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Research Article

Thermoluminescence of Novel Zinc Oxide Nanophosphors Obtained by Glycine-Based Solution Combustion Synthesis

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High-dose thermoluminescence dosimetry properties of novel zinc oxide nanophosphors synthesized by a solution combustion method in a glycine-nitrate process are presented for the very first time in this work. Sintered particles with sizes ranging between ~500 nm and ~2 μm were obtained by annealing the synthesized ZnO at 900°C during 2 h in air. X-ray diffraction patterns indicate the presence of the ZnO hexagonal phase, without any remaining nitrate peaks observed. Thermoluminescence glow curves of ZnO obtained after being exposed to beta radiation consists of two maxima: one located at ~149°C and another at ~308°C, the latter being the dosimetric component of the curve. The integrated TL fading displays an asymptotic behavior for times longer than 16 h between irradiation and the corresponding TL readout, as well as a linear behaviour of the dose response without saturation in the studied dose interval (from 12.5 up to 400 Gy). Such features place synthesized ZnO as a promising material for high-dose radiation dosimetry applications.

1. Introduction

A wide variety of luminescent materials used as thermoluminescent dosimeters (TLD) can be applied in several areas such as environmental and clinical dosimetry (low dose dosimetry), as well as applications related with high radiation doses such as nuclear reactors facilities, food sterilization plants, materials testing, and space dosimetry [1, 2]. In the case of high-dose dosimetry, thermoluminescence (TL) dose response should not exhibit a sublinear behaviour with a saturation trend, nor superlinear response in the range of interest because the real dose absorbed by the dosimeter can be underestimated or overestimated, respectively. Some materials, in particular conventional TL dosimeters, show a remarkable superlinearity at high-dose levels: thus, the number of available materials for high-dose dosimetry is limited [1, 2]. Nowadays, the search for new materials for high-dose TL dosimetry applications with high saturation limits represents a considerable challenge in the field of materials science. There are a considerable number of reports regarding the TL response of zinc oxide under exposure with different types of radiation sources [3–6].

Moreover, further investigations related to TL dosimetry features of pure and doped ZnO nanophosphors obtained by different soft chemistry-based methods had been carried out, proposing this oxide as a promising material for high-dose radiation dosimetry applications [7–15].

As an alternative to soft chemistry methods, solution combustion synthesis (SCS) is a technique in which a highly exothermic redox chemical reaction is carried out between a metal nitrate and a fuel, resulting in nanocrystals with composition consistent with the initial reagents. SCS begins with the complexation of the metallic species (oxidizing agent) prior to the combustion with an organic compound (reducing agent) functioning as the fuel. A large variety of technologically important inorganic compounds can be produced by SCS, such as ceramic oxides, aluminates, cromites, ferrites, manganites, and carbides [16].

Recently, Jagannatha Reddy et al. reported nanocrystalline ZnO powders which have been synthesized by a low temperature solution combustion method using oxalyldihydrazide as fuel. Thermoluminescence (TL) glow curves of gamma irradiated ZnO nanoparticles exhibit a single broad glow peak at ~343°C [14].

SCS based on a glycine-nitrate process represents a mechanistic advantage referring to the chemistry of the process in comparison with the combustion using urea or carboxylate azides such as oxalyldihydrazide as the complexant/fuel. The "zwitterionic" character of glycine allows the effective complexation of metals depending on the ionic size. Alkaline and alkaline-earth ions are more effectively complexed by the carboxylic acid group, while many transitions metals are more effectively complexed by the amino group [17].

Thereby, motivated by the antecedents mentioned above, the purpose of this work is to present for the very first time high-dose TL dosimetry properties of novel zinc oxide obtained by a glycine-nitrate solution combustion synthesis.

