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Solid-state synthesized HAP and β-TCP phosphors doped with lanthanides for thermoluminescent dosimetry

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HIGHLIGHTS

- HAP and β-TCP were synthesized by the solid-state method and doped with Ce, La, Gd, and Dy ions.
- TL properties of the samples were investigated in the high-dose range of 20-1500 Gy under gamma irradiation.
- β-TCP samples generally exhibited superior thermoluminescence response compared with HAP samples.
- HAP doped with 2% Ce and β-TCP doped with 1% and 3% Dy showed the best dosimetric performance.
- Lanthanum and gadolinium dopants showed minimal improvement in the thermoluminescence properties.

ABSTRACT

Calcium phosphates are promising candidates for thermoluminescent dosimetry due to their capacity to host dopants that enhance the thermoluminescent (TL) response, their similarity to bone mineral composition, favorable synthesis conditions, and the flexibility of available synthesis methods. Optimizing the TL response of these materials is a central objective in thermoluminescence research. In this study, hydroxyapatite (HAP) and -tricalcium phosphate (β-TCP) were synthesized via a solid-state method and doped with cerium (Ce), lanthanum (La), gadolinium (Gd), and dysprosium (Dy) at molar concentrations of 1%, 2%, and 3%. The samples were irradiated over a dose range of 20-1500 Gy, relevant for industrial and agricultural applications, and evaluated in terms of sensitivity, linear dose-response range, and glow-curve characteristics. The results indicate that β-TCP generally exhibits superior TL response compared to HAP. Notably, HAP doped with 2% Ce and -TCP doped with 1% and 3% Dy were identified as optimal compositions. Lanthanum and gadolinium doping had minimal impact on the TL properties of HAP. Overall, while HAP provides a favorable structural framework for dopant incorporation, the highest-performing samples were observed in the β-TCP series.

KEYWORDS

Thermoluminescence
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1 Introduction

The widespread use of nuclear technology in energy, industry, medicine, agriculture, and scientific research highlights the importance of accurate measurement of ionizing and non-ionizing radiation doses. Precise dosimetry is essential for assessing radiation-related risks and ensuring accurate dose delivery to target materials or organs in industrial and therapeutic applications. Therefore, dosimetry plays a fundamental role in radiation protection and in the safe and effective implementation of radiation-based practices (IAEA, 2004; Alencar, 2009). A variety of dosimetric techniques are available, among which thermoluminescent dosimeters (TLDs) have received considerable attention because of their high sensitivity, small size, reusability, and ease of use. TLDs can operate over a broad dose range and do not require electrical connections during irradiation, which makes them suitable for personal, environmental, and clinical radiation monitoring. Their resistance to common environmental factors and cost-effectiveness further support their widespread use (**??**).

Thermoluminescence is typically represented by a glow curve containing one or more peaks, which describe the variation of emitted light intensity with temperature. These peaks are associated with the release of trapped charge carriers from different energy levels within the material. The main peak, usually the most intense one, is generally more stable and less affected by fading, and is therefore commonly used for dose evaluation (Bakr and

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Omer, 2020; Pagonis and Kitis, 2012; Alam and Bauk, 2010).

Thermoluminescent dosimetric materials are generally insulators or semiconductors, since suitable charge trapping and luminescent behavior are not expected in highly conductive metals. Many TL materials exhibit first-order kinetic behavior, although higher-order kinetics have also been reported. In first-order systems, the peak temperature (Tm) remains nearly constant over a broad dose range, and the overall glow-curve shape does not change systematically with dose (Fernández et al., 2016; Furetta, 2010; Jones, 1996; Kry et al., 2020; Obryk et al., 2014; Pagonis and Kitis, 2012).

Various sulfate, sulfide, fluoride, phosphate, and halophosphate compounds have been investigated as thermoluminescent materials because of their favorable luminescent and trapping properties. Among them, calcium phosphates are of particular interest due to their compositional and structural similarity to the mineral phase of bone, which makes them promising biocompatible dosimeters for medical and biological radiation monitoring (Chand et al., 2021, 2022; Madhukumar et al., 2007).

Calcium phosphates, particularly hydroxyapatite and its derivatives, have attracted considerable interest because of their excellent biocompatibility and structural similarity to natural bone mineral. In addition to their established use in medical and dental applications, these materials have also been investigated for dosimetric purposes, especially in view of the widespread use of X-rays in diagnosis and therapy. Their favorable luminescent and trapping properties have further supported their application in retrospective dosimetry for reconstructing past radiation exposures (Barrera-Villatoro et al., 2018; Chand et al., 2022; Daneshvar et al., 2019b, 2020, 2019a; Ghovvati and Manouchehri, 2014; Islam et al., 2017; Madhukumar et al., 2007; Shafaei et al., 2016; Taghipour et al., 2022).

β-Tricalcium phosphate (β-TCP) is a promising calcium phosphate material due to its biocompatibility, thermal stability, and structural capacity to incorporate impurity ions. These characteristics make it an effective host for dopants in photoluminescent and thermoluminescent applications (Hegedűs et al., 2022; Hesaraki et al., 2009; Roohani et al., 2022; Tan et al., 2023).

The favorable dosimetric performance of calcium phosphate materials, together with their ability to host impurity ions and their compositional similarity to bone mineral, provides strong motivation for further investigation of these compounds as thermoluminescent dosimeters. In addition, the availability of raw materials and the flexibility of synthesis methods make them promising candidates for dosimetric applications (Chand et al., 2021, 2022).

Calcium phosphates can be synthesized by various methods (Khanafari et al., 2014). In this study, a solid-state route was used, where calcium and phosphate precursors were combined in predetermined stoichiometric ratios to obtain the desired compounds (Chand et al., 2021, 2022; Chen et al., 2023).

This study aims to comparatively evaluate the thermoluminescent dosimetric properties of synthesized hydroxyapatite and β-tricalcium phosphate powders, with emphasis on the effects of host composition, dopant type, and dopant concentration in order to identify the most promising samples for dosimetric applications.

