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Li_3PO_4: M (M=Tb, Cu) phosphors for radiation dosimetry

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Abstract The dosimetric phosphors Li_3PO_4:M (M = Tb, Cu) were produced by modified solid-state method. The structural and morphological characterization was carried out through X-ray diffraction (XRD) and scanning electron microscope (SEM). Additionally, the photoluminescence (PL), thermoluminescence (TL) and optically stimulated luminescence (OSL) properties of powder Li_3PO_4 doped with Tb and Cu were studied. It is advocated that Li_3PO_4: Cu phosphor not only shows higher OSL sensitivity (25 times or more) but also gives faster decay in OSL signals than that of Li_3PO_4: Tb^{3+} phosphor. The minimum detectable dose (MDD) of Li_3PO_4:M (M = Tb, Cu) phosphors is found to be 21.69×10^{-3} and 3.33×10^{-6} $J{\cdot}kg^{-1}$, respectively. In OSL mode, phosphor shows linear dose response in the range of 0.02–20.00 $J{\cdot}kg^{-1}$. In TL mode, sensitivity of Li_3PO_4: Cu phosphor is more than that of Li_3PO_4: Tb phosphor. The kinetics parameters such as activation energy and frequency factors were determined by peak shape method, and photoionization cross sections of prepared phosphor were calculated.

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Keywords Optically stimulated luminescence; Radiation dosimetry; Modified solid-state method; Minimum detectable dose

1 Introduction

The optically stimulated luminescence (OSL) technique has found general application in a various radiation dosimetry fields (personal, environmental and space dosimetry) [1]. Since the first suggested use of OSL for personal dosimetry, various OSL materials were developed and are currently used in dosimeter applications such as personnel and environmental monitoring applications [2–7].

Li_3PO_4 is often used as a material for personal dosimetry due to its low effective atomic number (Z_{eff} = 10.6), and phosphor exhibits useful thermoluminescence (TL)/OSL properties in personal dosimetry of ionizing radiations [8]. This phosphor also shows various luminescence properties such as mechanoluminescence, lyoluminescence and photoluminescence (PL) [9]. The majority of earlier studies were focused on the PL, TL and OSL properties of this phosphor doped with rare earth (RE) ions. This phosphor was developed by co-precipitation method and solid-state reaction.

To our knowledge, luminescence properties of Tb- and Cu-doped Li_3PO_4 dosimetric phosphors under beta irradiation were rarely reported. In addition, there are few published results concerning the Tb-doped luminescence properties of this host phosphor. In the present work, the comparative luminescence properties of Tb- and Cu-doped Li_3PO_4 phosphor under beta irradiations were reported and developed using modified solid-state method. This synthesized technique was built up to reduce the time required for the synthesis which is about 12 h without any special other atmosphere for synthesis.

2 Experimental

Li_3PO_4 phosphor doped with RE ions was synthesized by modified solid-state method. High-purity starting materials lithium nitrates ($LiNO_3 \cdot 3H_2O$), ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) and terbium nitrates ($Tb_4O_7 + HNO_3$) were used. The starting materials were taken in a proper stoichiometric ratio and mixed in china basin, small amount of acetone was added, and then clear solution was obtained. This mixture was heated on hot plate at 100 °C for 30 min, and then, the sample was placed in muffle furnace at 200 °C for 2 h, 400 °C for 2 h, 800 °C for 3 h and 950 °C for 1 h. Two times intermediate regrinding was done during this process, and the sample was suddenly quenched at room temperature. The same process was repeated for the copper nitrate ($Cu(NO_3)_2$) dopant.