2. Experimental

2.1. Zinc Oxide Synthesis. An initial 0.25 M zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, ACS grade, Sigma-Aldrich) solution was prepared using deionized water inside a 400 mL beaker, where 0.42 g of glycine ($C_2H_5NO_2$, ACS grade, Sigma-Aldrich) was added to the metallic nitrate solution to get a fuel-lean elemental stoichiometric coefficient value ($\Phi_e = 1.75$) for the fuel-oxidizer mixture [18]. The resulting solution was placed in a hot plate and stirred magnetically at 360 RPM during 30 min inside a fume hood. After the stirring process, the solution temperature was increased from room temperature up to 200°C during 1 h, and when most of the water content of the solution was evaporated, the temperature was increased up to 500°C until a green flame was observed. Once the combustion finished, only the inorganic material powder remained at the bottom of the beaker. The solid within the beaker was then cooled to room temperature and the solid was collected and finally crushed with a pestle in an agate mortar. Powder samples obtained by the SCS technique were thermally annealed inside a Thermolyne 1300 furnace in air at 900°C during 2 h. After each annealing, the samples were cooled slowly inside the furnace.

2.2. Materials Characterization. X-ray diffraction data were obtained using a Bruker D8 Advance with Cu Ka radiation ($\lambda = 1.542$ Å). Scanning electron microscopy (SEM) images were obtained using JEOL JSM-5410LV equipment. A Risø TL/OSL model TL/OSL-DA-20 unit equipped with a ^{90}Sr beta radiation source was used to perform beta irradiations, thermoluminescence (TL) measurements, and the TL dosimetry characterization. Aliquots of 60 mg of sample in stainless steel cups were used for the readouts. All irradiations were accomplished using a 5 Gy/min dose rate at room temperature (22°C). The TL readouts were carried out under N_2 atmosphere using a heating rate of 5°C/s.

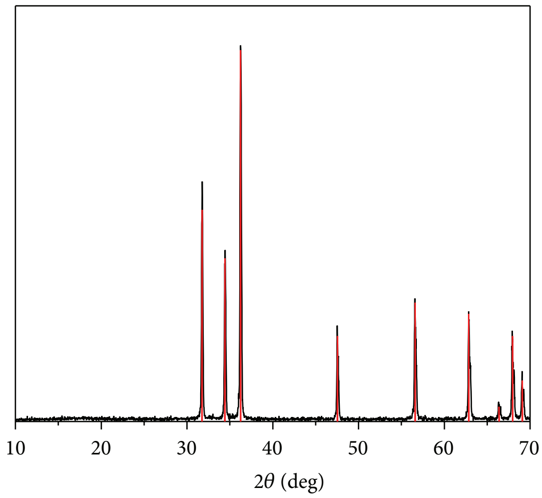

Figure 1: X-ray diffraction pattern of annealed samples obtained by SCS. Red vertical lines indicate the diffraction pattern of *zinc oxide or zincite* (PDF number 036-1251).

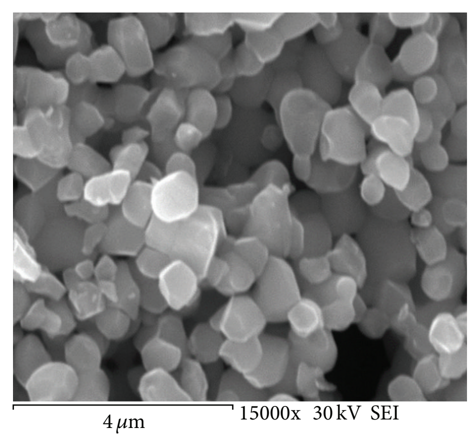

Figure 2: SEM image of ZnO samples synthesized by SCS.

3. Results and Discussion

As can be seen in Figure 1, the X-ray diffraction pattern obtained from annealed powder samples obtained by SCS consists of sharp well-defined peaks, which indicates high crystallinity.

Experimental diffraction data correspond to hexagonal zinc oxide or zincite (PDF number 036-1251) represented by red vertical lines, with a remarkable phase purity, since remaining nitrate or organic material diffraction peaks were not observed.

Figure 2 shows the SEM image of ZnO samples. Sintered particles with sizes ranging between ~500 nm and ~2 μm can be observed, with well-defined particle shapes and no visible porosity.

