

Luminescent and dosimetric properties of $\text{CaSO}_4\text{:RE,Mn}$ (RE = Dy, Tb, Tm, Yb, Eu, Ce) phosphors synthesized by the slow evaporation method

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ABSTRACT

This study investigates the luminescent and dosimetric properties of $\text{CaSO}_4\text{:Dy,Mn}$, $\text{CaSO}_4\text{:Tb,Mn}$, $\text{CaSO}_4\text{:Tm,Mn}$, $\text{CaSO}_4\text{:Yb,Mn}$, $\text{CaSO}_4\text{:Eu,Mn}$ and $\text{CaSO}_4\text{:Ce,Mn}$ composites synthesized via the slow evaporation route. Structural and compositional characterization was performed using X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS). The dosimetric performance of the materials was evaluated using Teflon-based pellets through thermoluminescence (TL) glow curve measurements. Additionally, Continuous Wave Optically Stimulated Luminescence (CW-OSL) measurements were conducted to assess their optical stimulation behavior. The TL emission spectra revealed characteristic transitions associated with both RE^{3+} and Mn^{2+} ions, with emission features strongly dependent on the specific dopant. The TL glow curves exhibited well-defined peaks in the UV and visible regions, with Tm,Mn, Dy,Mn and Tb,Mn codoped samples showing enhanced emissions at higher temperatures, a desirable feature for dosimetric applications. CW-OSL measurements demonstrated intense luminescence responses, particularly for the $\text{CaSO}_4\text{:Tm,Mn}$ and $\text{CaSO}_4\text{:Ce,Mn}$ compositions. A comprehensive dosimetric evaluation was conducted, including reproducibility, linearity and signal fading. Among the studied samples, $\text{CaSO}_4\text{:Tm,Mn}$ exhibited the most stable TL response, while $\text{CaSO}_4\text{:Dy,Mn}$ showed the superior OSL signal stability. Overall, the results demonstrate that these newly developed CaSO_4 -based RE,Mn composites possess excellent dosimetric characteristics, highlighting their strong potential as TL/OSL radiation detectors.

1. Introduction

Ionizing radiation dosimetry plays a fundamental role in agriculture, industry, and medicine to ensure compliance with radiation safe exposure limits, particularly for Occupationally Exposed Individuals (OEIs). Among the available techniques, luminescent dosimetry based on thermoluminescence (TL) and optically stimulated luminescence (OSL) are key tools in this field (Yukihara and McKeever, 2011). Current studies in this field have focused on the development and characterization of new luminescent materials for this dosimetry, alongside exploring practical applications for existing ones (Lalic et al., 2019).

Calcium sulfate (CaSO_4) is a well-known host matrix for thermoluminescent detectors (TLDs), especially when doped with rare-earth elements (RE). A systematic study conducted by Lakshmanan (1999)

demonstrated that CaSO_4 doped with lanthanides such as Tm^{3+} and Dy^{3+} exhibits high TL sensitivity, while $\text{CaSO}_4\text{:Tb}$ also showed promising performance despite being less explored at the time. Subsequent studies showed that co-doping strategies could further enhance the dosimetric characteristics of CaSO_4 by increasing the TL sensitivity and stabilizing trapping centers. Junot et al. (2020) reported that the incorporation of silver (Ag) into $\text{CaSO}_4\text{:Eu}$ increased thermally stimulated emission intensity by approximately four times compared to Ag-free samples. Similarly, investigations by Prokić (2000), Wang et al. (2011) and Junot et al. (2024) demonstrated that $\text{CaSO}_4\text{:RE,Li}$ systems exhibit superior thermoluminescent properties compared to singly doped CaSO_4 materials. Despite these advances, the interaction mechanisms between multiple dopants within the CaSO_4 lattice are not yet well understood.

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Recently, the $\text{CaSO}_4\text{:Mn}$, one of the earliest synthetic thermoluminescent dosimeters, has returned to the scientific community's spotlight (Bahl et al., 2017; Silva et al., 2022). Silva et al. (2023) reported that the issues of $\text{CaSO}_4\text{:Mn}$'s low-temperature peak and significant TL signal fading, which led to its previous de-emphasis in research, can be partially mitigated through optimized synthesis routes, such as the slow evaporation method, leading to improved trap stability and reduced fading.

Beyond synthesis optimization, co-doping $\text{CaSO}_4\text{:Mn}$ with rare-earth (RE) ions has emerged as an effective strategy for enhancing its dosimetric. Building on previous work by Silva et al. (2024), it was shown that RE/Mn co-doping, particularly with Tb, results in increased luminescent efficiency and improved signal stability. Compared with single-doped $\text{CaSO}_4\text{:Mn}$ and $\text{CaSO}_4\text{:Tb}$, co-doped samples exhibited enhanced preservation of high-temperature TL components, indicating the formation of deeper and more stable trapping levels.

In this context, the present study aims to systematically investigate and compare the luminescence and dosimetric properties of $\text{CaSO}_4\text{:Dy}$, Mn , $\text{CaSO}_4\text{:Ce,Mn}$, $\text{CaSO}_4\text{:Yb,Mn}$, $\text{CaSO}_4\text{:Eu,Mn}$, $\text{CaSO}_4\text{:Tm,Mn}$, and $\text{CaSO}_4\text{:Tb,Mn}$ composites synthesized via the slow evaporation method, with emphasis on their potential application as TL and OSL radiation detectors.

2. Materials and methods

$\text{CaSO}_4\text{:RE,Mn}$ (RE = Dy, Tb, Tm, Yb, Eu, Ce) samples were synthesized by the slow evaporation method as described by Junot et al. (2016, 2019) and Silva et al. (2020). First, a precursor solution was prepared by dissolving calcium carbonate (CaCO_3) in sulfuric acid (H_2SO_4). Then, dysprosium oxide (Dy_2O_3), terbium oxide (Tb_4O_7), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), europium oxide (Eu_2O_3), and manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were added as dopant sources. The concentration of both RE^{3+} and Mn^{2+} dopants was fixed at 0.1 mol% relative to calcium (Ca), corresponding to an RE:Mn molar ratio of 1:1. The resulting mixture was heated to 375 °C using a heating mantle and maintained at this temperature until complete evaporation of the acid. After cooling to room temperature, the solid product was washed with distilled water, ground, sieved, and finally calcined at 600 °C for 1 h.

