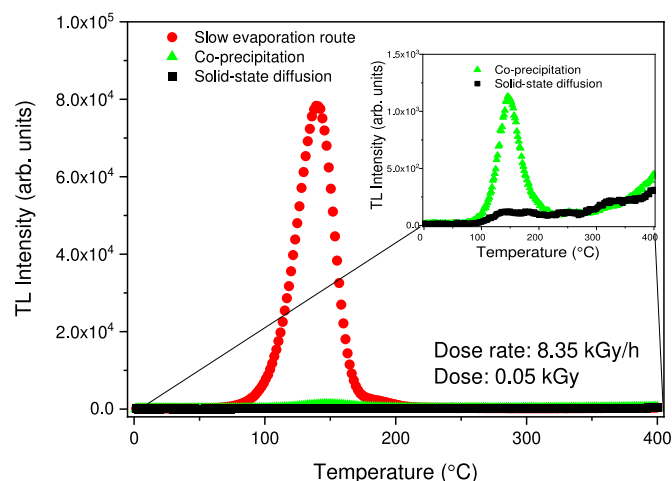


Fig. 10. TL glow curves of $\text{CaSO}_4\text{:Ce,Mn}$ samples prepared by different synthesis methods, irradiated with high-energy photons, to a dose of 50 Gy. TL readouts were performed using both a Schott BG-39 optical filter and a collimator with a 2 mm central aperture. Measurements were carried out 1 h after irradiation.

Linda V.E. Caldas: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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