2 Material and Methods

In this study, the dosimetric behavior of synthesized hydroxyapatite and β-tricalcium phosphate samples was evaluated. The samples were irradiated using a Gammacell cobalt-60 device (model GC-220, NORDION) located in the Radiation Systems Laboratory of the Radiation Application Research Institute, operating at a dose rate of approximately 1 Gy.s^{-1}. Source calibration was periodically performed using a reference ferrous dosimeter. The irradiation doses ranged from 20 to 1500 Gy. The selected irradiation doses (20, 100, 200, 400, 600, 800, and 1500 Gy) were chosen to provide representative coverage of the low-, intermediate-, and high-dose regions within the investigated range and to enable comparative evaluation of the studied compositions.

Post-irradiation readings were conducted using a Harshaw model 4500 reader, housed in the Dosimetry and Radiological Evaluation Laboratory of the same institute. Measurements were performed over a temperature range of 50-350 °C with a heating rate of 5 °C.s^{-1}. To prevent potential damage to the reader due to the high response of some samples, neutral density filters with ratios of 10:1 and 100:1 were employed. Additionally, pre-irradiation readings were obtained for all samples, and the background signal was subtracted from the total reading to determine the net thermoluminescent response.

For the synthesis of hydroxyapatite and β-tricalcium phosphate via the solid-state method, calcium nitrate tetrahydrate, diammonium hydrogen phosphate, and sodium bicarbonate were employed as precursor materials, according to the following stoichiometric reaction (Eq. (1)):

$$
\begin{aligned}
6(NH_4)_2HPO_4 + Ca(NO_3)_2.4H_2O + 8NaHCO_3 \\
\longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_4NO_2 \\
+ 8NaNO_2 + 8CO_2 + 10H_2O
\end{aligned}
\tag{1}
$$

The required quantities of the starting materials, as listed in Table 1, were accurately weighed using an analytical balance. Diammonium hydrogen phosphate and sodium bicarbonate were initially transferred into a porcelain mortar and ground for 20 minutes. Subsequently, calcium nitrate was added, and the grinding process was continued until the mixture was homogenized, yielding a frothy white suspension.

For the preparation of doped samples, the desired molar fraction of calcium nitrate was reduced according to the intended impurity concentration, and an equivalent amount of the dopant was incorporated into the mixture during the addition of calcium nitrate. The specific compositions corresponding to 1%, 2%, and 3% impurity levels are detailed in Table 2.

Table 1: Weight of starting material for synthesis.

Materials	Hydroxyapatite (g)	β-Tricalcium (g)
Calcium Nitrate	70.845	70.845
Diammonium Hydrogen Phosphate	20.162	20.162
Sodium Bicarbonate	23.769	26.421

Table 2: Weight of Impurities for the Synthesis of Doped Calcium Phosphate Samples.

Materials	1% (g)	2% (g)	3% (g)
Cerium	1.30	2.60	3.90
Lanthanum	1.29	2.58	3.87
Gadolinium	1.35	2.70	4.05
Dysprosium	1.04	2.08	3.12

The synthesized material was initially aged at room temperature for 24 hours. To remove residual by-products, the material was washed using a centrifuge at 3000 rpm for 15 minutes. This washing procedure was repeated twice with ethanol, twice with deionized water, and once with distilled water. The washed material was subsequently dried in an oven at 80 °C for 8-24 hours, depending on its initial moisture content, to ensure complete dehydration. The dried powder was then subjected to thermal treatment in a furnace. Based on our previous optimization study (Taghipour et al., 2022), hydroxyapatite was calcined at 600 °C and β-tricalcium phosphate at 900 °C for 3 h, as these conditions provided the highest fraction of the desired crystalline phases for subsequent TL investigations.

Each composition was synthesized as a single batch, and the successful synthesis was verified by structural characterization analyses. The irradiation conditions were kept constant for all samples. Since the main aim of this work was a comparative investigation of thermoluminescent behavior, each sample was irradiated once at each selected dose, and the TL readout was repeated three times under identical conditions to assess measurement repeatability.

To facilitate comparison and maintain brevity throughout the manuscript, the synthesized samples are labeled using a systematic code: "Matrix-Dopant-Concentration". Hydroxyapatite is denoted as HAP, and β-tricalcium phosphate is denoted as BTC (or β-TCP). The dopant elements are represented by their chemical symbols (Dy, Gd, La, Ce), followed by their nominal concentration in weight percent (1, 2, or 3 wt%). Pure, undoped samples are designated with the suffix "P". The labeling scheme representing all 26 compositions is summarized in Table 3.

3 Results and Discussion

In this study, calcium phosphate samples, in the forms of hydroxyapatite and β-tricalcium phosphate, were synthesized both in their pure form and doped with cerium, lanthanum, gadolinium, and dysprosium at molar concentrations of 1%, 2%, and 3% for each dopant, yielding a total of 26 powder samples. The samples were irradiated with doses ranging from 20 to 1500 Gy, and the thermoluminescent output was subsequently measured.

For each measurement, a powder sample weighing between 25 and 35 mg (measured using an analytical balance with a precision of 0.1 mg) was loaded into a small metallic mold. This setup ensured a uniform thickness and geometry, and the mold was positioned precisely at the center of the heating planchet to maintain identical geometrical conditions relative to the photomultiplier tube.

The recorded signals were normalized to the mass of each sample. For each sample at each dose point, the TL readout was repeated three times under identical conditions. The variation among these repeated measurements is shown as error bars in the dose-response plots. The resulting data were analyzed to evaluate key dosimetric characteristics, including linearity, dose sensitivity, and glow curve peak properties. Comparisons among the samples were conducted to identify the optimal composition. Dose-response curves and representative glow curves at an intermediate dose of 400 Gy are presented. The dose level of 400 Gy was chosen as a representative reference because it lies in the middle of the investigated dose range, offering a strong and clear TL signal for all compositions while minimizing the risk of signal saturation.