Structural characterization was performed using X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS). XRD patterns were obtained with a Rigaku RINT 2000/PC diffractometer using $\text{Cu-K}\alpha$ radiation (60 kV, 30 mA) over the 20°–80° (2 θ) range with a step size of 0.02° (2 θ). Phase identification was conducted by comparison with the JCPDS reference card no. 01-072-0916. Elemental composition and dopant incorporation were verified by EDS analysis using a JSM-IT700HR system, allowing assessment of compositional homogeneity and detection of possible impurities.

For luminescence characterization, the synthesized powders were mixed with polytetrafluoroethylene (PTFE) to enhance mechanical stability and facilitate handling. Pellets (~30 mg, 6 mm in diameter) were formed under a uniaxial pressure of 0.5 ton and sintered at 400 °C for 1 h. Thermoluminescence (TL) and optically stimulated luminescence (OSL) measurements were conducted using a Risø DA-20 TL/OSL reader. Luminescence signals were detected with a bialkali photomultiplier tube (Electron Tubes, 9235QB). Irradiations were carried out using a $^{90}\text{Sr}/^{90}\text{Y}$ beta source ($E_{\text{max}} = 2.27$ MeV), delivering a dose rate of ~4.33 Gy min^{-1} .

TL glow curves were recorded by heating the samples from room temperature up to 400 °C at a constant rate of 5 °C s^{-1} under nitrogen atmosphere. To control the spectral response and minimize scattered light, a Schott BG-39 bandpass filter (330–600 nm) was used for visible emissions; while a Hoya U-340 filter (270–380 nm) was used for ultraviolet emissions. OSL measurements were conducted in continuous-wave (CW-OSL) using optical stimulation provided by blue LEDs (470 nm, FWHM $\approx$ 30 nm) with power density of ~90 mW cm^{-2} , with the luminescence signal detected through a Hoya U-340 bandpass filter to

selectively measure ultraviolet emissions and suppress contributions from the stimulation light.

For the fading studies, irradiated pellets were placed on acrylic holders, stored at room temperature under ambient laboratory humidity, protected from light and without any additional thermal or optical stimulation. After each TL or OSL run, the pellets were annealed at 400 °C for 1 h in a 671 IRD/CNEN furnace to restore their dosimetric properties for reuse.

3. Results and discussion

3.1. Structural and elemental characterization

The XRD patterns presented in Fig. 1 demonstrate that all $\text{CaSO}_4\text{:RE}$, Mn samples crystallize in a single orthorhombic phase, in agreement with reference data from the JCPDS card no. 01-072-0916. The absence of additional diffraction peaks associated with secondary phases, such as RE- or Mn-rich oxides or sulfates, indicates that the dopants are incorporated into the CaSO_4 lattice without inducing phase segregation. This suggests that the relatively low dopant concentration (0.1 mol% for each dopant) does not introduce detectable lattice distortion at the resolution of conventional XRD. Given the difference in ionic radii between Ca^{2+} and the $\text{RE}^{3+}/\text{Mn}^{2+}$ ions, the absence of structural perturbations implies that charge compensation mechanisms, likely involving point defects such as cation vacancies or interstitials, occur without disrupting the long-range crystallographic order. This result confirms that the slow evaporation synthesis route is effective in producing structurally homogeneous CaSO_4 -based phosphors, even in the presence of dual dopants.

The elemental compositional analysis obtained by EDS (Fig. 2a–f) further supports the successful incorporation of the intended dopants into the CaSO_4 host matrix. In all samples, the characteristic peaks of Ca, S, and O were detected, confirming the CaSO_4 host structure. Furthermore, the dopant elements were successfully identified in each sample: Eu and Mn in Fig. 2a, Ce and Mn in Fig. 2b, Tb and Mn in Fig. 2c, Tm and Mn in Fig. 2d, Yb and Mn in Fig. 2e, and Dy and Mn in Fig. 2f. No additional impurity peaks were observed in the EDS spectra, confirming the chemical purity of the synthesized materials. The absence of extraneous elemental signals indicates high chemical purity and excludes contamination effects that could otherwise influence the luminescent response. In addition, the elemental mapping images shown in Fig. 2 provide additional insight into dopant distribution. The homogeneous spatial distribution of Mn and RE ions suggests that the dopants are well dispersed within the host matrix rather than forming clusters or segregated regions. This uniformity is particularly important for luminescent dosimeters, as dopant clustering can lead to concentration quenching,

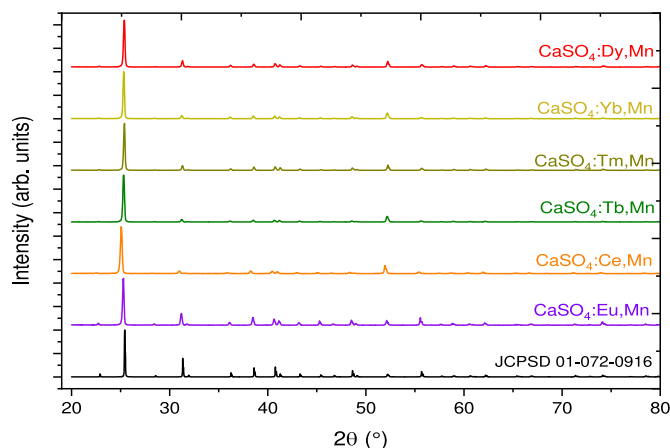


Fig. 1. X-ray diffractograms of crystalline samples of $\text{CaSO}_4\text{:RE,Mn}$ (RE = Dy, Tb, Tm, Yb, Eu, Ce).

