

Investigation of the thermoluminescence properties Ti⁴⁺ doped MgO synthesized solid-state assisted solution combustion synthesis method

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Abstract

In this study, undoped MgO and titanium (Ti⁴⁺) doped MgO ceramics were synthesized using the solid state-assisted solution combustion synthesis method. The structural characteristics were investigated using X-ray diffraction (XRD) and scanning electron microscope (SEM). TL curves of the MgO:Ti⁴⁺(0.1% wt) ceramic consist of three TL peaks located at 70, 250 and 290 °C with a heating rate of 2 °C/s after 1 Gy beta dose. Radioluminescence (RL) characteristic of the MgO:Ti⁴⁺(0.1% wt) ceramic was studied with excitations between 200 - 1000 nm. It was found to be the four emission bands the maximums located at 327 nm (~3.79 eV), 694 nm (~1.78 eV), 715 (~1.73 eV), and 745 (~1.66 eV). Some dosimetric characteristics such as TL curve, reusability, dose-response, of the ceramic were investigated using the thermoluminescence (TL) technique using beta radiation of ⁹⁰Sr/⁹⁰Y. Dose-response characteristics showed the integrated TL signals between 170-350 °C exhibited a linear up to 20 Gy. The experimental results showed that if it is developed of the MgO:Ti⁴⁺(0.1% wt) ceramic can be considered as a dosimetric material with suitable properties in personal and medical applications.

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1. Introduction

Thermoluminescence dosimeters (TLDs) are used in many fields such as clinical, radiological as well as environmental. The materials close to tissue equivalent ($Z_{\text{eff}}:7.25$) are very important in clinical applications such as radiological examinations and therapeutic treatments. Magnesium oxide (MgO) known as magnesia, a p-type semiconductor with a wide bandgap ($E_g = 7.8$ eV), has been received great attention because of its fundamental and practical applications. As well as chemical stability, it has non-toxicity, tissue-equivalent with 10.7. It has a melting point of ~ 2850 °C. It has a single phase, with rock salt structure (fcc) like oxides of other alkaline earth metals, cubic structure with lattice parameters $a=b=c$ 4.23 Å. MgO ceramic is one of the investigated host materials in radiation dosimetry. But pure MgO does not exhibit high luminescence TL sensitivity to ionizing radiation, so researchers have been synthesized it with various dopants to improve the radiation sensitivity [1-6]. In the literature, there are many synthesis methods such as solution combustion, precipitation sol-gel, solid-state., etc. Wang et al.,

(2009) reported titanium doped MgO synthesized with a chemical coprecipitation method [7]. They studied

the structure analysis of the synthesized nanopowders using XRD, X-ray fluorescence (XRF), differential thermal analysis (DTA) and transmission electron microscope (TEM). Bokhimi et al., (1999) reported the MgO-TiO₂ system produced by sol-gel. They produced a stable phase of the MgO-TiO₂ system such as periclase, anatase, and rutile [8]. Barron et al., 2016 reported that TL dosimetric properties of MgO:Ce³⁺ synthesized by the solution combustion synthesis. They calcined it at 900 °C for 2 h in the air atmosphere. They have been studied its structural characterization with XRD and SEM. They were found to be linear between 0.08 and 5.33 Gy [2]. Rao et al., (1992) reported using various magnesium salts such as Mg(NO₃)₂ and their combination with magnesium oxide in a presence flux. They studied their emission characteristic. Structural characterization produced materials studied with XRD analysis. The emission spectra of Tb doped MgO as six peaks have been recorded [6]. Recently, Mokokeng et al., (2020) reported the thermoluminescence properties of MgO:Al,Li synthesized by microwave-assisted