Thermoluminescence glow curves of ZnO nanophosphors after being exposed to beta radiation in the dose range from 12.5 up to 400 Gy are shown in Figure 3. Two maxima are observed, one located at ~149°C and another at ~308°C. These maxima shift their positions to lower temperatures

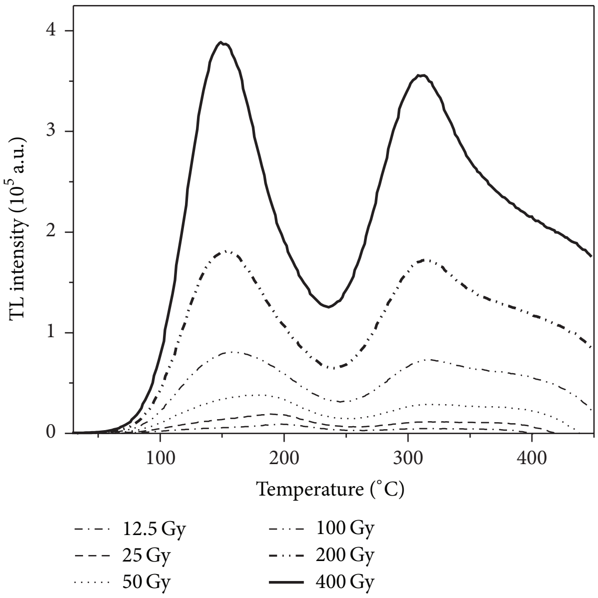

Figure 3: Thermoluminescence glow curves of ZnO nanophosphors obtained by SCS.

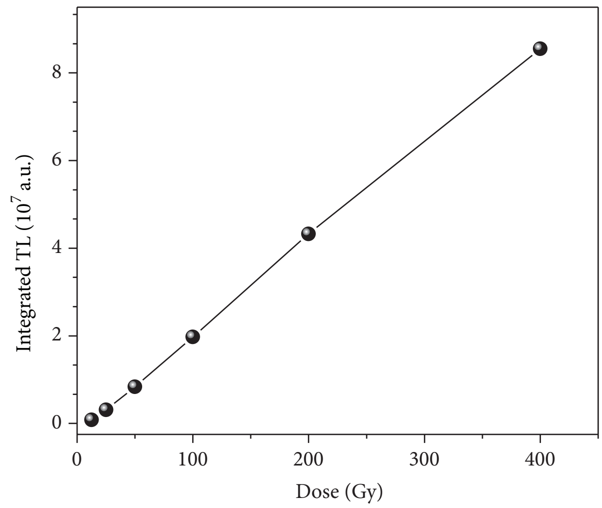

Figure 4: Dose response of ZnO nanophosphors obtained by SCS.

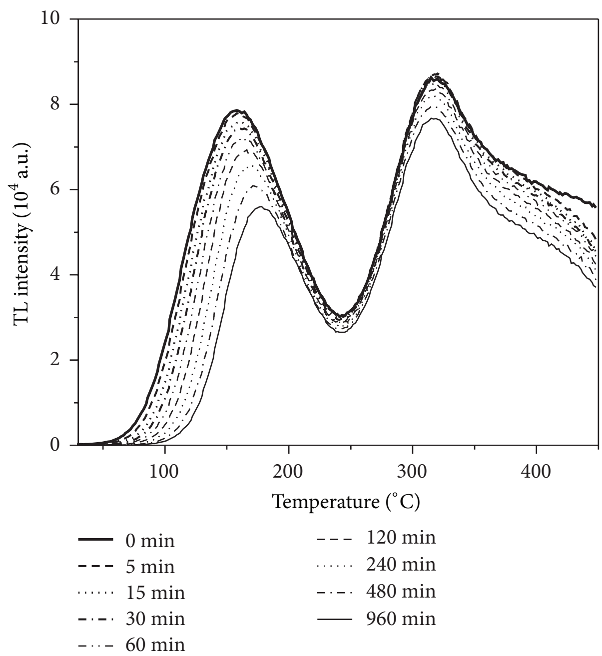

Figure 5: TL glow curve evolution of ZnO nanophosphors, previously exposed to 50 Gy of beta radiation after each elapsed time between irradiation and the corresponding TL readout (inner text).

as the dose increases, experimental evidence that second-order kinetics is predominating in the TL processes, although further glow curve deconvolution studies are necessary to better support such assumption [19].