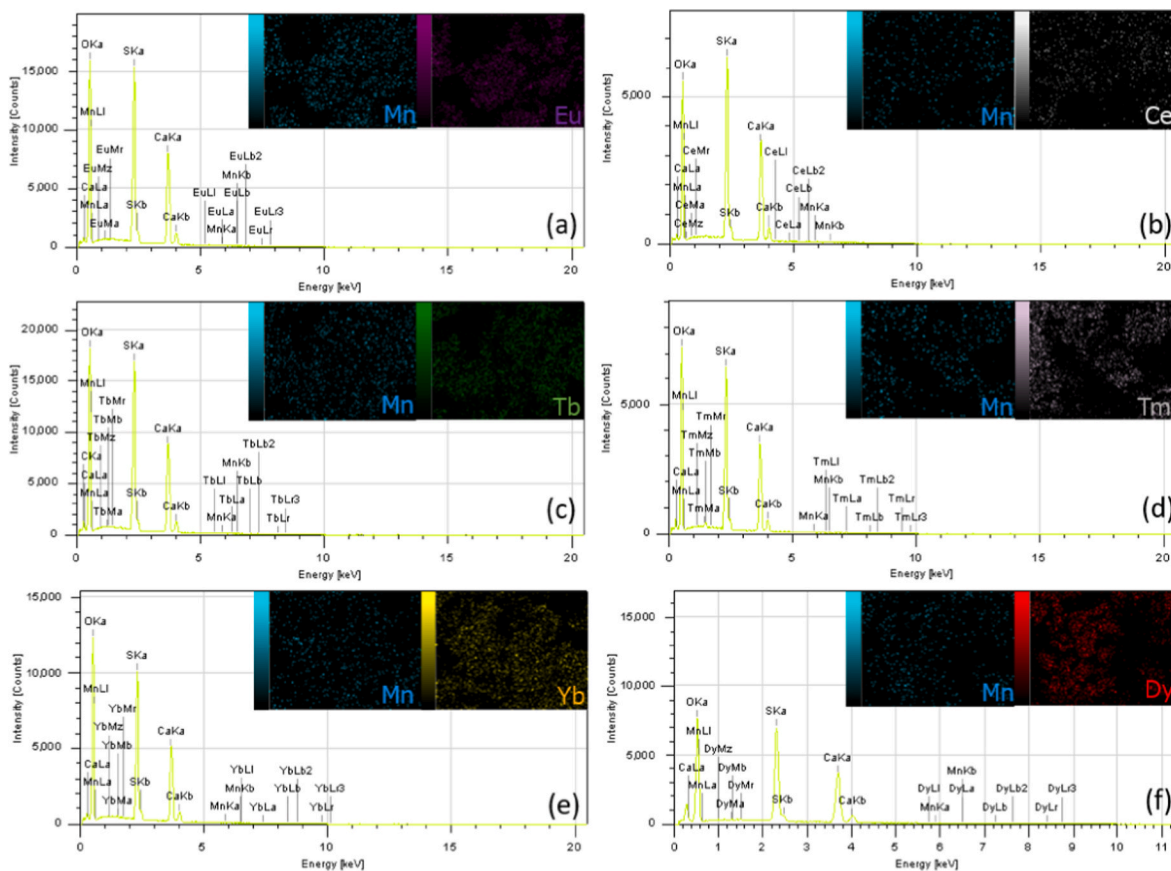


Fig. 2. EDS spectra of CaSO_4 samples doped with different ions: (a) $\text{CaSO}_4\text{:Eu,Mn}$, (b) $\text{CaSO}_4\text{:Ce,Mn}$, (c) $\text{CaSO}_4\text{:Tb,Mn}$, (d) $\text{CaSO}_4\text{:Tm,Mn}$, (e) $\text{CaSO}_4\text{:Yb,Mn}$ and (f) $\text{CaSO}_4\text{:Dy,Mn}$.

non-radiative recombination centers, or unstable trapping sites.

Although EDS is a semi-quantitative technique and has limited sensitivity at low dopant concentrations, the consistent detection of both Mn and RE signals across all samples confirms the reproducibility of the synthesis procedure. Combined with the XRD results, the structural and elemental analyses indicate that the CaSO_4 lattice acts as a host capable of accommodating multiple dopants while maintaining crystallographic integrity.

3.2. Thermoluminescence and optically stimulated luminescence

Fig. 3 shows the TL emission spectra of $\text{CaSO}_4\text{:RE,Mn}$ samples presented in a 3D representation (TL intensity versus wavelength and temperature). A common feature observed in all samples is the presence of a visible band centered at ~ 500 nm, corresponding to the $^4\text{T}_1 \rightarrow ^6\text{A}_1$ transition of Mn^{2+} ions (Luchechko et al., 2019; Menon et al., 2005; Zahedifar et al., 2011). The persistence of this band across a wide temperature range confirms the role of Mn^{2+} as a dominant luminescent center in the CaSO_4 matrix. For the Dy doped sample (Fig. 3a), the emission lines are attributed to Dy^{3+} transitions: $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (~ 480 nm) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (~ 570 nm), with additional weaker emissions at ~ 660 nm and ~ 750 nm assigned to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{9/2}$ transitions, respectively (Kano, 1999). A strong near-infrared emission band in the 900–1000 nm region is observed of in the Yb doped sample (Fig. 3b), corresponding to the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of Yb^{3+} ions (Huang et al., 2016).

Fig. 3c shows that the Tm doped sample exhibits emissions with the main band at 455 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_4$), accompanied by weaker bands at 348 nm ($^1\text{I}_6 \rightarrow ^3\text{F}_4$), 355 nm ($^1\text{D}_2 \rightarrow ^3\text{H}_6$), 482 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$), and 788 nm ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) (Junot et al., 2024). For the Tb doped sample (Fig. 3d), the most intense emission occurs at 544 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$). Additional weaker

transitions are detected at 378 nm ($^5\text{D}_3 \rightarrow ^7\text{F}_6$), 412 nm ($^5\text{D}_3 \rightarrow ^7\text{F}_5$), 435 nm ($^5\text{D}_3 \rightarrow ^7\text{F}_4$), 453 nm ($^5\text{D}_3 \rightarrow ^7\text{F}_3$), 470 nm ($^5\text{D}_3 \rightarrow ^7\text{F}_2$), 488 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 586 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$), 619 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$), and 653 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_2$).

The Ce doped sample (Fig. 3e) presents emission bands in the 290–340 nm region, associated with the permitted $5\text{d} \rightarrow ^2\text{F}_{5/2}$ and $5\text{d} \rightarrow ^2\text{F}_{7/2}$ transitions of Ce^{3+} ions. The emission in the infrared region (900–1000 nm) over 350 °C is related to the incandescence of the heating plate. Finally, for the Eu doped sample (Fig. 3f), a broad band between 450 and 580 nm is observed, superimposed with the Mn^{2+} emission at ~ 497 nm ($^4\text{T}_1 \rightarrow ^6\text{A}_1$). One could attribute the 450–580 nm emission to the $\text{Eu}^{2+} 4\text{f}^6 5\text{d}^1 \rightarrow 4\text{f}^7$ transition, as it is consistent with the presence of a single low-temperature TL peak at around 150 °C. According to Bastani et al. (2019), low-temperature TL peaks in Eu-doped CaSO_4 are commonly associated with Eu^{2+} -related recombination processes. In the present material, however, the emission in this temperature region involves overlapping Eu^{2+} and Mn^{2+} related transitions. Furthermore, in Eu^{2+} -doped samples, the energy of the $4\text{f}^6 5\text{d}^1$ excited state is strongly influenced by the interaction of the 5d electron with the host material's surrounding ions (crystal field splitting). The stronger this interaction, the further the emission band shifts to longer wavelengths (redshift) (Dorenbos, 2003). Although numerous studies report Eu^{2+} emission in CaSO_4 matrices at ~ 385 nm (Mandlik et al., 2020; Junot et al., 2020; Guckan et al., 2023), such a signal was not observed in the samples produced here. Therefore, an exclusive attribution of the observed band to Eu^{2+} cannot be conclusively established, and overlapping Mn^{2+} transitions likely play a substantial role.