3.1 *Fourier Transform Infrared (FTIR) Spectroscopy and X-Ray Diffraction Analysis*

The Fourier-transform infrared (FTIR) spectra of the synthesized HAP and β-TCP powder samples are presented in Fig. 1 and show good agreement with reported standard spectra. Characteristic vibrational bands corresponding to the phosphate (PO_4^{3-}) groups are observed at 570 cm^{-1} and 1040 cm^{-1}, while the hydroxyl (OH^-) groups appear at 720 cm^{-1} and 3460 cm^{-1}. These features confirm the successful synthesis and high quality of the prepared compounds.

The X-ray diffraction (XRD) patterns of the synthesized material are shown in Fig. 2. Comparison with the reference pattern (PDF #09-0169) confirms that the synthesized compound corresponds to β-tricalcium phosphate, indicating successful phase formation.

3.2 *Dosimetry Results of Hydroxyapatite Samples*

To evaluate the dosimetric performance of the synthesized samples, both glow curves and dose-response curves were plotted. Key parameters, including the linear dose-response range, coefficient of determination (R^2) for linearity, average glow peak temperature, and the standard deviation of the peak temperature, are summarized in corresponding tables to facilitate direct comparison among the samples.

Analysis of the dose-response and glow curves for the pure and cerium-doped hydroxyapatite samples (Fig. 3) reveals that the glow peak of the undoped sample occurs at approximately 230 °C, with a linear dose-response up to 200 Gy. Incorporation of 1% cerium enhances the sensitivity by a factor of 2.5 and extends the linear dose-response

Table 3: Summary of sample compositions and their corresponding labeling nomenclature (totaling 26 samples).

Base Matrix	Dopant	Concentrations (wt%)	Representative Sample Labels	Total Samples
HAP	Undoped (Pure)	0%	HAP-P	1
	Dy, Gd, La, Ce	1%, 2%, 3%	HAP-Dy1, HAP-Gd2, HAP-La3, HAP-Ce1, etc.	12
β-TCP (BTC)	Undoped (Pure)	0%	BTC-P	1
	Dy, Gd, La, Ce	1%, 2%, 3%	BTC-Dy1, BTC-Gd2, BTC-La3, BTC-Ce1, etc.	12
Total			26	

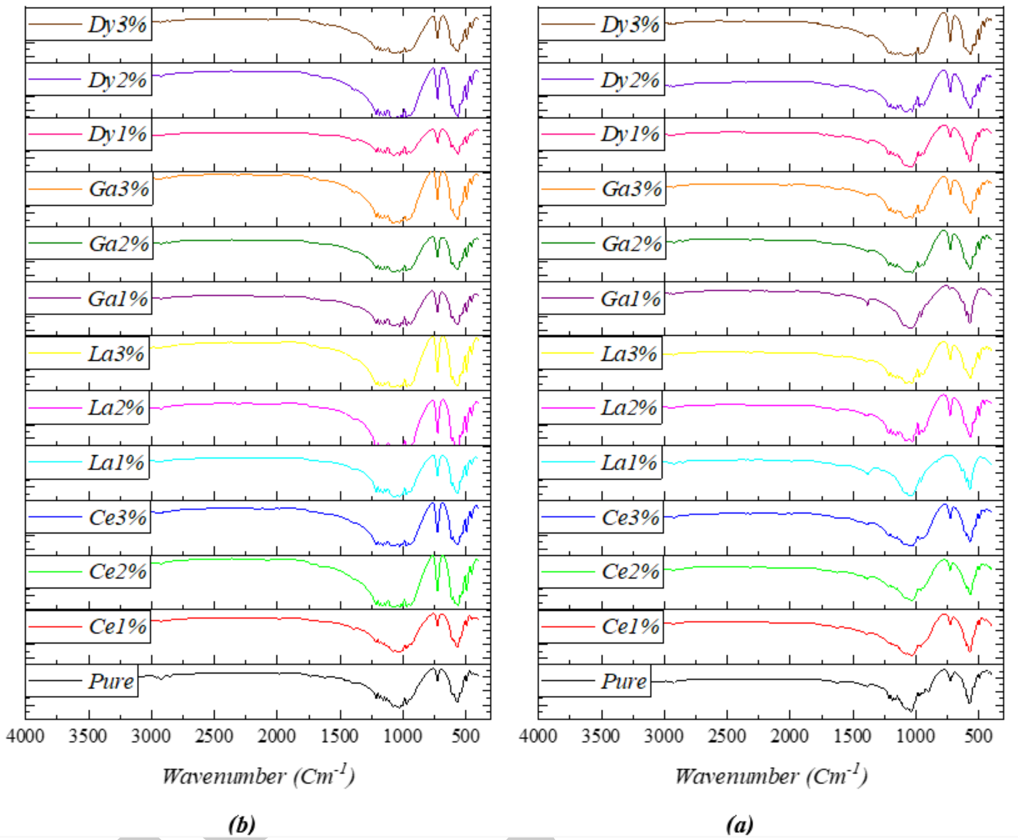

Figure 1: FTIR Analysis Results: (a) Hydroxyapatite, (b) Beta-Tricalcium Phosphate.

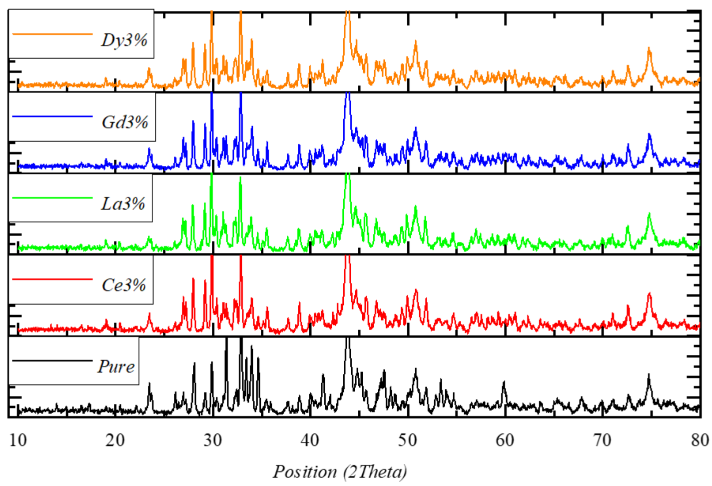

Figure 2: XRD Analysis Results of Beta-Tricalcium Phosphate.