Phase purity of Li_3PO_4:M (M=Tb, Cu) samples was measured by means of X-ray diffractometer (XRD, Rigaku MiniFlex II) with Cu Kα ($\lambda = 0.15405$ nm) radiation operated at 5 kV. The data were collected in a 2θ range of 10°–90°. The structural and morphological characteristics, i.e, particle size and shape of particles, were studied using scanning electron microscope (SEM). The measurements were taken using a ZEISS EVO/18 Research at Department of Physics, RTM University, Nagpur, and sample in powder form (100–150 μm) was placed directly into a SEM for imaging. Irradiations of all samples were performed at room temperature using a calibrated $^{90}Sr/^{90}Y$ beta source in-housed in RISO TL/OSL Reader (DA-15 Model). The activity of the source was 1.480×10^6 Bq, and the dose rate was 0.02000 $J \cdot kg^{-1}$. All TL/OSL measurements were taken using an automatic Risø TL/OSL-DA-15 reader system which can accommodate up to 48 discs. Blue light-emitting diodes (LEDs) emitting at 470 nm (full width at half maximum, FWHM = 20 nm) were arranged in four clusters, and each contains seven individual LEDs. PL and PL excitation (PLE) spectra were measured on fluorescence spectrophotometer (Hitachi F-7000) with a 450-W xenon lamp, in the range of 200–700 nm, with spectral slit width of 1 nm and PMT voltage of 700 V at room temperature.

3 Results and discussion

3.1 XRD analysis

XRD patterns of Li_3PO_4:M (M=Tb, Cu) phosphors synthesized by modified solid-state reaction are presented in Fig. 1. The patterns well match with the International Center for Diffraction Data (ICDD) with Card No. 01-083-0339. The structure of Li_3PO_4:M (M=Tb, Cu) is orthorhombic system with space group of *Pmnb*(62) and lattice parameters of $a = 61.110$ nm, $b = 104.612$ nm, $c = 49.200$ nm, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 90°$. However, in Li_3PO_4: M (M=Tb, Cu) lattice, the ionic radius of Cu^{2+} (0.0770 nm) is nearer to that of Li^{3+} (0.0760 nm) than that of Tb^{3+} (0.0923 nm) for sixfold coordinations. Based on the effective ionic radii, it is assumed that Li is more preferably replaced by Cu. The average crystallite sizes of Li_3PO_4:M (M=Tb, Cu) phosphors are determined from Debye–Scherrer formula [10] and found to be 87.70 and 79.42 nm, respectively.

3.2 Surface morphology

Figure 2 shows SEM images of Li_3PO_4:M (M=Tb, Cu) phosphors prepared by modified solid-state reaction. The photograph reveals that the morphology remains quite same in Li_3PO_4: M (M=Tb, Cu) phosphors, and the phosphors do not show any drastic change due to the change of dopant. There is no change in morphological effect in both

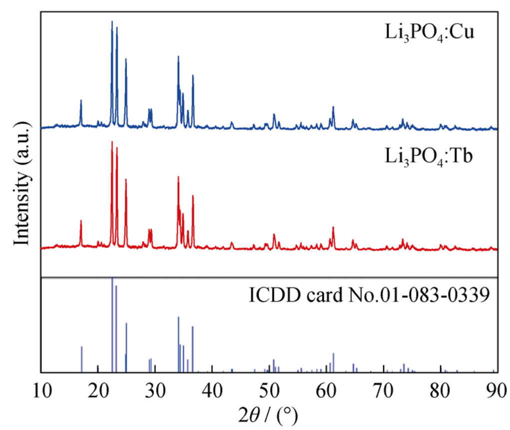

Fig. 1 XRD patterns of Li_3PO_4: M (M=Tb, Cu) phosphors

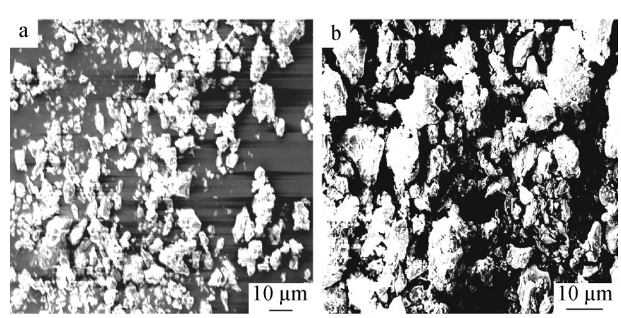

Fig. 2 SEM images of surface morphology of Li_3PO_4: M (M=Tb, Cu) phosphors: **a** Li_3PO_4:Tb and **b** Li_3PO_4:Cu

REEs-doped phosphors, as the concentration variation of RE in the phosphor is very less. Consequently, there is no effect on the morphology of host lattices. It is observed that the microstructure of the phosphor consists of irregular grains with heavy agglomeration. The average sizes of as-prepared particles are found to be in the range of 2–10 μm.