Overall, the TL emission maps clearly demonstrate that RE/Mn codoping enables fine control over the recombination pathways in CaSO_4 -based phosphors. The presence of intense RE-specific emissions at elevated temperatures, particularly for Tm^{3+} , Tb^{3+} , and Dy^{3+} ,

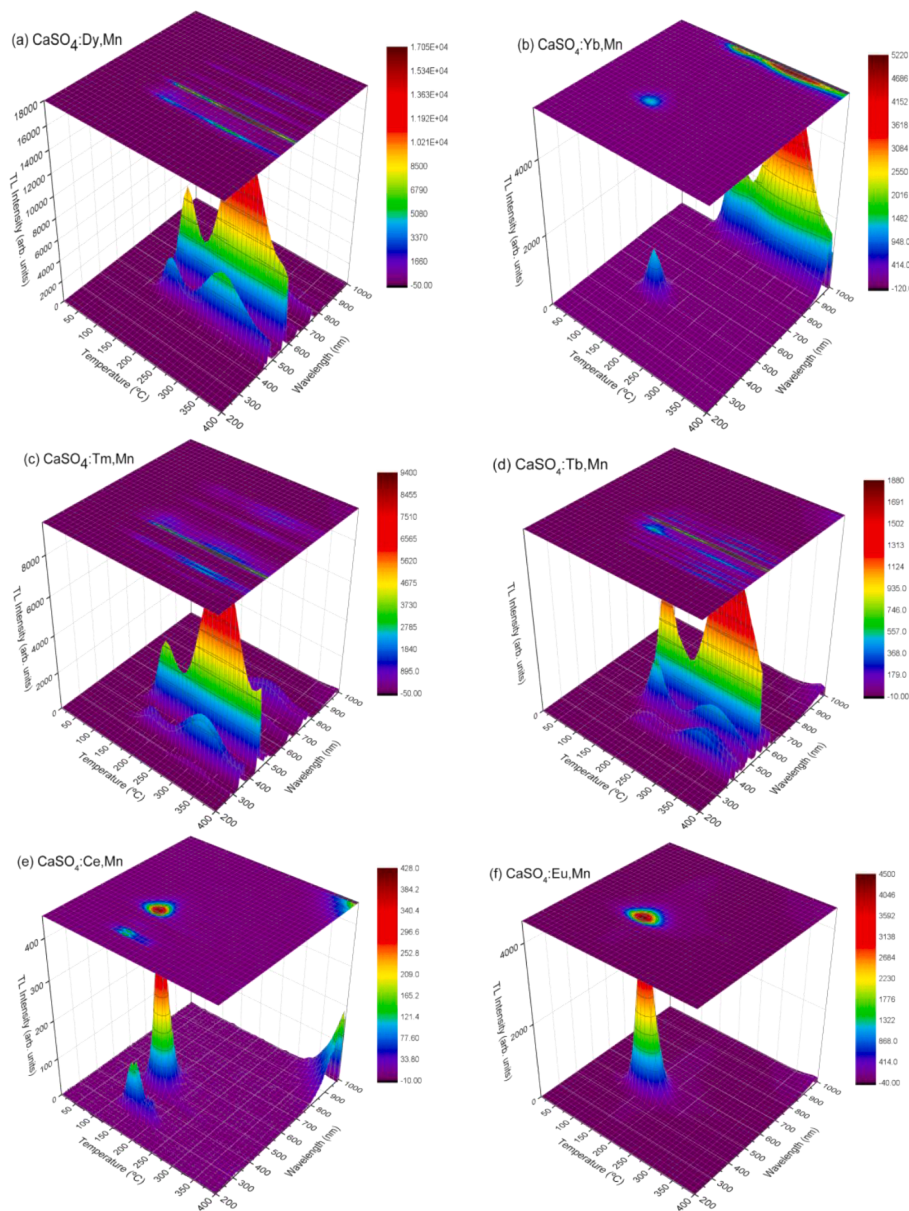


Fig. 3. TL emission spectra of the $\text{CaSO}_4\text{:RE,Mn}$ (RE = Dy, Tb, Tm, Yb, Eu, Ce) samples after irradiation with 100 Gy ($^{90}\text{Sr}/^{90}\text{Y}$).

indicates the formation of deeper and more stable trapping centers, which are essential for high-performance dosimetric materials.

Fig. 4 shows the TL glow curves of $\text{CaSO}_4\text{:RE,Mn}$ samples irradiated with a beta dose of 500 mGy, recorded using two distinct optical filters: Hoya U-340 (UV region) and Schott BG-39 (visible region). The use of different filters allows selective observation of recombination pathways associated with specific luminescent centers, providing deeper insight into the trap structure and recombination mechanisms induced by RE/Mn co-doping. Fig. 4 clearly demonstrates that the incorporation of different rare-earth co-dopants results in pronounced variations in the TL glow curves in terms of intensity, shape and the position of the TL peak temperatures. In the UV region, only the $\text{CaSO}_4\text{:Tb,Mn}$ and $\text{CaSO}_4\text{:Tm,Mn}$ samples exhibited significant peaks. This behavior is consistent with the TL emission spectra discussed previously, where Tb^{3+} and Tm^{3+} exhibit strong UV and blue emissions associated with specific intra-4f transitions. In the visible region (Fig. 4b), the TL glow curves of the $\text{CaSO}_4\text{:Dy,Mn}$, $\text{CaSO}_4\text{:Tb,Mn}$, and $\text{CaSO}_4\text{:Tm,Mn}$ samples exhibit intense and well-resolved peaks that are shifted toward higher temperatures. These shifts are associated with deeper and more thermally

stable trapping centers, which are less susceptible to spontaneous charge release at room temperature. This characteristic is particularly advantageous for dosimetric applications, as it minimizes signal fading during storage and enhances the reliability of dose reconstruction.