range to 800 Gy, with the peak shifting to 240 °C. The 2% cerium-doped sample exhibits a linear response also up to 800 Gy, with sensitivity approximately twice that of the pure sample, and a peak around 220 °C. In contrast, the 3% cerium-doped sample displays linearity only up to 400 Gy, with a sensitivity 1.5 times that of the pure sam-

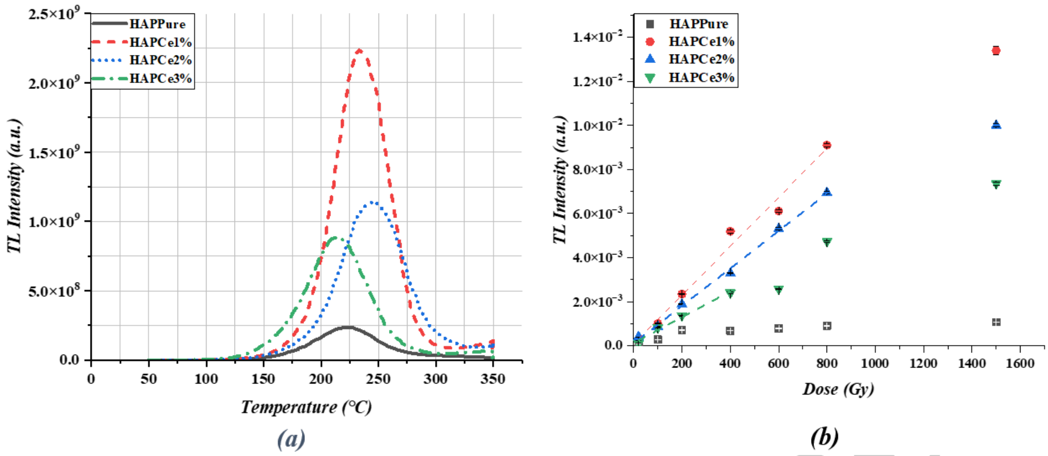

Figure 3: (a) Glow Curve and (b) Dose-Response Curve of Cerium-Doped Hydroxyapatite Samples.

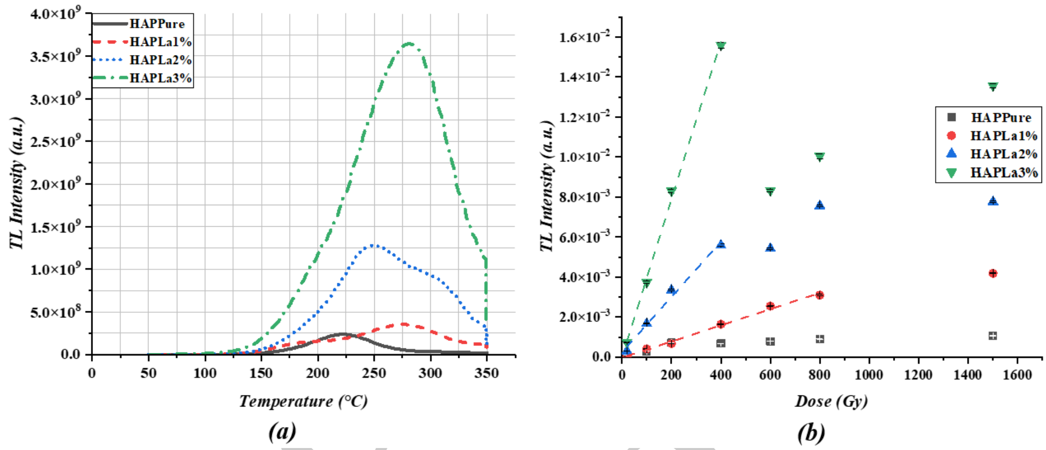

Figure 4: (a) Glow Curve and (b) Dose-Response Curve of Lanthanum-Doped Hydroxyapatite Samples.

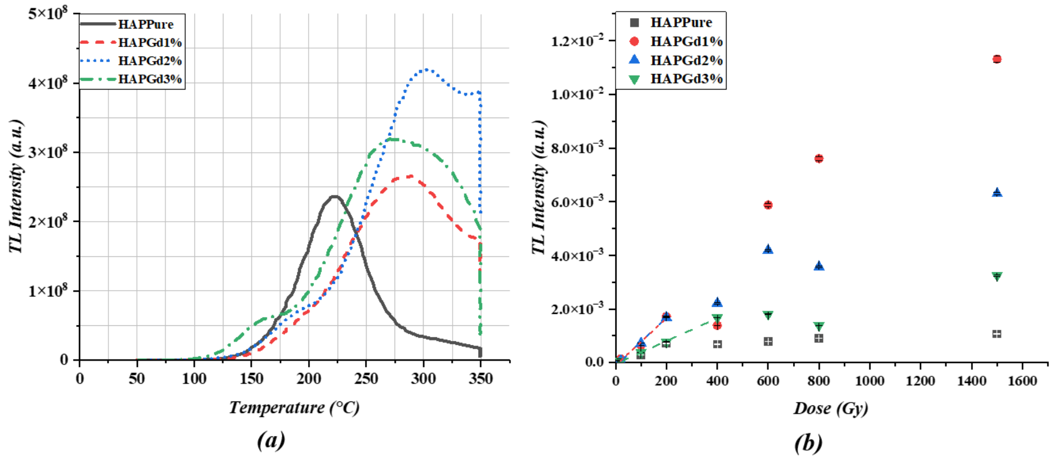

Figure 5: (a) Glow Curve and (b) Dose-Response Curve of Gadolinium-Doped Hydroxyapatite Samples.

ple; although the peak occurs near 240 °C, the peak shape becomes broader and less defined. These observations indicate that cerium doping up to 2% significantly enhances the thermoluminescent performance of hydroxyapatite.

