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Thermoluminescence and photoluminescence of ZrO_2 nanoparticles

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ABSTRACT

This work describes the thermoluminescence (TL) and photoluminescence (PL) of zirconium oxide (ZrO_2) nanoparticles synthesized using the propellant chemical combustion method. They were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD result shows a nanocrystalline material with a major tetragonal phase along with a small portion of monoclinic phase, while SEM images display particles of spherical shapes of diameters in the 25–35 nm range. Samples from this powder were exposed to different doses of γ-rays from a ^{137}Cs source in the range of 0.01 Gy–1 kGy. The induced TL glow curve has a single broad peak at around 600 K. TL response curve of this peak shows sublinearity for all the recorded doses, while its fading over two months is negligible. The intensity and structure of the TL glow curve did not change after several cycles of exposures and readout. PL excitation and emission spectra were also recorded and are investigated. When the material was excited by different wavelengths, several emission bands are observed in the range of 300–500 nm. The new nanocrystalline material shows excellent characterization such as good TL sensitivity, low fading and reusability making it a promising TL dosimeter.

1. Introduction

Nanomaterials are defined as those materials whose length scale lies within the nanometric range, i.e. from one to a hundred nanometers. Within this length scale, the properties of matter are considerably different from the individual atoms, molecules and bulk materials. The physical, chemical, electrical and optical properties of these materials are size and shape dependent and they often exhibit important differences in the bulk properties. The materials at such scale have attracted many workers in various fields from material science to biotechnology and genetics (Fonseca et al., 2005; Kerman et al., 2004; Christopher et al., 2003; Xu and Ejaz Huq, 2005; Salah et al., 2009a). Currently, the importance of nanomaterials in the field of luminescence has been increased, especially, as they exhibit enhanced optical, electronic and structural properties. They have potential as efficient phosphors in display applications such as new flat panel displays with low-energy excitation sources, solar energy converters, optical amplifiers and thermoluminescent dosimeters (Russell and Boyd, 1996; Gong et al., 2000; Hadjipanayis and Siegel, 1993; Salah, 2011; Yi et al., 2001; Gershenfeld and Chaung, 1997). Many new physical and chemical methods of preparations have also been developed in the last two decades, nanoparticles and nanorods (powders) of several ceramic materials have been produced (Wu et al., 2003). More recent studies have revealed that optical, luminescence and other properties get modified by its shape and size, incorporation of impurity(ies) at different site(s) and also due to the presence or absence of certain defects (Yatsui et al., 2002; Qu et al., 2002; Fox et al., 1988).

Thermoluminescence (TL) is the thermally stimulated emission of light from an insulator or semiconductor, following the previous absorption of energy from ionizing radiation such as γ -rays, X-rays, β-rays, α-particles, neutrons and energetic ions. This phenomenon has been utilized for the dosimetry of ionizing radiations, since the TL intensity on stimulation (heating) is proportional to the radiation flux (doses). There are a number of commercially available thermoluminesent dosimeters (TLD) for this purpose under different trade names, the most popular ones are LiF:Mg,Ti (TLD-100), LiF:Mg,Cu,P (TLD-700H), $CaSO_4$:Dy (TLD-900), CaF_2:Dy (TLD-200), Al_2O_3:C (TLD-500) and so on (Noh et al., 2001; Madhusoodanan et al., 1999). However, efforts are still being made either by improving the TL characteristics of these phosphors by preparing them using different methods or by doping with different impurities or developing some new ones (Lakshmanan et al., 2002; Shinde et al., 2001; Kima et al., 2004; Sahare and Moharil, 1990a, 1990b; Dhoble et al., 1993; Hasan et al., 1985). However, all these phosphors have 'dose-ranges' depending on their 'sensitivity' and 'response characteristics' (linearity and saturation) to high-energy radiations. At low doses, very low signal to noise makes it difficult to estimate doses, while

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at higher doses the saturation of the TL signal makes it difficult. For example, Hasan et al. (1985) have suggested the use of high temperature peak of $CaSO_4$:Dy for estimating such high doses of γ-rays but it is also not very accurate and convenient as there is not much variation in TL intensity with doses, and undesired changes in the glow structure also makes it difficult. Moreover, the black body radiation from the heating plate may add some inaccuracies at higher temperatures.