From a dosimetric perspective, the observed glow curve characteristics align well with established criteria for thermoluminescent materials. According to McKeever et al. (1995), an optimal dosimetric peak should correspond to a single, well-defined peak in the 200–300 °C temperature range, balancing thermal stability and readout efficiency. In this context, the $\text{CaSO}_4\text{:Dy,Mn}$, $\text{CaSO}_4\text{:Tb,Mn}$, and $\text{CaSO}_4\text{:Tm,Mn}$ compositions meet these requirements most effectively, exhibiting intense, stable, and suitably positioned TL peaks.

Fig. 5 presents the relative TL intensities of the different samples recorded with both UV (Hoya U-340) and visible (Schott BG-39) transmitting filters. The results clearly demonstrate that both the magnitude and the spectral distribution of the TL signal strongly depend on the nature of the rare-earth co-dopant. In the UV region, the $\text{CaSO}_4\text{:Tm,Mn}$ sample exhibited the highest TL intensity among all investigated compositions. This behavior is consistent with the TL emission spectra

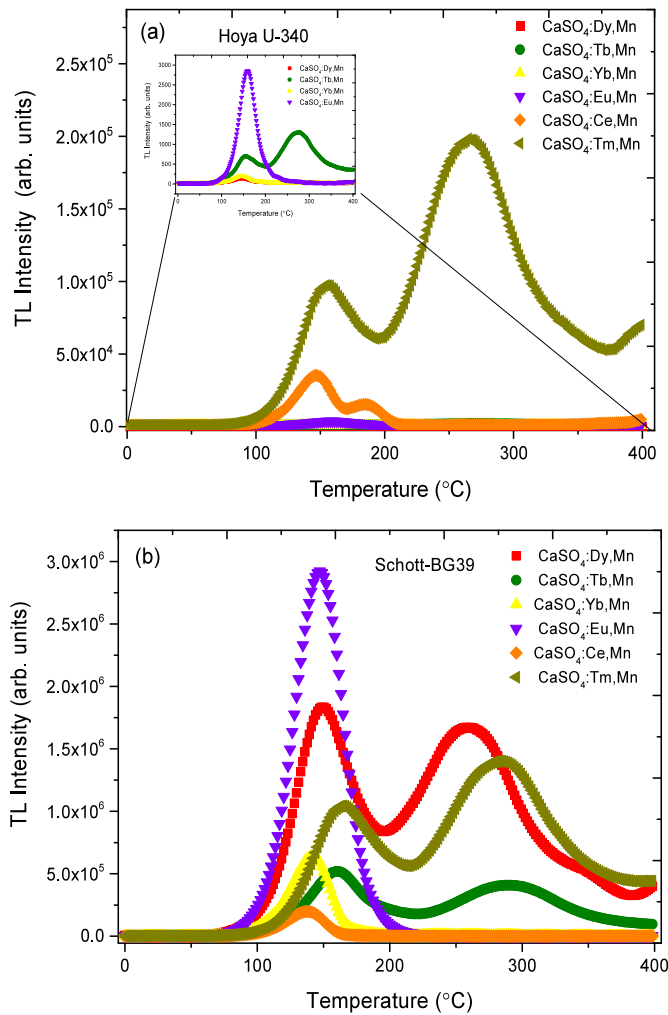


Fig. 4. TL glow curves of the $\text{CaSO}_4\text{:RE,Mn}$ samples irradiated with 500 mGy of beta radiation, recorded using: (a) a Hoya U-340 optical filter (270–380 nm transmission) and (b) a Schott BG-39 optical filter (330–600 nm transmission).

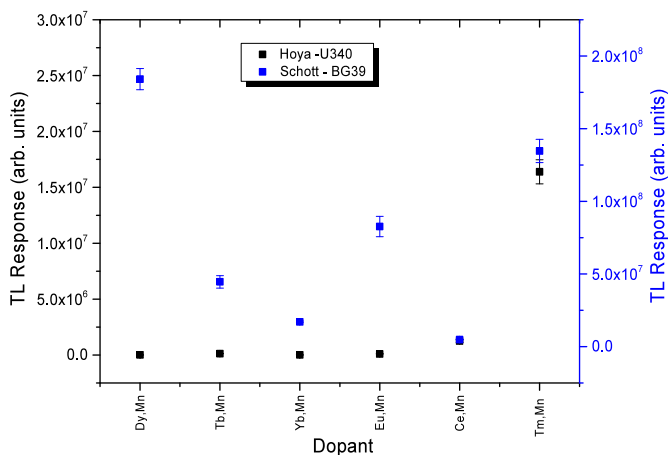


Fig. 5. TL signal obtained by integrating the area under the emission curve of the $\text{CaSO}_4\text{:RE,Mn}$ samples irradiated with 500 mGy using Schott BG-39 (visible range) and Hoya U-340 (UV range) optical filters.

(Fig. 3) and glow curves (Fig. 4a), which show strong UV and blue emissions from Tm^{3+} transitions persisting up to relatively high temperatures. In the visible range, the $\text{CaSO}_4\text{:Dy,Mn}$ and $\text{CaSO}_4\text{:Tm,Mn}$

samples showed the strongest intensities. This observation is in good agreement with previous reports, such as those by Bastani et al. (2019), who reported enhanced thermoluminescent emission in the visible region for Dy^{3+} and Tm^{3+} activated CaSO_4 based phosphors. Additionally, the $\text{CaSO}_4\text{:Eu,Mn}$ sample also exhibited a high TL intensity in the present study, despite its peak occurring at lower temperatures. This suggests that Eu-related recombination processes, possibly involving Eu^{2+} -associated centers and overlapping Mn^{2+} emission, are highly radiative, even though they are linked to shallower trapping levels.

The beneficial effect of Mn^{2+} co-doping is particularly evident in the $\text{CaSO}_4\text{:Tm,Mn}$ composition. Compared to singly doped $\text{CaSO}_4\text{:Tm}$ reported in the literature (Junot et al., 2024), the introduction of Mn^{2+} leads to a substantial enhancement of both UV and visible TL intensities. This enhancement can be attributed to Mn^{2+} acting as an efficient recombination center, as well as to its role in modifying the trap structure by promoting the formation of deeper and more stable trapping levels through defect complex formation.