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solution combustion synthesis. They studied XRD, Energy band gap using Kubelka-Munk relation and some dosimetric properties such as dose-response [4]. Depending on the synthesis methods TL glow curve shape varies significantly in such way that synthesized by many researchers: Barron et al (2016) [2] reported 74 °C for MgO, 103 °C for MgO:Ce and 243 °C for MgO:Ce,Li; Oliviere et al., (2019) [5] reported the main dosimetric TL Peak 80 °C for MgO:Ce,Tm; 180 °C for MgO:Ce,Sm; 180 °C for MgO:Tb,Sm; 180 °C for MgO:Ce,Sm,Li; and 460 °C for MgO:Ce,Yb,Li; Barron reported the main dominant TL peak 80,215,270 °C for MgO:Ce,Li; Barron et al., (2011) [9] reported the temperature TL Peak at 70 °C for undoped MgO, 75 °C for MgO:Tm,Li, (70 and 220) °C for MgO:Tb,Li; and 330 °C for MgO:Eu,Li and Recently Mokofeng et al., (2020) [4] reported the dominant TL Peak TL 105 °C for MgO:Al,Li.

In the literature, there are many synthesis methods for the synthesis of luminescent materials. The material cannot be synthesized in a single step in methods such as sol-gel and solid state, which are problems of energy and time consumption. Unlike this method, solution combustion synthesis (SCS) is a versatile, simple and rapid process, time- and energy saving method which allows the effective synthesis of a variety of nanosized/polycrystal materials. It can be used that chemicals can be dissolved in water such as nitrate in the SCS method. In this study, the SCS method could not be used directly because of the Ti^{4+} ion (TiO_2) cannot be dissolved in water to obtain MgO: Ti^{4+} ceramic. Ti^{4+} activated MgO ceramic was able to synthesis using the solid state assisted solution combustion synthesis method. Solid state assisted solution combustion synthesis method has been effectively used to produce powders in shorter times in comparison with the solid-state synthesis methods. In this study, the structural characterization of the synthesized MgO: Ti^{4+} ceramic was studied with x-ray diffraction (XRD) and scanning electron microscope (SEM). Besides, radioluminescence (RL) was also studied. Some dosimetric properties of the ceramic were investigated using TL techniques.

2. Materials and Methods

Undoped and titanium (Ti^{4+}) doped MgO ceramics were synthesized as follows using solid-state assisted solution combustion method: To produce undoped MgO powder with the solution combustion synthesis method (SCS), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, ACS reagent, 99%, Sigma Aldrich) as the source of Mg, glycine ($C_2H_5NO_2$, ReagentPlus, 99%, Sigma Aldrich) as a fuel was dissolved via

magnetic fish in the 200 ml ionized water and placed on the hot plates at 100 °C for 30 minutes. After 30 min, the temperature of the hot plate was increased up to 250 °C until the water of the solution was held up. The powder materials were calcined at 800 °C for 2 hours to remove CO_2 , N_2 , i.e gases. Because Titanium oxide (TiO_2 , powder, 99.8% trace metals basis, Sigma Aldrich) cannot be dissolved in water, the obtained the powders to TiO_2 as a dopant pre-determined weight of Titanium in the range of 0.1 to 1 %wt by using the solid-state method was doped. Mix powders at agate mortar were kindly mixed separately. The pellets with using 30 mg powder were done under 860 kP using Carver Machine. Pellet samples were sintered at 1200 °C for 2 h to obtain the crystal form of MgO: Ti^{4+} (0.1%wt). In the end of this temperature process, ceramics, i.e., undoped MgO, MgO: Ti^{4+} (0.1%), MgO: Ti^{4+} (0.5%) and MgO: Ti^{4+} (1%) ceramics were obtained. Solid state assisted solution combustion synthesis method has been effectively used to produce powders in shorter times in comparison with the solid-state synthesis methods.