3.3 PL properties

The combined excitation and emission spectra of Li_3PO_4:M (M=Tb, Cu) phosphors are shown in Fig. 3. In case of Cu-doped phosphor, excitation was monitored under 256 nm and emission was monitored under 367 nm. Emission spectra of Li_3PO_4:Cu consist of broad band from 325 to 600 nm which corresponds to spin-forbidden $3d^94s$-$23d^{10}$ transitions of Cu ions. In case of Tb-doped phosphors, excitation and emission are observed under 544 and 225 nm, respectively. The excitation spectra consist of broad peak from 200 to 250 nm, and high-intensity peak appears at 225 nm which corresponds to the $4f^8$-$4f^75d^1$ transition of Tb^{3+} [11]. The emission spectrum consists of a relatively strong peaks at 488, 544, 584 and 621 nm corresponding to $^5D_4$ to ^7F_J ($J = 6, 5, 4, 3$) transition within the $4f^8$ configurations of Tb^{3+}. Among the emission lines from the $^5D_4$ state, the dominant emission is observed at 544 nm, corresponding to the $^5D_4$ to $^7F_5$ transition observed at 225-nm excitation.

3.4 TL results

TL glow curve is plotted between intensity of the emitted light and temperature. This curve is an indication that whether a material can be used for TL dosimetry or not and glow curve is characteristic of the different trap levels that lie within the forbidden gap of the material. These trap parameters were characterized by certain physical parameters like activation energy (E) and frequency factor (s) [12]. Figure 4 represents TL glow curves of Li_3PO_4:M (M=Tb, Cu) phosphors under beta irradiations. It can be seen that Li_3PO_4:Cu phosphor is sensitive than Li_3PO_4: Tb phosphor. TL glow curve of Li_3PO_4:Cu phosphor consists of overlapping peaks in the temperature range of 100–250 °C, and glow curve of Li_3PO_4:Tb phosphor consists of two peaks, appearing at 157 and 263 °C, respectively.

Kinetics parameters of Li_3PO_4:M (M=Cu, Tb) phosphors could be determined by peak shape method [13, 14] based on the value of the symmetry factor (μ_g). TL glow curve was deconvoluted by origin software as shown in Fig. 5. To determine these parameters (activation energy, frequency factor, order of kinetics), the following shape