As shown in Fig. 4, the incorporation of 1% lanthanum into hydroxyapatite extends the linear dose-response range to 800 Gy and enhances the thermoluminescent response for doses above 200 Gy, with the glow peak occurring at 280 °C. Increasing the lanthanum concentration to 2% further increases the sensitivity to approximately 2.5 times that of the pure sample; however, the linear dose-response range is reduced to 400 Gy, with the glow peak forming at 247 °C. The 3% lanthanum-doped sample also exhibits linearity up to 400 Gy, with a sensitivity approximately

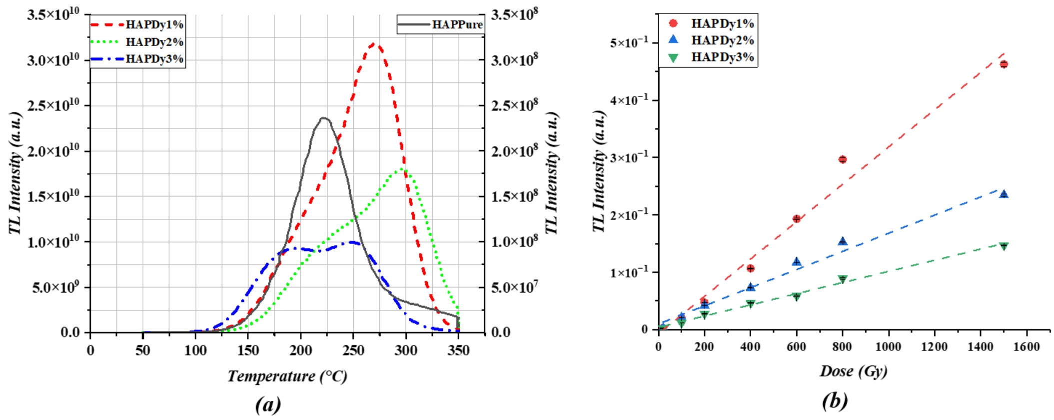

Figure 6: (a) Glow Curve and (b) Dose-Response Curve of dysprosium-Doped Hydroxyapatite Samples.

Table 4: Characteristics Obtained from the Dose-Response Curve of Hydroxyapatite Powder Samples.

Sample	Linear Response Range	Linear Relationship	R^2	Average Peak Temperature	Standard Deviation of Peak Temperature
Pure	20-200	$y = 4E - 06x - 2.0E - 05$	0.9854	234.5714	16.5414
Ce 1%	20-800	$y = 1E - 05x + 9.0E - 05$	0.9843	242.7142	17.9509
Ce 2%	20-800	$y = 8E - 06x + 1.0E - 04$	0.9972	220.8571	16.3240
Ce 3%	20-400	$y = 6E - 06x + 1.0E - 04$	0.9861	237.5714	32.0460
Gd 1%	20-200	$y = 9E - 06x - 1.0E - 04$	0.9807	269.7142	21.2737
Gd 2%	20-200	$y = 9E - 06x - 1.0E - 04$	0.9977	293.2857	39.1267
Gd 3%	20-400	$y = 4E - 06x - 5.0E - 05$	0.9987	301.4285	23.5786
La 1%	20-800	$y = 4E - 06x - 3.0E - 05$	0.9933	283.8571	19.3858
La 2%	20-400	$y = 1E - 05x + 2.0E - 04$	0.9876	247.8571	16.7075
La 3%	20-400	$y = 4E - 05x + 7.0E - 06$	0.9979	255.0000	17.9907
Dy 1%	20-1500	$y = 0.0003x - 6.9E - 04$	0.9845	266.2857	26.8744
Dy 2%	20-1500	$y = 0.0002x + 1.0E - 02$	0.9826	250.2857	23.0630
Dy 3%	20-1500	$y = 1E - 04x + 4.3E - 04$	0.9914	248.0000	32.1143

10 times higher than the undoped sample, and a glow peak at 255 °C. A notable drawback of lanthanum doping is the formation of glow peaks at undesirably high temperatures. Moreover, the 1% and 2% samples display non-single-peaked glow curves, with a shoulder appearing alongside the main peak. Despite the observed increases in sensitivity and, in some cases, extension of the linear dose-response range, these factors collectively indicate that lanthanum doping does not produce a significant overall improvement in the thermoluminescent properties of hydroxyapatite.

As illustrated in Fig. 5, the incorporation of 1% and 2% gadolinium into hydroxyapatite did not alter the linear dose-response range, which, similar to the pure sample, remained linear only up to 200 Gy. However, the sensitivity of these samples increased by a factor of approximately 2.25. The glow peaks shifted to 270 °C and 300 °C for the 1% and 2% samples, respectively, and the curves deviated from a single-peak structure. For the 2% sample, the temperature range of the glow peak exhibited undesirable broadening across different doses. The 3% gadolinium-doped sample extended the linear dose-response range to 400 Gy, with sensitivity comparable to that of the pure sample, but its glow peak remained around 300 °C and also lost the single-peak characteristic. Overall, these results indicate that gadolinium doping negatively affects the thermoluminescent properties of hydroxyapatite, causing an increase in average peak temperature and the appearance of multiple peaks in the glow curves, thereby diminishing the performance relative to the undoped material.

As presented in Fig. 6, the incorporation of 1% dysprosium into hydroxyapatite produced a substantial enhancement in thermoluminescent response, with sensitivity increasing approximately 75-fold relative to the pure sample. This doping extended the linear dose-response range up to 1500 Gy, although the glow peak shifted to 266 °C. Increasing the dysprosium concentration to 2% maintained linearity up to 1500 Gy, with sensitivity reduced to 50 times that of the pure sample. The glow peak occurred at 250 °C, and a shoulder appeared on the left side of the peak. For the 3% dysprosium-doped sample, linearity up to 1500 Gy was preserved, but the sensitivity further decreased to 25 times that of the undoped sample. The peak temperature remained around 250 °C, while the peak broadening increased across different doses, and the shoulder observed in the 2% sample evolved into a distinct secondary peak in the glow curve. These results indicate that dysprosium doping significantly enhances the thermoluminescent properties of hydroxyapatite, with an optimal

