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Thermoluminescence properties of TiO_2 nanopowder

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Abstract

Titanium oxide (TiO_2)-based ceramics have many desirable and potential applications. Their mechanical properties are strongly affected by composition and microstructure, and can thus be tailored. The optical properties of TiO_2 are useful, being colorless, transparent, and possessing a high refractive index. These properties and the ability to tailor the structure make TiO_2-based ceramics suitable for a wide range of applications. Interest in titanium oxide-based ceramics has increased considerably in recent years as possible thermoluminescence (TL) dosimeters which could be used in a wide variety of research activities and applications of ionizing radiation dosimetry. The aim of this work is to investigate some dosimetric properties of manganese doped titanium oxide (TiO_2: Mn) nanopowder concerning the TL phenomenon related to its structural, morphological, and luminescent characteristics. Powder of TiO_2: Mn was prepared using a co-precipitation method from titanium oxysulfate–sulfuric acid complex ($TiOSO_4 \times H_2SO_4 \times H_2O$) and manganese(II)chloride $\cdot$ $6H_2O$. Formation of the compound was confirmed by studying the X-ray diffraction patterns. Diffraction patterns obtained suggested a mixture of anatase and rutile structure of the TiO_2 powder analyzed. Assuming the particles are stress-free, the size was estimated from a single diffraction peak using Scherrer's equation. Powder with the average nanopolycrystalline sizes from 10 nm up to about 80 nm was obtained. The glow curve of TiO_2: Mn nanopowder exposed to gamma radiation exhibited one main peak centered at 240 °C and a lower intensity peak at about 258 °C. The intensity of the main peak increases as the dose increases. TL glow curve intensity of TiO_2: Mn powder submitted to 1000 °C was found to be more intense than that of the amorphous material, with the intensity increasing with the increase of crystallization temperature.

Keywords: Thermoluminescence; Metallic oxides; Dosimetry

1. Introduction

Thermoluminescence (TL) dosimetry has become a reliable and routine method for measuring ionizing and non-ionizing radiation (Azorin, 1990; Furetta and Weng, 1998), and many solid-state materials (pellets and powders) have been employed. Interest in metallic oxides, mainly in titanium oxide (TiO_2) has increased considerably in recent years, conducting to its possible use as TL dosimeters. Properties like grain size, porosity, texture, specific surface area, and chemical and thermal stability can be tailored to desired applications. However, attainment of these properties is strongly dependent on the growth conditions.

Nanomaterials can form new metastable crystal structures and have potential as efficient phosphors in many applications. In addition, these materials are more stable with high luminescent intensity and low photo-bleaching (Chandler et al., 1993). Many new physical and chemical methods of preparations have also been developed in the last one decade, and nanoparticles and nanorods (powders) of several ceramic materials have been produced (Brinker and Sherrer, 1989).

Titanium oxide (TiO_2)-based ceramics have many desirable and potential applications. The optical properties of TiO_2 are useful, being colorless, transparent, and possessing a high refractive index. It is the combination of its properties, and the ability to tailor the structure, that makes TiO_2-based ceramics suitable for a wide range of applications (Chen et al., 2004). Interest in titanium oxide-based ceramics has increased considerably in recent years as possible TL dosimeters which could

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be used in a wide variety of research activities and applications of ionizing radiation dosimetry.

Interest in co-precipitation method to produce TiO_2: Mn from titanium oxysulfate–sulfuric acid complex ($TiOSO_4 \times H_2SO_4 \times H_2O$) and manganese(II)chloride $\cdot$ $6H_2O$ arises from the relatively low cost and the approach allows the chemical content and concentration ratio of the elements of the derived powders to be tailored, with ready fabrication into different solutions (Vekawa et al., 2002).

It is known that the TL process in phosphors is in general related to the defect centers created due to ionizing radiation (Azorin, 1990). TL investigations have also shown that defect centers play a crucial role in TL. The formation and the stability of the defect centers also depend on the method of preparation of phosphors and dopants (Furetta and Weng, 1998).

Therefore, the objective of the present work is to investigate the TL properties of TiO_2 nanopowder concerning the TL phenomenon related to its structural, morphological, and luminescent characteristics and to propose it as a good candidate TL dosimeter for gamma radiation field.

2. Experimental procedures

2.1. Samples preparation

Co-precipitation method was used to produce TiO_2: Mn from titanium oxysulfate–sulfuric acid complex ($TiOSO_4 \times H_2SO_4 \times H_2O$) and manganese(II)chloride $\cdot$ $6H_2O$ due to its relatively low cost and the approach that allows the chemical content and concentration ratio of the elements of the derived powders to be tailored, with ready fabrication into different solutions.

2.2. Thermal annealing

To study the crystallization pathway, successive annealing treatments of the fresh samples were performed in air by heating at temperatures in a range of 100–1000 °C.

2.3. Structural characterization

The TiO_2: Mn powders obtained from the above processing route were characterized using EDS analysis and X-ray diffractograms which were obtained with a Siemmens D-5000 diffractometer, using CuK_α radiation ($\lambda = 0.1548$ nm) at 40 kV and 30 mA, with intervals of 0.03° in a range of $5° < 2\theta < 70°$, using an integration time of 0.3 s for each point.