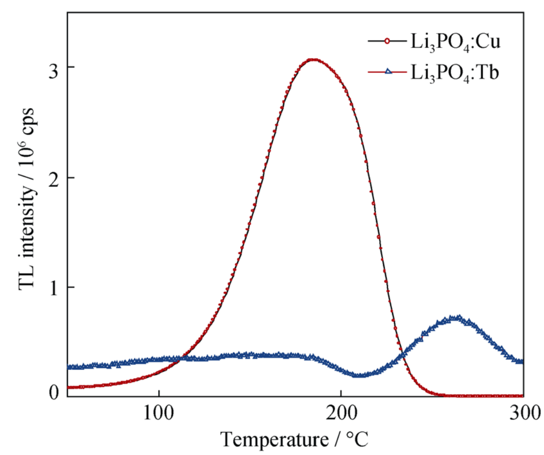

Fig. 4 TL glow curves of Li_3PO_4: M (M=Tb, Cu) phosphors under beta irradiation

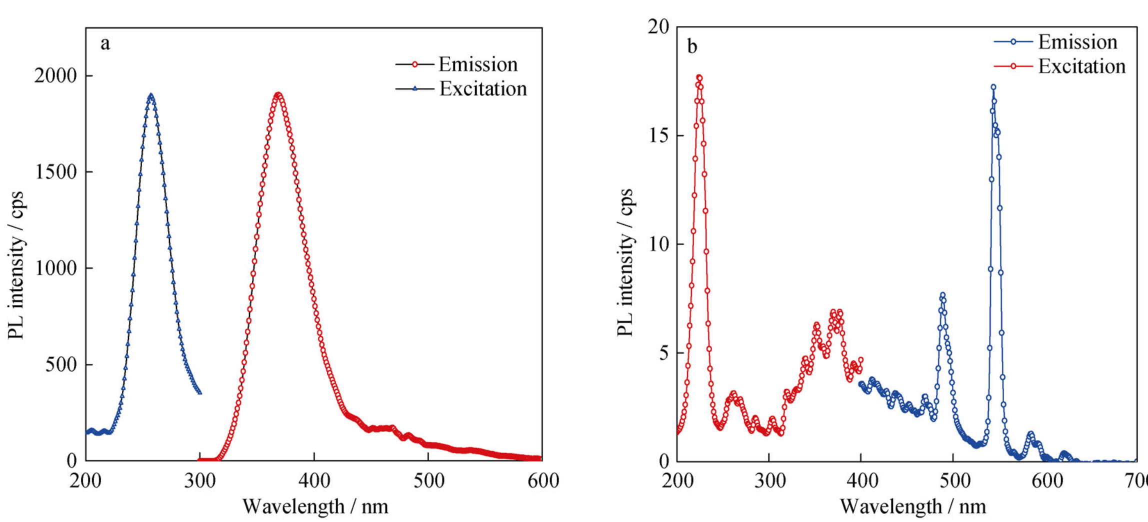

Fig. 3 Excitation and emission spectra of Li_3PO_4: M (M=Tb, Cu) phosphors synthesized by solid-state reaction: **a** Li_3PO_4:Cu and **b** Li_3PO_4:Tb

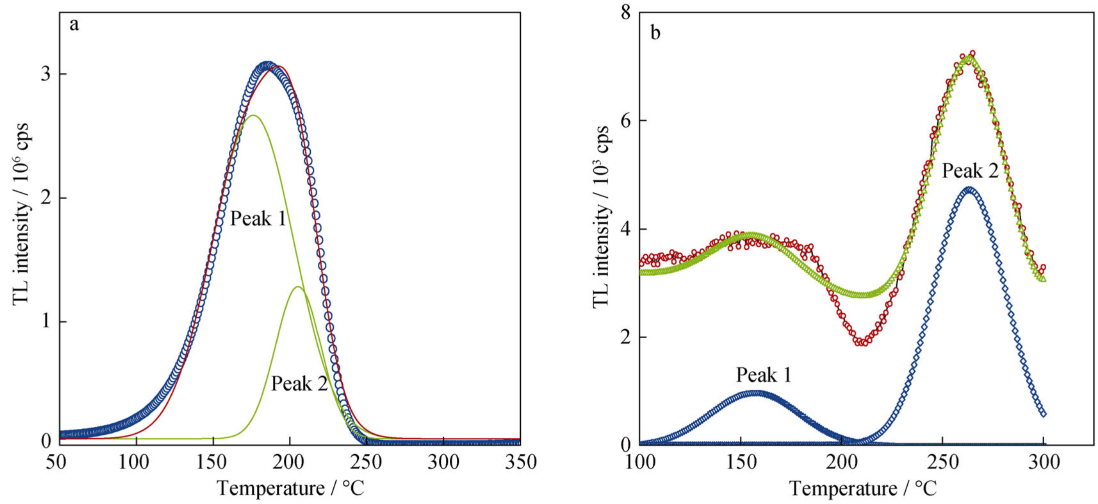

Fig. 5 Deconvoluted glow curves of Li_3PO_4: M (M=Tb, Cu) phosphors by origin software: **a** Li_3PO_4:Cu and **b** Li_3PO_4:Tb

Table 1 Kinetic parameters of Li_3PO_4: M (M=Tb, Cu) phosphors

Phosphors	Peaks	E/eV	s/s^{-1}	T_m/°C	μ_g
Li_3PO_4:Cu	1	0.885	1.62×10^9	177	0.48
	2	1.799	3.59×10^{18}	204	0.54
Li_3PO_4:Tb	1	1.007	1.56×10^{11}	157	0.50
	2	1.941	1.62×10^{17}	263	0.51

parameters were determined: the total half intensity width ($\omega = T_2 - T_1$), the high-temperature half-width ($\delta = T_2 - T_m$), the low-temperature half-width ($\tau = T_m - T_1$), where T_m is the peak temperature, and T_1 and T_2 are temperatures on either side of T_m corresponding to half peak intensity. The kinetic parameter values obtained for Peaks 1 and 2 are given in Table 1. The values of μ_g for the first- and second-order kinetics are 0.42 and 0.52, respectively.