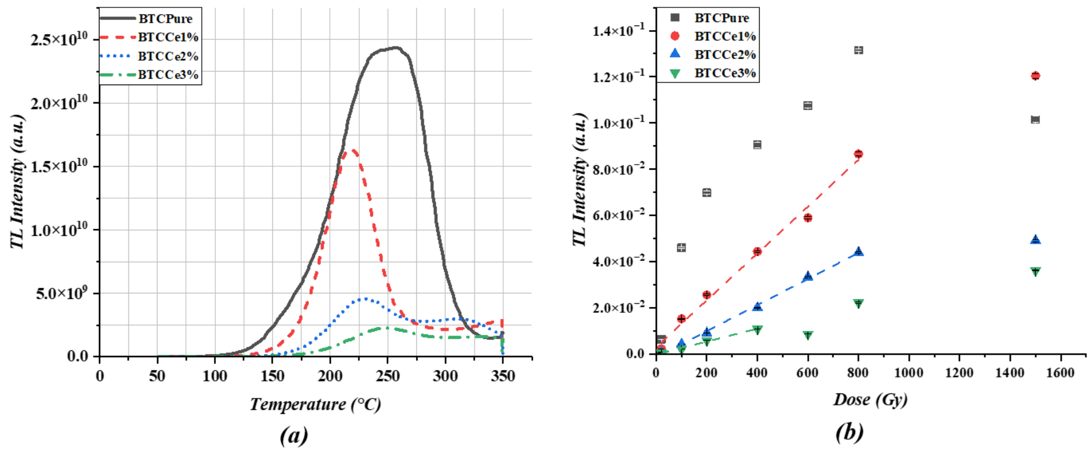

Figure 7: (a) Glow Curve and (b) Dose-Response Curve of Cerium-Doped Beta-Tricalcium Phosphate Samples.

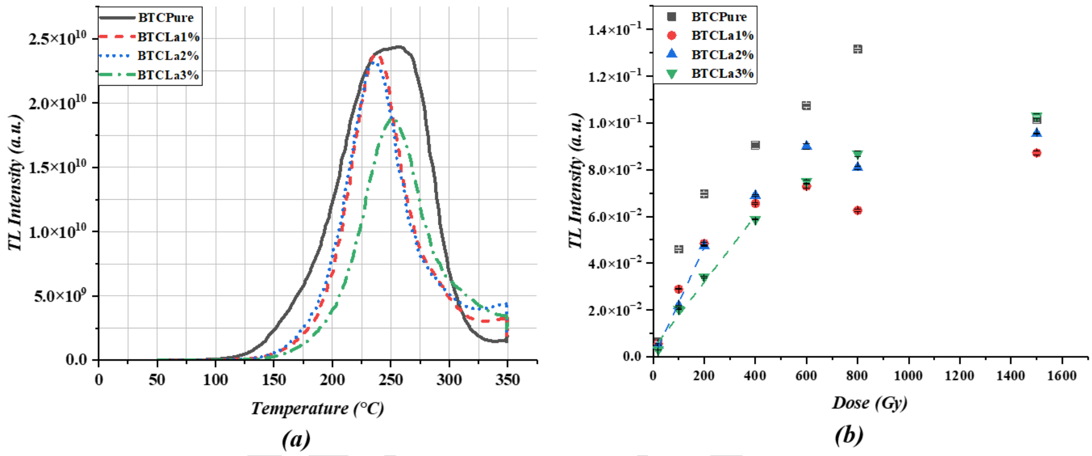

Figure 8: (a) Glow Curve and (b) Dose-Response Curve of Lanthanum-Doped Beta-Tricalcium Phosphate Samples.

effect observed at low impurity concentrations.

As summarized in Table 4, the dysprosium-doped hydroxyapatite samples exhibit the most favorable thermoluminescent performance in terms of both linear dose-response range and sensitivity among all tested compositions. Cerium-doped samples at 1% and 2% also demonstrate good linearity, with sensitivities exceeding those of the pure samples. In contrast, gadolinium-doped samples perform poorly in extending the linear dose-response range, and their average peak temperatures, along with associated variations, are undesirable. Lanthanum-doped samples show relatively better behavior compared to gadolinium-doped samples, but overall their performance is comparable to that of the undoped material. Increasing impurity concentrations enhances the TL response only in the case of lanthanum; for the other dopants, raising the concentration to 2% or 3% generally reduces the TL response and, consequently, the sensitivity. With the exception of gadolinium, increasing the dopant concentration either maintains or decreases the linear dose-response range. Notably, the glow peak temperature decreased only for the 2% cerium-doped sample; in all other cases, the peak temperature increased.

3.3 Dosimetry Results of Beta-Tricalcium Phosphate Samples

As illustrated in Fig. 7, pure β-tricalcium phosphate exhibits a non-linear dose-response, with its glow peak appearing around 250 °C. Incorporation of 1% cerium decreases the sensitivity to approximately 50% of the pure sample, but the dose-response becomes linear up to 800 Gy, and the glow peak shifts to 232 °C. Increasing the cerium concentration to 2% further reduces the sensitivity to 30% of the pure sample while maintaining linearity up to 800 Gy; the glow peak shifts to 217 °C, and a secondary, smaller peak emerges to the right of the main peak. At 3% cerium, the linear dose-response range decreases to 400 Gy, with sensitivity dropping to 15% of the pure sample. The glow peak occurs around 237 °C, exhibiting increased peak dispersion across different doses, and the curve retains the dual-peak structure observed in the 2% sample. These results suggest that cerium doping up to 2% positively influences the thermoluminescent properties of β-tricalcium phosphate.