The X-ray diffraction (XRD) pattern of the MgO: Ti^{4+} (0.1%wt) ceramic was recorded with a PANalytical EMPYREAN XRD diffractometer equipped with a copper and cobalt X-ray tube using Cu- $K\alpha$ radiation ($\lambda=0.1541$ nm). XRD pattern was recorded in the range from 20° to 80° with the step of 0.0001° in the powder form of the MgO: Ti^{4+} (0.1%wt) ceramic. The structural characterization of the ceramic was performed using a FEI Quanta 650 SEM instrument, field-emission with 30–100 kV accelerating voltage and 100 nA probe current. SEM image of the powder MgO: Ti^{4+} (0.1%wt) ceramic was taken at 5.000X magnification. The radioluminescence (RL) spectra of the undoped MgO and MgO: Ti^{4+} (0.1%wt) pellet ceramics were taken using a homemade RL system that has an attached Ocean Optics model QE Pro (Ocean Optics USB-2000, Inc.,Dunedin, FL, USA) by f/2 collimator in front of fiber optic cable (1mm core diameter, transmission between 200 and 1100 nm) throughout the CCD detector while irradiating by mini x-ray tube operated at from 4 kV up to 40 kV for stimulating the ceramics. RL measurements of ceramic pellets were recorded in the range from 200 to 1000 nm. All TL measurements were carried out by the Riso TL/OSL DA-20 device, equipped with a $^{90}S/^{90}Y$ beta source (40 mCi) in calibrated geometry and delivering a dose rate of 6.689 Gy/min. A Schoot BG 39 filter was used at all TL measurements in the front of Photo Multiple Tube (PMT), which is EMI 923QB. In this study, the dosimetric characteristic of MgO: Ti^{4+} (0.1%wt) pellet ceramics were investigated by taking the integrated TL

signals between 170-350 °C, which is the main dosimetric TL peak of ceramic. In this study, unless otherwise stated, all TL measurements were recorded using pellet ceramic. The same samples ceramics were used all TL experiments and before ceramics were annealed at 400 °C for 20 min. TL curves were recorded with the heating rate of 2 °C/s after preheating 170 °C, following 1 Gy dose.

3. Results and Discussion

3.1. X- ray diffraction (XRD)

X-ray diffraction (XRD) analysis was carried out to determine whether the material has the targeted crystal structure after a series of temperature process to obtain crystal form and also whether the amount of dopant ions concentration changes the main crystal structure. The MgO:Ti⁴⁺(0.1%wt) ceramic synthesized using solid-state assisted SCS after calcination at 800 °C for 2 h and following it sintered at 1200 °C for 2 h was determined using the XRD analysis. Fig. 1 shows the XRD pattern of the MgO:Ti⁴⁺(0.1% wt) ceramic. The diffraction peaks of the MgO:Ti⁴⁺(0.1% wt) ceramic matched to the standard ICDD number of 98-015-7523 in terms of peak position and intensity. The crystal structure was cubic with lattice parameters a=b=c=4.235 Å. The XRD results indicated the crystalline phase of MgO:Ti⁴⁺(0.1% wt) the dominating for these temperature processes. XRD results showed that Ti⁴⁺ introduced to MgO lattice did not significantly change the crystal lattice of MgO. As a result, the material was successfully synthesized using the solid state assisted solution combustion synthesis method.

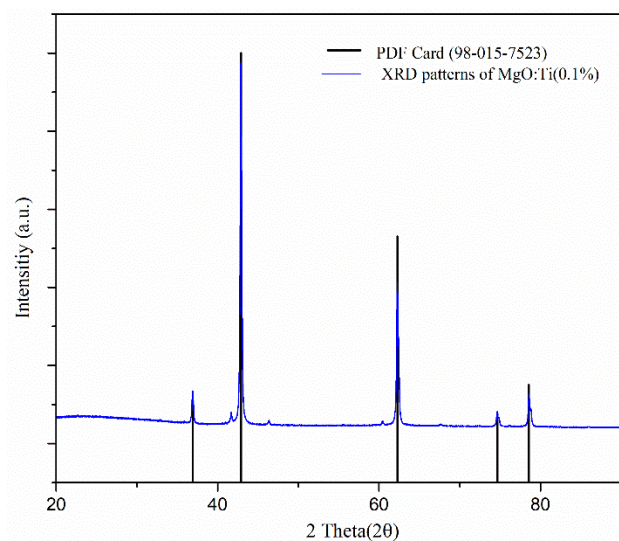


Figure 1. XRD patterns of the MgO:Ti⁴⁺(0.1% wt) ceramic with reference peaks (PDF Card No:98-015-7523).