Fig. 6a presents the CW-OSL decay curves of the $\text{CaSO}_4\text{:RE,Mn}$ samples, recorded with a 40 s stimulation period. The decay profiles clearly reveal that both the intensity and the temporal behavior of the OSL signal are strongly dependent on the nature of the rare-earth co-dopant, reflecting differences in trap depth, optical cross section, and recombination pathways. Among the investigated compositions, $\text{CaSO}_4\text{:}$

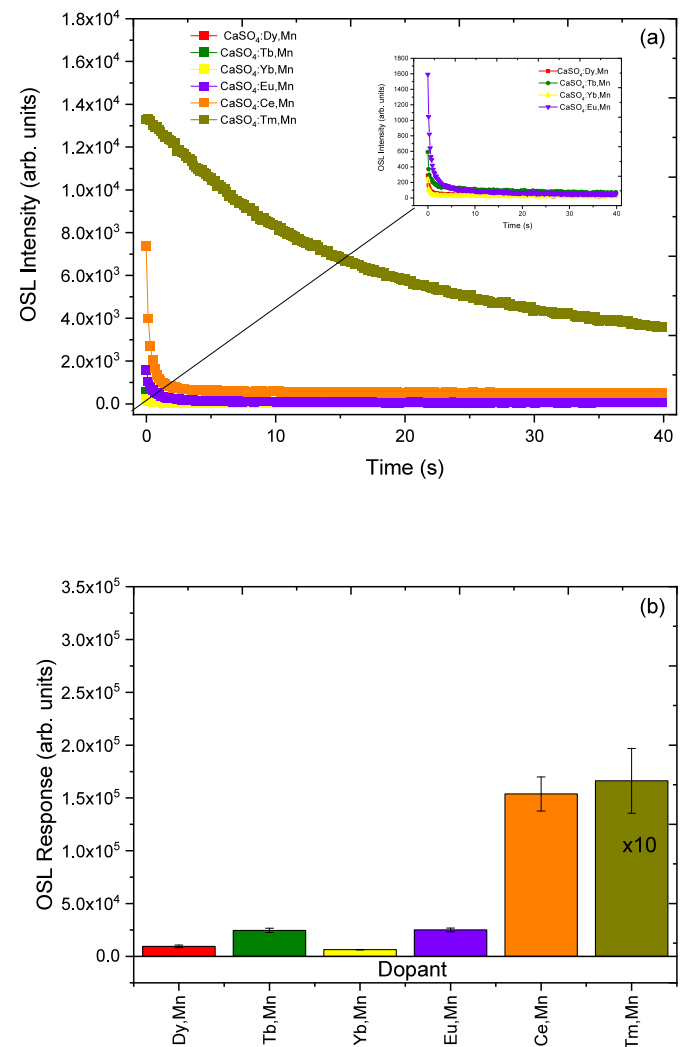


Fig. 6. (a) CW-OSL decay curves of the $\text{CaSO}_4\text{:RE,Mn}$ samples irradiated with 500 mGy. (b) Corresponding integrated OSL signals recorded with a Hoya U-340 filter.

Tm,Mn exhibits by far the most intense and persistent OSL response, followed by $\text{CaSO}_4\text{:Ce,Mn}$. This trend is consistent with the TL emission profiles obtained with the Hoya U-340 filter, indicating a correlation between TL and OSL responses for these compositions. Such consistency suggests that, for these compositions, the same population of deep traps contributes significantly to both thermally and optically stimulated recombination processes. The CW-OSL decay curves exhibit a characteristic non-linear, quasi-exponential behavior, which is commonly associated with the progressive depletion of optically active traps under constant stimulation (Yukihara and McKeever, 2011).

Interestingly, the $\text{CaSO}_4\text{:Tm,Mn}$ sample did not show a predominant fast decay component typically associated with shallow traps that are easily emptied at the onset of optical stimulation. Instead, the decay profile is governed by a slower component, associated with prolonged signal persistence. This suggests that the traps responsible for the luminescent centers in this material are not easily stimulated by blue LED excitation, which points to the presence of deeper or more stable trap distributions. Fig. 6b provides a quantitative comparison of the OSL responses through the integrated area under the decay curves, highlighting the pronounced dependence of OSL efficiency on dopant selection. The integrated OSL signal of $\text{CaSO}_4\text{:Tm,Mn}$ is an order of magnitude higher than that of most other compositions, reinforcing its outstanding performance as an OSL detector. $\text{CaSO}_4\text{:Ce,Mn}$ also shows a significant integrated response, likely due to the efficient optical excitation of Ce-related centers and possible energy transfer involving Mn^{2+} .

3.3. Reusability, fading, and linearity

In radiation dosimetry, an essential requirement is that TL/OSL dosimeters be reusable. This means that under identical irradiation and measurement conditions they should yield consistent responses over repeated cycles. Fig. 7 summarizes the reusability performance of the $\text{CaSO}_4\text{:RE,Mn}$ pellets over five consecutive cycles, each consisting of irradiation with a 0.5 Gy beta dose, evaluated through integrated TL signals measured with the Schott BG-39 (visible) and Hoya U-340 (UV)

filters, as well as through normalized OSL responses. Each data point represents the average of five pellets, and error bars correspond to the experimental standard deviations.

The TL results obtained with the Schott BG-39 filter (Fig. 7a) demonstrate that all investigated compositions maintain stable visible TL responses throughout the cycling process. Similarly, the TL responses recorded with the Hoya U-340 filter (Fig. 7b) exhibit good reproducibility in the ultraviolet region. This stability suggests that the annealing protocol at 400 °C for 1 h is effective in restoring the initial trap population without inducing permanent structural or chemical modifications in the phosphors. The normalized OSL responses shown in Fig. 7c further corroborate the excellent reusability of the $\text{CaSO}_4\text{:RE,Mn}$ samples. All compositions display nearly constant OSL signals over the five cycles, with no evidence of cumulative signal loss or sensitivity change. Quantitatively, all samples exhibit coefficients of variation (CV) below 10 % for both TL and OSL measurements, which is well within the acceptable limits for practical dosimetric materials. These results confirm the good reproducibility and reusability of the synthesized phosphors over repeated irradiation and readout cycles.