As shown in Fig. 8, β-tricalcium phosphate doped with 1% and 2% lanthanum exhibits sensitivities comparable to that of the pure sample, with the linear dose-response

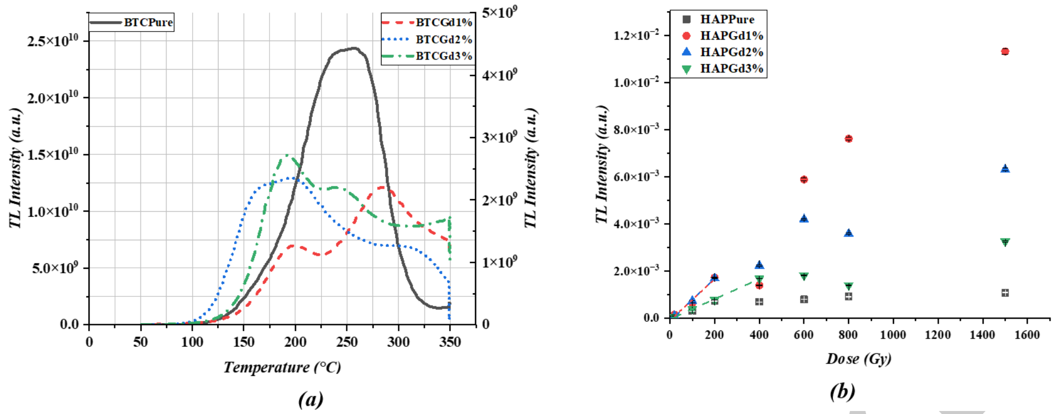

Figure 9: (a) Glow Curve and (b) Dose-Response Curve of Gadolinium-Doped Beta-Tricalcium Phosphate Samples.

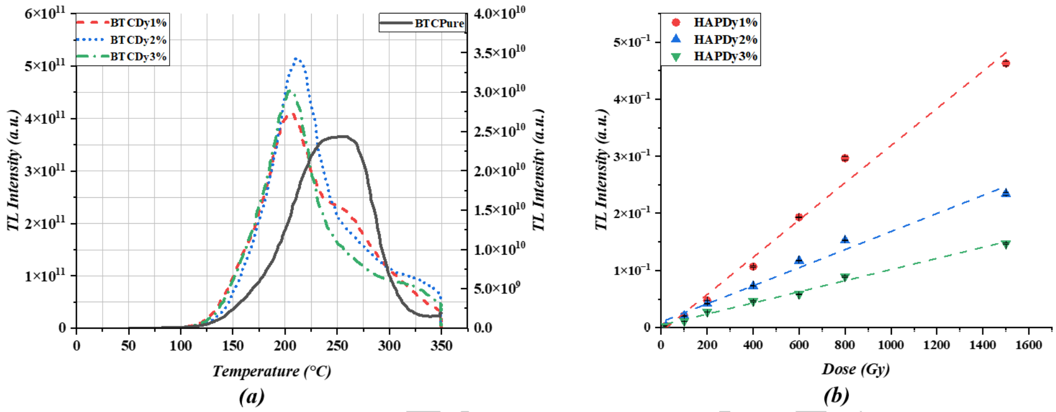

Figure 10: (a) Glow Curve and (b) Dose-Response Curve of Dysprosium-Doped Beta-Tricalcium Phosphate Samples.

Table 5: Characteristics Obtained from the Dose-Response Curve of β-TCP Powder Samples.

Sample	Linear Response Range	Linear Relationship	R^2	Average Peak Temperature	Standard Deviation of Peak Temperature
Pure	-	-	-	221.1428	18.2704
Ce 1%	20-800	$y = 1E - 4x + 0.003$	0.99	232.8571	18.4339
Ce 2%	20-800	$y = 6E - 05x - 0.0014$	0.9973	217.5714	15.4148
Ce 3%	20-400	$y = 3E - 05x - 0.0003$	0.993	237.0000	34.9809
Gd 1%	-	-	-	236.5714	26.1652
Gd 2%	20-200	$y = 5E - 05x + 0.0007$	0.9815	204.0000	29.6872
Gd 3%	20-400	$y = 4E - 05x + 0.0007$	0.9824	174.5714	29.8153
La 1%	20-200	$y = 2E - 4x + 0.0024$	0.9867	232.2857	6.6511
La 2%	20-200	$y = 2E - 4x - 0.00$	0.997	241.8571	19.7435
La 3%	20-400	$y = 1E - 4x + 0.0034$	0.9846	228.1428	20.7880
Dy 1%	20-800	$y = 4.3E - 3x - 0.1134$	0.9962	222.2857	31.0145
Dy 2%	20-1500	$y = 3.3E - 3x + 0.1629$	0.9851	205.2857	15.4996
Dy 3%	20-1500	$y = 3E - 3x - 0.0742$	0.9875	218.1428	19.8614

range limited to 200 Gy for both concentrations. The corresponding glow curves display a single peak, occurring at approximately 230 °C and 240 °C, respectively. Increasing the lanthanum concentration to 3% reduces the sensitivity to 50% of the pure sample, while extending the linear dose-response range to 400 Gy; the average glow peak temperature for this sample is 228 °C. Overall, these results indicate that the incorporation of 1% lanthanum has a favorable effect on the thermoluminescent properties of β-tricalcium phosphate.

As illustrated in Fig. 9, the incorporation of 1% gadolinium into β-tricalcium phosphate does not produce a linear dose-response, while simultaneously reducing sensitivity and shifting the glow peak to higher temperatures, resulting in the appearance of two peaks in the glow curve. At 2% and 3% concentrations, the dose-response becomes linear up to 200 Gy and 400 Gy, respectively, but the thermoluminescent response remains reduced. The corresponding glow peak temperatures shift to 204 °C and 174 °C, and both samples retain the dual-peak structure

Table 6: Guidelines for scoring variables.

Linear Response Range	20-1500	5
	20-800	4
	20-600	3
	20-400	2
	20-200	1
Peak Temperature	190-210	4
	180-190 or 210-220	3
	170-180 or 220-230	2
	160-170 or 230-240	1
	<170 or >240	0
Slope of the Linear Curve	1E-4 - 9E-4	4
	1E-5 9E-5	3
	1E-6 - 9E-6	2
	1E-7 9E-7	1
Standard Deviation of Peak Temperature	3-9	4
	9-15	3
	15-20	2
	>20	1
Number Of Peaks	1	2
	>1	1

observed in the 1% sample. Collectively, these findings indicate that gadolinium doping does not improve the thermoluminescent properties of β-tricalcium phosphate.