2.4. TL readout

TL measurements were made in a Harshaw TL analyzer, model 3500, connected to a PC to record and process the experimental data. The TL signal was integrated from room temperature up to 350 °C using a heating rate of 10 °C/s. All TL measurements were made in nitrogen atmosphere in order to reduce the spurious signals resulting from the heating planchet of the TL reader.

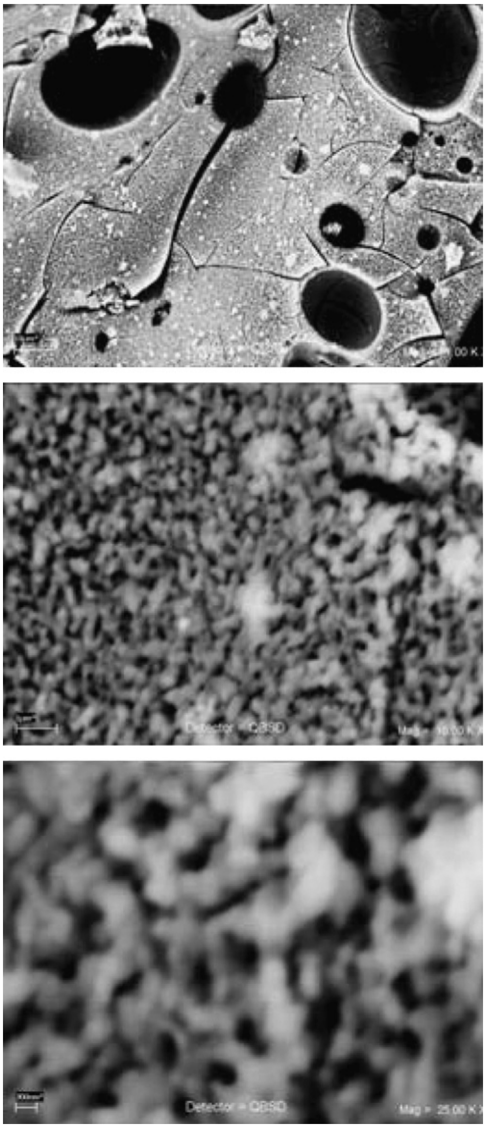

Fig. 1. SEM micrographs of TiO_2: Mn powders. It is possible to observe a porous material (a). In the solid regions of the sample, fine granulated zones are observed (b, c).

2.5. Dosimetric properties

Previous to determination of dosimetric properties, the samples were submitted to a thermal treatment consisting in heating at 120 °C for 2 h and in immediate readout in order to obtain background signal.

Dosimetric properties studied were: glow curve, sensitivity, linearity, fading, and repeatability. Each experimental data point represents the average of at least 10 measurements.

To investigate glow curve and other TL properties of TiO_2: Mn powder, samples were exposed to ^{137}Cs gamma radiation source. Sensitivity was tested by irradiating samples of TiO_2: Mn powder jointly with a similar (same mass) batch of commercial LiF:Mg,Ti (TLD-100) with ^{137}Cs gamma radiation at an absorbed dose of 10 Gy. To determine the TL response as a function of absorbed dose, the samples were exposed to ^{137}Cs

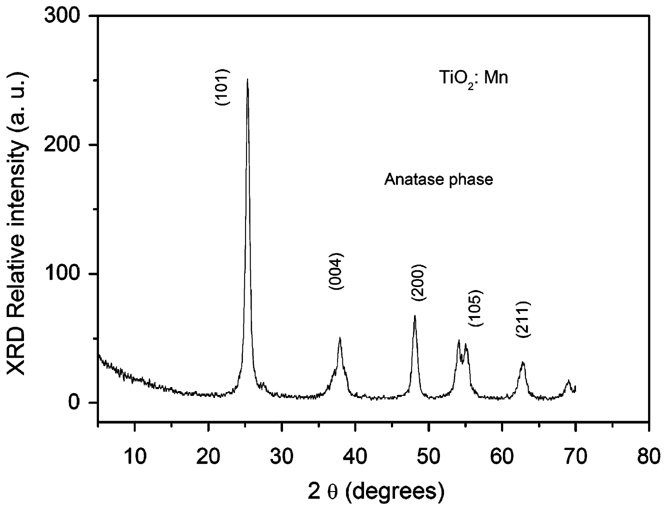

Fig. 2. X-ray diffraction pattern for TiO_2: Mn powder. This powder shows the TiO_2 anatase phase.