The maximum located at ~308°C, mainly due to electron recombination from deep trapping states, is expected to be the stable peak since it is located at a temperature higher than 200°C, whereas the peak located at ~149°C can be considered as a low temperature peak and not suitable for TL dosimetry, mainly due to electron recombination from shallow traps [19, 20].

It is worth mentioning that there is no evidence of saturation in the 12.5–200 Gy dose interval for ZnO TL glow curves obtained in the present work.

TL glow curves obtained in this work are different compared to the curves of ZnO synthesized by a combustion process, but using oxalyl dihydrazide ($C_2H_6N_4O_2$) as fuel, reported by Jagannatha Reddy et al. In that work, TL glow curve consists of a single broad peak located at ~343°C. Also, there is evidence of TL signal saturation as the dose increases in the dose interval studied (10–50 Gy), according to the glow curves shown [14], which is lower than the interval used in the present study.

The integrated TL as a function of the dose, namely, the dose response of ZnO nanophosphors, is shown in Figure 4. Each point in the plot represents the integrated TL or the area beneath each TL glow curve shown in Figure 3. A linear behavior as well as proportionality in the 12.5–200 Gy dose interval can be observed. There is a sublinear behaviour evidence for doses above 200 Gy. Moreover, a further study is necessary to carry out to determine which is the optimal annealing prior to irradiation in order to eliminate the effect of the peak located at ~149°C and, therefore, the sublinear trend for doses above 200 Gy.

Figure 5 shows the TL glow curve evolution obtained previously exposing ZnO nanophosphors to 50 Gy of beta radiation, increasing the elapsed time between each irradiation and the corresponding TL readout until 16 h. It can be observed that TL intensity of the component located at ~149°C decreases in a higher proportion as time increases, compared to the maximum at ~308°C which is a more stable component since it represents recombination of charge carriers such as electrons previously trapped at deeper localized metastable energy states within the band gap of ZnO.

Figure 6 shows the total TL signal as a function of the elapsed time between irradiation and the corresponding TL

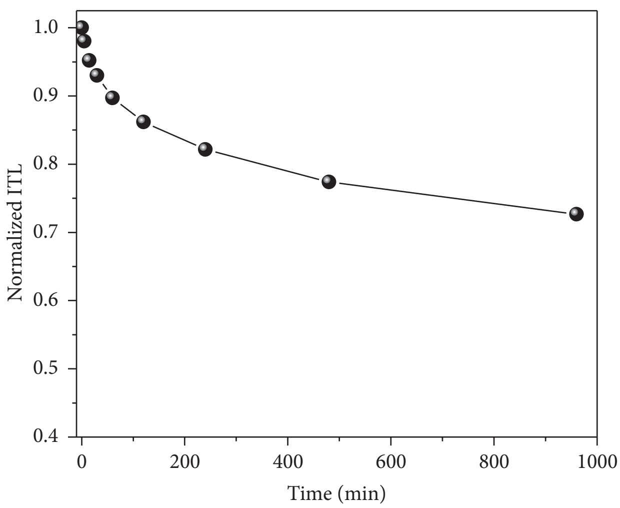

Figure 6: Normalized integrated TL as a function of the elapsed time between irradiation and the corresponding TL readout of ZnO nanophosphors.

readout of ZnO nanophosphors. Each point in the plot represents the integrated TL or the area beneath each TL glow curve shown in Figure 5. The signal faded down 25% past 9 h after irradiation, with an asymptotic behaviour for times longer than 16 h. Such behaviour is mainly due to the ~308°C peak which can be suitable for dosimetry applications such as radiotherapy and food irradiation industry.

4. Conclusions

It was feasible to synthesize through a glycine-nitrate combustion process novel ZnO nanophosphors with phase purity and with remarkable TL dosimetry properties under beta-particle irradiation, according to the results obtained in this work. Dose response without saturation evidence and a linear trend for doses up to 200 Gy as well as the asymptotic behaviour of the TL fading for times longer than 16 h are experimental evidence for proposing annealed ZnO as a promising material aimed for high-dose radiation dosimetry applications such as radiotherapy and food irradiation industry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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