3.2. Scanning electron microscope (SEM)

The scanning electron microscopy (SEM) was used to examine the surfaces of the MgO:Ti⁴⁺(0.1%wt) ceramic. The surface morphology of the MgO:Ti⁴⁺(0.1%wt) ceramic powder was taken at 5.000X magnification. Fig. 2 shows the SEM image of the ceramic synthesized using solid-state assisted SCS after calcination at 800 °C for 2 h and following it sintered at 1200 °C for 2 h. As seen in Fig. 2, the SEM images show the non-homogeneous and irregular shape structure. These structures were likely attributed to the non-uniform temperature distribution during synthesis.

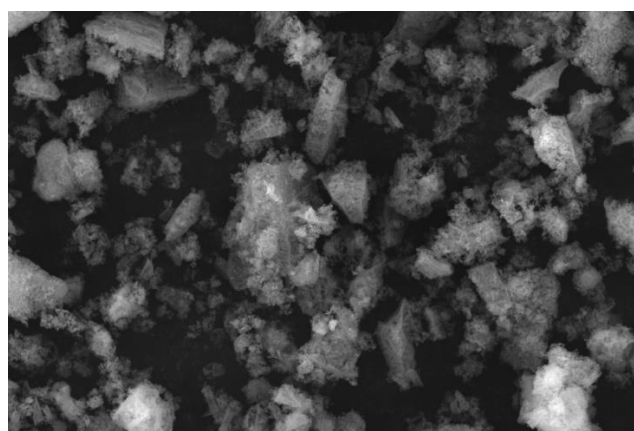


Figure 2. SEM image of the MgO:Ti⁴⁺(0.1% wt) ceramic. Magnification is 5.000X.

3.3. Radioluminescence (RL)

Radioluminescence (RL), known as also X- ray Luminescence (XL), spectra were measured to study the morphology of bulk and surface defects involved in the luminescence processes stimulated by the volume penetrated by ionizing radiation. RL spectra of the undoped MgO and MgO:Ti⁴⁺(0.1% wt) pellet ceramics were recorded in the range from 200 nm to 1000 nm at room temperature. Fig 3. shows the RL spectra of the undoped MgO and MgO:Ti⁴⁺(0.1% wt) ceramics. The three emission peaks for undoped MgO was recorded at near-infrared regions at 694, 715, 745 nm. When Ti⁴⁺ was introduced to MgO lattice crystal, the four emission peaks were located at 327, 694, 715 and 745 nm. As seen in Fig. 3, both undoped MgO and MgO:Ti⁴⁺(0.1% wt) ceramics show similar peak shape and maximum, which indicates that the luminescence most likely originated from the same groups of traps.

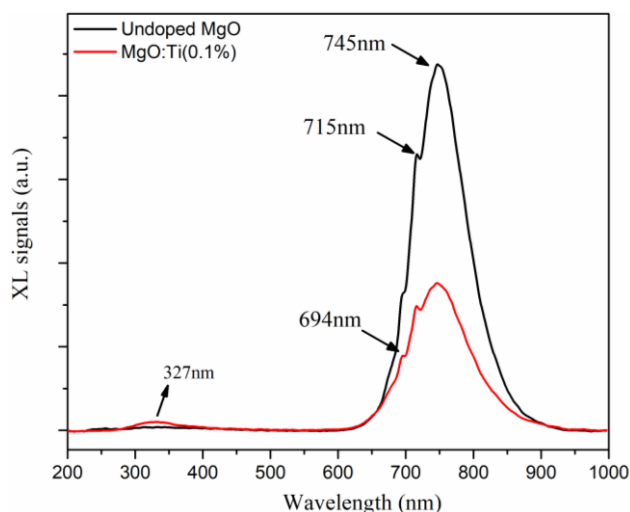


Figure 3. Radioluminescence (RL) spectra of the undoped MgO and MgO:Ti⁴⁺(0.1% wt) ceramics in the range of 200-1000 nm.