Fig. 8 shows the integrated TL/OSL responses of the $\text{CaSO}_4\text{:RE,Mn}$ pellets as a function of the beta dose ranges. Each data point represents the average of three pellets, and the error bars indicate the corresponding standard deviations. For the TL measurements (Fig. 8a), all samples exhibited a linear response in the absorbed dose range from 0.1 up to ~50 Gy, with correlation coefficients ranging from $R^2 = 0.985$ to 0.999. These high linearity values confirm that the trapping and recombination mechanisms remain stable over this dose interval and that no significant saturation of trapping centers occurs. The upper dose limit of 50 Gy is imposed by the high sensitivity of the material combined with limitations of the reader system. In the case of OSL (Fig. 8b), the response remained linear up to ~100 Gy, with correlation coefficients between $R^2 = 0.970$ and 0.998. Despite the overall linear behavior, notable differences in OSL sensitivity are observed among the different compositions, as reflected by the slopes of the dose–response curves. Specifically, the $\text{CaSO}_4\text{:Eu,Mn}$ and $\text{CaSO}_4\text{:Tb,Mn}$ samples

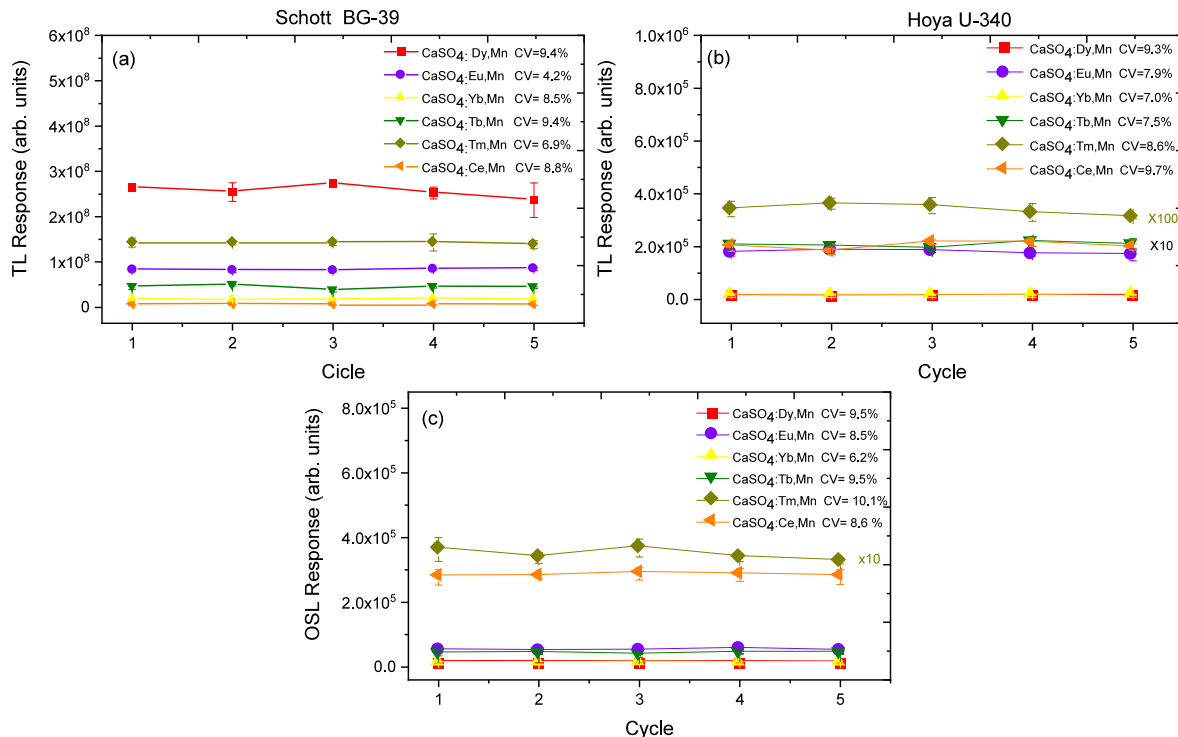


Fig. 7. Reusability of $\text{CaSO}_4\text{:RE,Mn}$ pellets over five irradiation–readout–annealing cycles (0.5 Gy). (a) TL response measured with the Schott BG-39 filter. (b) TL response measured with the Hoya U-340 filter. (c) Normalized CW-OSL response as a function of cycle number. Error bars represent standard deviations. The coefficient of variation (CV) for each sample is indicated in caption.

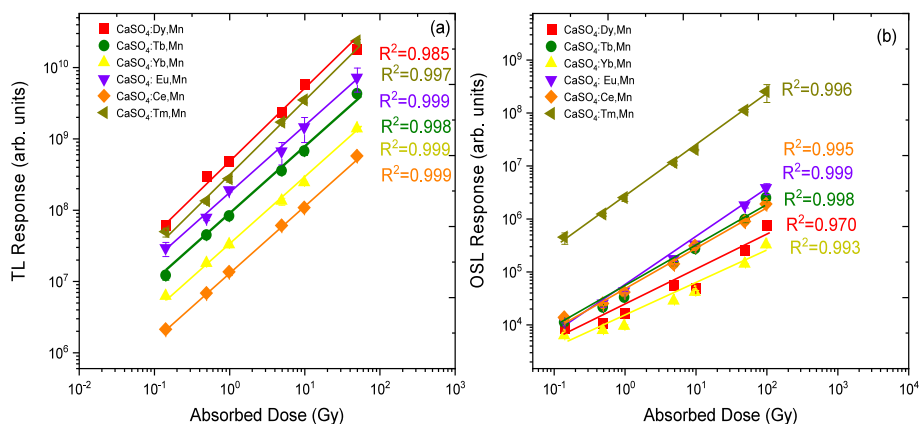


Fig. 8. Dose–response curves of CaSO₄:RE,Mn pellets under beta irradiation. (a) Integrated TL response in the 0.1–50 Gy dose range. (b) Integrated OSL response in the 0.1–100 Gy dose range. Solid lines indicate linear fits.

display steeper slopes than CaSO₄:Ce,Mn, indicating higher OSL sensitivity at increasing radiation doses. This enhanced sensitivity can be attributed to more efficient recombination pathways involving Eu- and Tb-related luminescent centers, as well as to differences in trap depth and optical stimulation cross sections introduced by the specific RE/Mn co-doping combinations. Overall, the demonstrated linear TL response up to 50 Gy and linear OSL response up to 100 Gy, together with high correlation coefficients and reproducible behavior, confirm that CaSO₄:RE,Mn phosphors are well suited for beta radiation dosimetry over a broad dose range.

Fig. 9 shows the fading behavior of the TL and OSL signals of CaSO₄:RE,Mn samples by comparing measurements performed immediately after beta irradiation with those obtained after 30 days of storage at room temperature. The black bars correspond to the normalized signals

measured immediately after irradiation (reference = 1.0), while the red and blue bars represent the TL signals measured after 30 days using Schott BG-39 and Hoya U-340 filters, respectively. The magenta bars depict the corresponding OSL signals.