3.5 Continuous stimulated OSL (CW-OSL)

The sample was studied for its OSL response using blue LED stimulation (470 nm). Figure 6a shows the typical CW-OSL response of Li_3PO_4: M (M=Tb, Cu) for 0.10000 J·kg^{-1} beta dose. The sensitivity of Li_3PO_4:Cu phosphor is 25 times that of Li_3PO_4:Tb phosphor. Figure 6b, c represents second- and third-order exponentially decay curves of Li_3PO_4:M (M=Cu, Tb) phosphors. Li_3PO_4:M (M=Tb, Cu) phosphors possess three and two OSL components with photoionization cross sections of 0.442×10^{-17}, 4.42×10^{-17}, 26.54×10^{-17} cm^2 (M=Cu) and 0.1769×10^{-17}, 0.4424×10^{-17} cm^2(M=Tb).

3.5.1 *Dose response*

To study the dose response, the discs made up of Li_3PO_4: M (M=Tb, Cu) phosphors were used and they are exposed to beta ray in the dose range of 0.02 to 20.00 J·kg^{-1}. Figure 7 represents dose response of Li_3PO_4:M (M=Tb, Cu) phosphors for variations of dose. The data were fitted linearly, and the slopes are 0.996 for Li_3PO_4:Tb and 0.995 for Li_3PO_4:Cu, indicating that the nonlinearity in the dose versus OSL response is found to be 0.4 % and 0.5 %, respectively.

3.5.2 *Minimum detectable dose*

The lowest level of detections known as the minimum detectable dose was calculated using the relation given by Rawat et al. [15]. MDDs of Li_3PO_4:M (M=Tb, Cu) phosphors are found to be 21.69×10^{-3} and 3.33×10^{-6} J·kg^{-1}, respectively (dose corresponding to 3σ of the background, where σ is the standard deviation in background counts integrated for time).

3.5.3 *Reusability*

Reusability is one of the most important parameters for any dosimetric material. This study was carried out by exposing the discs to 20.00×10^{-3} J·kg^{-1} doses, and its OSL was recorded for 60 s, after that again measure was hold for 100 s so that the discs were bleached completely. Ten such cycles

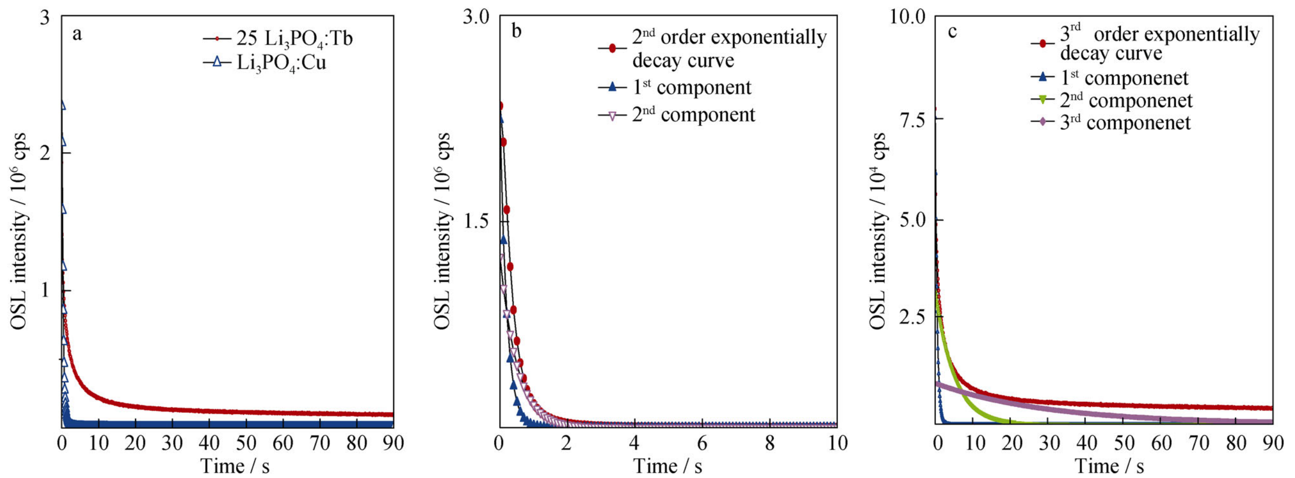

Fig. 6 OSL response of Li_3PO_4: M (M=Tb, Cu) phosphors under beta irradiation: **a** CW-OSL response of Li_3PO_4: M (M=Tb, Cu) phosphors, **b** second-order exponentially decay curves of Li_3PO_4:Tb, and **c** third-order exponentially decay curves of Li_3PO_4:Cu phosphor