3.4. TL glow curve

Fig. 4 shows the comparison TL curves of undoped MgO, MgO:Ti⁴⁺(0.1% wt), MgO:Ti⁴⁺(0.5% wt) and MgO:Ti⁴⁺(1% wt) ceramics after 1 Gy beta dose with a heating rate of 2 °C/s from room temperature to 450 °C. TL curve of the undoped MgO consists of three TL peaks located at 90 °C, 250 °C and 290 °C, respectively. The main dosimetric TL peak characteristic of undoped MgO is 250 °C and 290 °C does not significantly change when the Ti⁴⁺ ions are introduced to the crystal lattice of MgO. TL signals of the main dosimetric TL peak that located between 190 and 350 °C has been increased by ~7.5, 5.6 and 4.2 times for MgO:Ti⁴⁺(0.1% wt), MgO:Ti⁴⁺(0.5% wt) and MgO:Ti⁴⁺(1% wt), respectively while TL signals at 90 °C is decreasing by ~ 0.4, 0.24 and 0.14 times for MgO:Ti⁴⁺(0.1%), MgO:Ti⁴⁺(0.5% wt) and MgO:Ti⁴⁺(1% wt), respectively. The best TL signal was recorded for MgO:Ti⁴⁺(0.1% wt). With the incorporation of Ti⁴⁺ ions into the MgO lattice, Ti⁴⁺ doping can lead to increasing the trap centers (recombination centers) in the forbidden gap of the ceramic. Dosimetric characteristics of the MgO:Ti⁴⁺(0.1% wt) ceramics were investigated among the aforementioned ceramics. The high TL peaks of the MgO:Ti⁴⁺(0.1% wt) located at 250 and 290 °C are suitable for dosimetric investigation.

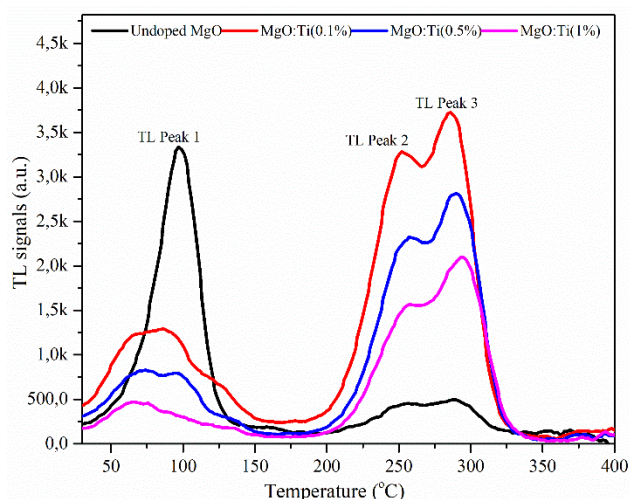


Figure 4. TL curves of the synthesized all ceramics, i.e., undoped MgO, MgO:Ti⁴⁺(0.1% wt), MgO:Ti⁴⁺(0.5% wt) and MgO:Ti⁴⁺(1% wt) after 1 Gy dose.

3.5. Preheat experiment

Preheat experiments are important for the study of thermal stability and in the identification of the nature of the traps responsible for the TL signals. In order to determine the preheat temperature of the MgO:Ti⁴⁺(0.1% wt) ceramic, TL curves were separately recorded after preheating at pre-determined temperatures between 50-300 °C with the step of 10 °C and 20 °C for preheating temperature time of 10 s after 1 Gy dose, following after the ceramic were annealed at 400 °C for 20 min. Then, a TL reading at a heating rate of 2 °C/s up to 450 °C was performed in order to delete residual signals each after TL measurements. The integrated TL signals between 170-350 °C were recorded. The graphic was drawn integrated TL signals vs preheat temperature (Fig 5.). As seen in Fig. 5., temperature about 200 °C has a stable region, if the temperature region >200 °C, the sharp reduce is recorded up to 300 °C. The main reason for this reduction is the decrease of trapped charge population in this range temperature. The preheat temperature of the MgO:Ti⁴⁺(0.1% wt) temperature was selected as a 170 °C. Guckan et al., (2020) [3] reported OSL preheat temperature of MgO:Na,Li ceramic as a 130 °C for 10s.