To quantitatively evaluate TL fading, the integrated area under the glow curves was used instead of the peak height. The glow curves were divided into low-temperature (0–200 °C) and high-temperature (200–400 °C) regions, which are commonly associated with shallow and deep traps, respectively. Overall, the high-temperature TL components exhibited less fading, indicating stability of the charge carriers in the traps throughout the storage period. In contrast, the low-temperature TL components exhibited more pronounced signal loss. Consequently, materials with dominant high-temperature TL peaks are more suitable for long-term dosimetric applications. Among the

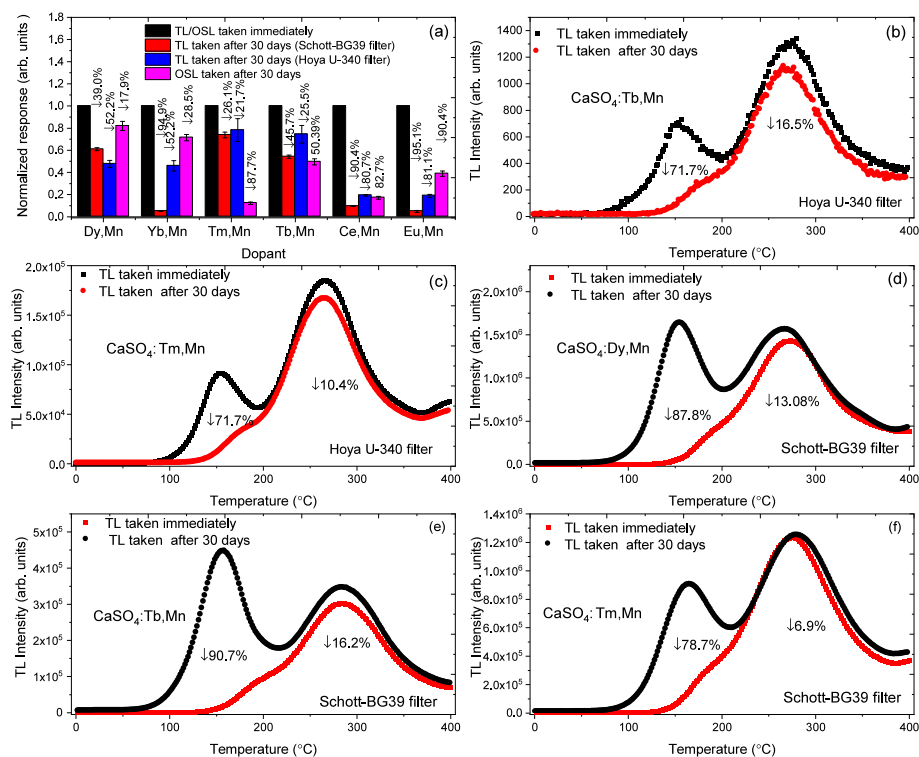


Fig. 9. Fading of TL and OSL signals of CaSO₄:RE,Mn samples after beta irradiation. (a) Normalized TL and OSL intensities immediately after irradiation (black) and after 30 days with Schott BG-39 (red) and Hoya U-340 (blue) filters; OSL signals after 30 days are shown in magenta. (b–f) TL glow curves for CaSO₄:Tb,Mn, CaSO₄:Tm,Mn, and CaSO₄:Dy,Mn immediately after irradiation (black) and after 30 days (red) using different filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

investigated compositions, $\text{CaSO}_4\text{:Tm,Mn}$, $\text{CaSO}_4\text{:Tb,Mn}$, and $\text{CaSO}_4\text{:Dy,Mn}$ samples demonstrated the highest TL stability in both the visible and UV spectral regions. This behavior is consistent with the TL glow-curve analysis and emission spectra discussed earlier, which showed pronounced high-temperature peaks and RE-specific emissions persisting at elevated temperatures. The OSL fading results confirmed that $\text{CaSO}_4\text{:Dy,Mn}$ and $\text{CaSO}_4\text{:Yb,Mn}$ samples exhibited the highest OSL signal stability after 30 days. This suggests that the optically active traps in these materials are deeper or have lower optical stimulation cross sections, making them less susceptible to spontaneous charge loss during storage. These results indicate that rare-earth co-doping with manganese promotes the formation of deeper and more stable traps, increases the concentration of charge carriers, thereby enhancing the long-term stability of both TL and OSL signals.

4. Conclusions

Calcium sulfate phosphors co-doped with rare-earth ions (RE = Dy, Tb, Tm, Yb, Eu, Ce) and manganese were synthesized via the slow evaporation method and evaluated for radiation dosimetry applications. X-ray diffraction confirmed the formation of a single-phase CaSO_4 crystal with an orthorhombic crystal structure for all compositions, while EDS analyses confirmed the effective incorporation of RE and Mn dopants without the presence of secondary phases or impurities, attesting to the chemical and structural homogeneity of the materials. The TL and OSL investigations revealed that the dosimetric performance of CaSO_4 is strongly dependent on the specific rare-earth co-dopant. RE/Mn co-doping significantly modifies the trap structure and recombination pathways, leading to marked differences in emission spectra, glow-curve characteristics, sensitivity, and signal stability. In particular, $\text{CaSO}_4\text{:Tm,Mn}$, $\text{CaSO}_4\text{:Dy,Mn}$, and $\text{CaSO}_4\text{:Tb,Mn}$ exhibited well-defined TL peaks at higher temperatures, indicating the presence of deep and thermally stable traps that are desirable for reliable dosimetry. These compositions also showed enhanced OSL responses with good temporal stability. All investigated samples showed good luminescent reproducibility and reusability, with coefficients of variation below acceptable dosimetric limits, as well as a linear TL and OSL dose–response behavior over a wide beta dose range. Fading studies further revealed that RE co-doping effectively suppresses the pronounced signal loss typically observed in $\text{CaSO}_4\text{:Mn}$, particularly for high-temperature TL components. Among the studied materials, $\text{CaSO}_4\text{:Tm,Mn}$ exhibited the most stable TL response, whereas $\text{CaSO}_4\text{:Dy,Mn}$ demonstrated superior OSL signal stability, highlighting their complementary strengths depending on the readout technique. Overall, these results confirm that rare-earth and manganese co-doped CaSO_4 phosphors constitute a versatile and promising class of TL/OSL dosimetric materials. Nevertheless, further studies addressing additional dosimetric parameters are required to fully establish their practical applicability in routine radiation monitoring.

CRedit authorship contribution statement

Anderson M.B. Silva: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Danilo O. Junot:** Writing – review & editing, Visualization, Validation, Investigation. **Neilo M. Trindade:** Conceptualization, Validation, Visualization, Writing – review & editing. **Divanizia N. Souza:** Writing – review & editing, Visualization, Resources, Project administration, Funding acquisition, Formal analysis. **Linda V.E. Caldas:** Visualization, Supervision, Resources, Project administration, Funding acquisition.

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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