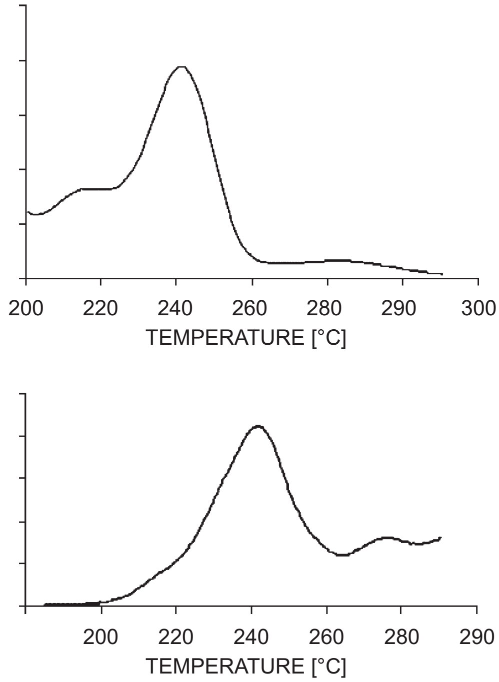

Fig. 3. Glow curves of TiO_2: Mn powder irradiated with ^{137}Cs gamma radiation at an absorbed dose of 10 Gy, obtained immediately after irradiation (a) and 2 h after irradiation (b).

gamma radiation by varying the absorbed dose. To investigate repeatability, a set of TiO_2: Mn powder samples was exposed repeatedly to the same absorbed dose (10 Gy) repeating up to 10 times the irradiation–readout–annealing cycle.

Fading was determined by means of the samples at an absorbed dose of 10 Gy of ^{137}Cs gamma radiation and storing at room temperature without the external light exposure. Then, readout at different time intervals was carried out.

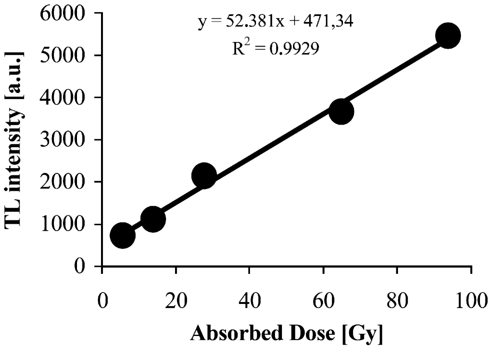

Fig. 4. TL response of TiO_2: Mn powder as a function of ^{137}Cs gamma radiation absorbed dose.

3. Results and discussion

Fig. 1 shows the SEM micrographs of TiO_2: Mn powder after annealing at 120 °C for 2 h in air. In this figure we can observe the surface morphology of the powders. It is possible to observe a porous material (Fig. 1a). In the solid regions of the sample, fine granulated zones are observed (Figs. 1b and c).

It is shown that the morphology of the TiO_2: Mn powder is basically polycrystalline constituted by nanocrystalline TiO_2 particles which include anatase TiO_2, with grain sizes of the order of nanometers. The powder size observed by SEM is highly accordant with that of the sample examined by XRD whose spectrum is shown in Fig. 2. Diffraction patterns obtained suggested anatase structure of the TiO_2 powder analyzed revealing a preferential (1 0 1) orientation of titanium oxide. The observed line broadening was used to estimate the average grain size. Assuming the particles are stress-free, the size was estimated from a single diffraction peak using the Scherrer's equation (Cullity, 1978). The crystallite size was in a range of about 10–80 nm.

Fig. 3 shows the glow curve of TiO_2: Mn nanopowder exposed to an absorbed dose of 10 Gy of ^{137}Cs gamma radiation.

This TL glow curve exhibited one main peak centered at 240 °C, and two lower intensity peaks at about 220 and 258 °C. The intensity of the peaks increases as the dose increases without change in the glow curve shape. The first peak disappears 2 h after irradiation. Fig. 3a shows the glow curve obtained immediately after the irradiation, meanwhile Fig. 3b presents the glow curve 2 h after the irradiation.

Sensitivity of TiO_2: Mn to ^{137}Cs gamma radiation was 0.14 nC/mg-mGy (0.5 relative to TLD-100). The TL response as a function of gamma radiation absorbed dose, determined as the height of the 240 °C peak, was linear in the range from 5 up to 100 Gy as is shown in Fig. 4. The fading characteristics of the TiO_2: Mn powder under gamma radiation effects was 20% during the first 2 h and was negligible after this time. Repeatability was ±3% after 10 cycles of annealing–irradiation–readout.

4. Conclusions

The chemical process for synthesizing TiO_2: Mn nanopowder has been developed using the co-precipitation of titanium oxysulfate–sulfuric acid complex ($TiOSO_4 \times H_2SO_4 \times H_2O$) and manganese(II)chloride $\cdot$ $6H_2O$, obtaining TiO_2: Mn polycrystalline powder constituted by nanocrystalline TiO_2 particles which include mainly anatase TiO_2, with grain sizes of the order of nanometers.

TL glow curve intensity of sintered TiO_2 powder submitted to thermal treatment was found to be more intense than that of the amorphous TiO_2; this intensity is increased as crystallization temperature applied was increased. The reason for this increasing intensity could be that under irradiation the crystalline TiO_2 ions in the lattice crystal cause defects and thus act as trapping sites by capturing the electrons released by the radiation.

The intense fading observed during the 2 h after irradiation could be due to the 220 °C peak which disappears completely after this elapsed time.

Results obtained for linearity, fading, and repeatability tests suggest that TiO_2: Mn is a good candidate to be used as a TL dosimeter for gamma radiation field.

Acknowledgement

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