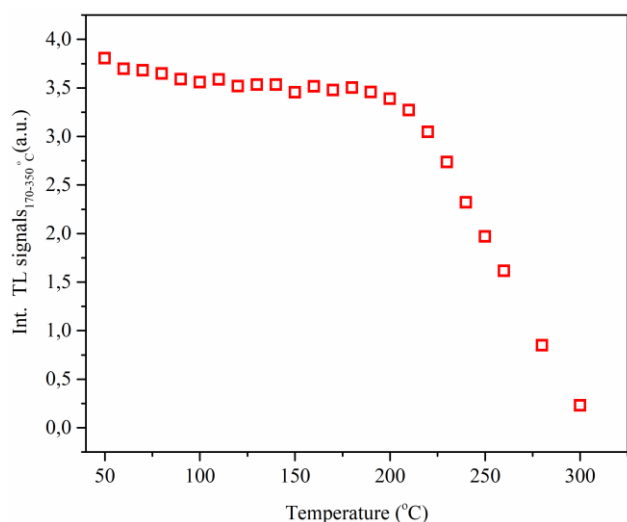


Figure 5. The graphic of preheating for MgO:Ti⁴⁺(0.1% wt) ceramic in the range from 50-300 °C after 1 Gy dose.

3.6. Dose-response experiment

TL sensitivity of thermoluminescent dosimeter (TLD) phosphor to ionizing radiation would ideally be linear over a range of doses. Dose-response of the MgO:Ti⁴⁺(0.1% wt) ceramic was studied in the range of 0.1 Gy–20 Gy. The dose values were taken as 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 Gy. TL curves were recorded after preheating at 170 °C for 10s with a heating rate of 2 °C/s from room temperature to 450 °C for each dose. Fig. 6 shows a graphic of the integrated TL signals between 170-350 °C data versus absorbed dose. The data points were fitted with a linear function which is given $y=a+bx$, where and its parameters were given as insert table in Fig 6. The slope of the plotted graphic was found to be 1.03. The results indicate the response of ceramics was linear in the 0.1 Gy to 20 Gy.

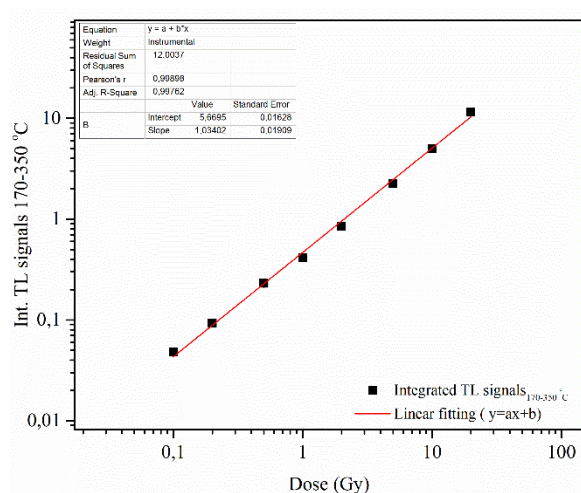


Figure 6. Dose-response of the MgO:Ti⁴⁺(0.1% wt) ceramic.