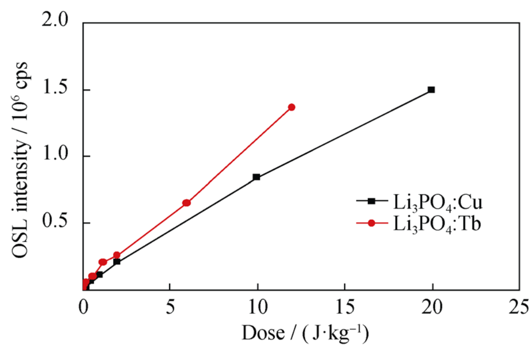

Fig. 7 Dose response of Li_3PO_4: M (M=Tb, Cu) phosphors

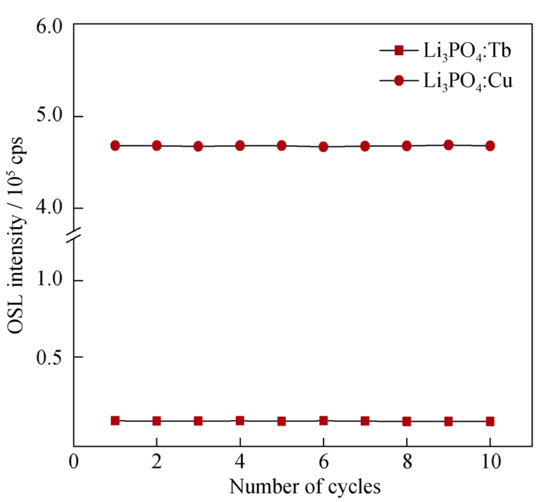

Fig. 8 Reusability study of Li_3PO_4: M (M=Tb, Cu) phosphors under beta irradiation

were carried out, as shown in Fig. 8. The studies show that the phosphor can be reused for 10 cycles without change in the OSL output in Li_3PO_4: M (M=Tb, Cu) phosphors.

Above results indicate that the prepared Li_3PO_4:Cu phosphor is highly sensitive in all modes of luminescence (PL, TL and OSL) than Li_3PO_4:Tb^{3+} phosphor because effective ionic radii of Li are very close to that of Cu instead of Tb [10].

4 Conclusion

Polycrystalline sample of Li_3PO_4: M (M=Tb, Cu) phosphors was successfully synthesized by modified solid-state diffusion method. The PL emission spectra of Li_3PO_4:Tb^{3+} phosphor show the strong prominent peak at 544 nm corresponding to $^5D_4$ to $^7F_5$ transition of Tb^{3+}, and the emission spectra of Li_3PO_4: Cu phosphor consist of broad band from 325 to 600 nm corresponding to spin-forbidden $3d^94s$-$23d^{10}$ transitions of Cu ions. Prepared phosphor shows good TL/OSL response under beta irradiations. In OSL mode, the sensitivity of Li_3PO_4: Cu phosphor is 25 times that of Li_3PO_4:Tb phosphor and the photoionization cross sections are found to be 0.4420×10^{-17}, 4.4200×10^{-17}, 26.5400×10^{-17} cm^2 for Li_3PO_4:Cu and 0.1769×10^{-17}, 0.4424×10^{-17} cm^2 for Li_3PO_4:Tb phosphor. In TL mode, Li_3PO_4: Cu phosphor is more sensitive than that of Li_3PO_4: Tb phosphor. Moreover, dose response is linear in the OSL mode and MDD is found to be 21.69×10^{-3} and 3.33×10^{-6} $J \cdot kg^{-1}$ for Li_3PO_4: M (M=Cu, Tb^{3+}) phosphor, respectively. Effective atomic number (Z_{eff}, ~10.6) of prepared phosphor is near about that of human tissue, and phosphors show excellent dosimetric properties such as sensitivity, dose linearity and reusability. Hence, this phosphor is suitable for dose measurements in radiation dosimetry.

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