As shown in Fig. 10, dysprosium doping significantly enhances the thermoluminescent response of β-tricalcium phosphate. Incorporation of 1% dysprosium increased sensitivity by approximately 21.5-fold and produced a linear dose-response up to 800 Gy, with the glow peak occurring at 220 °C. Increasing the dopant concentration to 2% and 3% further extended the linear dose-response range up to 1500 Gy, with sensitivities of 16.5 and 15 times that of the pure sample, respectively. The corresponding average glow peak temperatures were 205 °C and 218 °C, with a notable reduction in standard deviation across different doses. These results indicate that dysprosium is the most effective dopant for enhancing the thermoluminescent properties of β-tricalcium phosphate.

As summarized in Table 5, dysprosium-doped β-tricalcium phosphate samples exhibit the most favorable thermoluminescent performance in terms of linear dose-response range, sensitivity, and average glow peak temperature, and are the only doped samples to surpass the response of the pure material. Cerium-doped samples at 1% and 2% also demonstrate good linearity, although their sensitivities are lower than that of the undoped sample. Gadolinium-doped samples perform poorly in extending the linear dose-response range, and their average glow peak temperatures, along with associated variations, are undesirable. Lanthanum-doped samples show relatively better behavior than gadolinium-doped samples but remain comparable overall to the pure sample. Increasing the dopant concentration generally decreases sensitivity, and with the exception of cerium, higher concentrations either maintain or reduce the linear dose-response range. Although the average glow peak temperature in all doped samples is lower than in the pure sample, it remains outside the optimal range in most cases.

3.4 Determination of the Optimal Sample

Given the large number of samples and the diversity in their responses, in order to facilitate comparison and selection of the optimal sample, the characteristics under review were grouped into five key criteria, and a scoring range was defined for each variable (Table 6). Based on these criteria, all samples were scored accordingly (Table 7). The five criteria are as follows:

- Range of linear response
- The Slope of the Linear Curve as a Criterion for Sensitivity Peak temperature
- Standard deviation of peak temperature (as an indicator for the likelihood of following first-order kinetics)
- Number of peaks

It is worth noting that the evaluation of the optimal compositions was performed globally across the entire investigated dose range (20-1500 Gy). Compositions that exhibited a wide linear response range up to the maximum dose were prioritized in the scoring system, ensuring that the selected optimal samples are suitable for application across the entire studied dose interval .The slope-based scoring system was introduced as a relative and instrument-dependent ranking method to facilitate comparison among the large number of studied compositions. Since the dose-response slopes are expressed in arbitrary units, the assigned scores reflect the relative magnitude of the measured response within this dataset rather than an absolute physical threshold.

4 Conclusions

This study systematically investigated the effects of dopants on the TL properties of calcium phosphate mate-

Table 7: Scoring of Samples Based on the Analyzed Characteristics.

		Linear Response Range	Peak Temperature	Slope of the Linear Curve	Standard Deviation of Peak Temperature	Number of Peaks	Total
HAP	Pure	1	1	2	2	2	8
	Ce 1%	4	0	3	2	2	11
	Ce 2%	4	2	2	2	2	12
	Ce 3%	2	1	2	1	2	8
	Gd 1%	1	0	2	1	1	5
	Gd 2%	1	0	2	1	1	5
	Gd 3%	2	0	2	1	1	6
	La 1%	4	0	2	2	1	9
	La 2%	2	0	3	2	1	8
	La 3%	2	0	3	2	2	9
	Dy 1%	5	0	4	1	2	12
	Dy 2%	5	0	4	1	2	12
	Dy 3%	5	0	4	1	1	11
BTC	Pure			NON linear			
	Ce 1%	4	1	3	2	2	12
	Ce 2%	4	3	2	2	1	12
	Ce 3%	2	1	2	1	1	7
	Gd 1%			NON linear			
	Gd 2%	1	4	2	1	1	9
	Gd 3%	2	2	2	1	1	8
	La 1%	1	1	3	4	2	11
	La 2%	1	0	3	2	2	8
	La 3%	2	2	3	1	2	10
	Dy 1%	4	2	3	1	2	12
	Dy 2%	5	4	3	2	2	16
	Dy 3%	5	3	4	2	2	16

rials, specifically HAP and β-TCP. The focus was placed on linear dose-response range, sensitivity, and glow-curve characteristics. Samples were synthesized via the solid-state method and doped with cerium (Ce), lanthanum (La), gadolinium (Gd), and dysprosium (Dy) at molar concentrations of 1%, 2%, and 3%, followed by irradiation and TL measurements.

The results indicate that impurity doping generally shifts the glow peak of HAP towards higher temperatures and enhances the TL response. While Ce, La, and Gd increased the TL response by roughly one order of magnitude, Dy produced enhancements up to two orders of magnitude and expanded the dosimetric response range. Optimal HAP samples were identified as those doped with 2% Ce and 1-2% Dy. Although La and Gd occasionally improved linearity and sensitivity, the displacement of glow peak temperatures and the emergence of multiple peaks limited their overall dosimetric advantage relative to the pure sample.

For β-TCP, the undoped material inherently lacks a linear dose-response; however, doping with Ce and Dy induced linearity, whereas Gd at 2% did not. Except for Dy, other dopants had limited impact on increasing the TL response and, in some cases, even reduced it. The most favorable β-TCP samples were those doped with 1-2% Ce and 2-3% Dy. Overall, while the structural properties of HAP facilitate impurity incorporation and enhance TL response, the number of optimal powder samples is higher in the β-TCP series.

While fading is an essential parameter for determining the practical applicability of thermoluminescent dosimeters, it was not evaluated in the present study due to its screening nature covering 26 different compositions. Systematic fading investigations will be carried out in future work specifically for the optimized HAP and β-TCP compositions.

In conclusion, Dy emerged as the most effective dopant for both HAP and β-TCP, significantly enhancing sensitivity and extending the linear dose-response range. Ce also improves TL characteristics, particularly at low concentrations, whereas La and Gd have limited or negligible effects. These findings provide valuable guidance for the design of calcium phosphate-based thermoluminescent dosimeters for industrial, medical, and agricultural applications.

Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

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