3.7. Reusability experiment

Reusability is one of the most significant properties that almost every dosimetric material should possess. One of the biggest advantages of thermoluminescence dosimeters (TLDs) is that it can be used repeatedly. The reusability characteristic of the ceramics was studied up to ten experimental cycles under beta radiation. The TL curves were recorded with a heating rate of 2 °C/s after preheating 170 °C for 10 s after 1 Gy beta dose. Then A TL readout was done to delete the remaining signals after reading. Fig. 7 shows (a) the normalized integrated TL signals which are between 170-350 °C versus the number of experimental cycles (b) TL glow curves after reading. As seen in Fig. 7., the reusability showed at 4% standard deviation up to the first readout at the end of ten cycles. This deviation might originate from; (i) variations in the effective number of total traps, (ii) reader system.etc. This deviation was with acceptance limits of 5% [10]. As a result, the ceramic possesses a good reusability under the same experimental conditions.

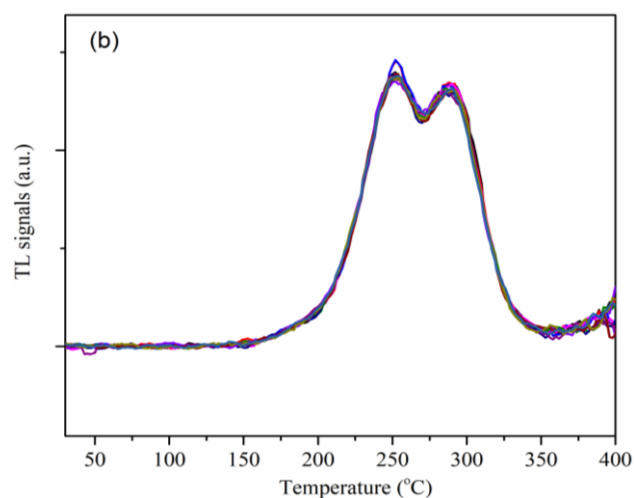
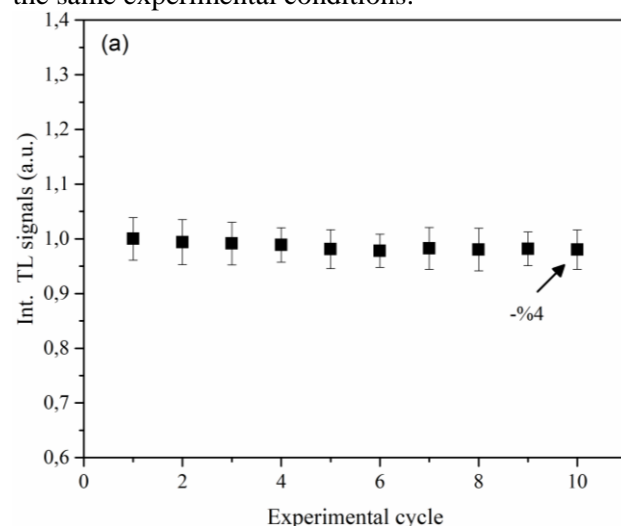


Figure 7. (a) Normalized TL signal (Integrated 170-350 °C) according to the first TL read, (b) TL glow curve after preheating 170 °C up to ten experimental cycles.

4. Conclusions

In this study, the SCS method could not be used directly because of the Ti^{4+} ion (TiO_2) cannot be dissolved in water to obtain the titanium doped MgO ceramics. Ti^{4+} doped MgO ceramic was able to synthesis the using the solid state assisted solution combustion synthesis method. The structural characterization of the synthesized ceramic was studied using the XRD and SEM techniques. XRD results showed that MgO: Ti^{4+} (0.1%wt) ceramic was successfully synthesized by the abovementioned method. RL characteristic of the ceramic showed four emission peaks located at 327, 694, 715 and 745 nm. Some dosimetric properties of the MgO: Ti^{4+} (0.1%wt) ceramic such as dose-response, reusability were reported. The dose-response was studied in the range from 0.1 to 20 Gy, showing a linear response over this range. The ceramic has good reusability up to 10 cycles with the standard deviation of 4% according to the first TL readout under the same experimental condition. The experimental results showed that if it is developed this ceramic can be considered as a dosimetric material with suitable properties in personal and medical applications.

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Conflicts of interest

The author state that did not have conflict of interests.

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