Recently, Salah and co-workers have synthesized nanocrystalline of some highly sensitive phosphors such as $CaSO_4$:Dy, LiF:Mg,Cu,P, MgB_4O_7:Dy, $Ba_{0.97}Ca_{0.03}SO_4$:Eu, $K_2Ca_2(SO_4)_3$:Eu, $BaSO_4$:Eu and K_3NaSO_4:Eu (Salah et al., 2006, 2007a, 2007b; Lochab et al., 2007a, 2007b; Sahare et al., 2007) and studied their TL response to different ionizing radiations. Some of them were tested for their response to sparsely ionizing radiations such as gamma rays and others to densely ionizing radiations like heavy charged particles. They have found very interesting results, especially the response of these nanomaterials to very high doses. The linear response over a large span of exposures along with negligible fading and their insensitivity to heating treatments makes the nanomaterial phosphors useful for their application to estimate high exposures of γ-rays and heavy charged particles (HCP). Therefore due to these preliminary remarkable results obtained in such nanomaterials it is of great importance to further study the TL properties of different nanomaterials to heavy doses of ionizing radiations.

Ultrafine zirconia (ZrO_2) particles or nanoparticles have been reported to have unique properties such as excellent refractoriness and chemical resistance, good mechanical strength, high ionic conductivity, low thermal conductivity at high temperature together with relatively high thermal expansion coefficient and good thermal stability (Tahmasebpour et al., 2008; Garcia et al., 2009). They have found a broad industrial applications including fabrication of dense ceramics, sensors, batteries, capacitors, corrosion-resistant and thermal barrier coatings, fuel cells, solid electrolytes, catalysts, etc. (Guo and Chen, 2005; Liang et al., 2003; Sadykov et al., 2005). It is therefore suggested to study the TL response of ZrO_2 nanoparticles to gamma rays. They were synthesized using the chemical combustion (propellant) method and characterized by XRD, SEM and PL. Samples from these nanomaterials were exposed to different doses from a ^{137}Cs gamma rays source and studied for their TL properties.

2. Experimental

The nanoparticles of ZrO_2 were prepared by the propellant chemical combustion technique. In this technique, appropriate amount of $ZrO(NO_3)_2 \cdot xH_2O$ (AR grade) was mixed in stoichiometric proportions with urea (5.8 g of $ZrO(NO_3)_2 \cdot xH_2O$ and 1.5 g of urea) and dissolved in a minimum amount of water (~20 mL) in a Pyrex dish. The stoichiometric composition of the redox mixtures was calculated from the total oxidizing and reducing valency of the total nitrate (oxidizer) and reducing agent, i.e. urea (fuel), which serves as a numerical coefficient for the stoichiometric balance so that the equivalence ratio is equal to unity ($O/F=1$) (Patil, 1993). The dish is introduced into a furnace preheated at 600 °C. The solution immediately started to boil and undergoes dehydration. This is quickly followed by decomposition of the metal nitrates, with a large release of gases (oxides of nitrogen and ammonia). The paste frothed and formed foam, which swelled and was then blazed up. A white flame occurred with the production of a foamy material, which swelled to the capacity of the dish. Then a fine powder is produced. This powder was then annealed at 800 °C for 1 h.

The produced nanomaterials were characterized by X-ray diffraction, using an Ultima-IV (Rigaku, Japan) diffractometer with Cu Kα radiation, while the morphology of the powder was analyzed with a field emission scanning electron microscopy (FESEM), JSM-7500F (JEOL, Japan) operated at 10 kV. For taking TL, samples were exposed to gamma rays from a ^{137}Cs source for various doses (0.01 Gy–1 kGy) at room temperature. The dose rate for gamma rays irradiation was 0.15 Gy/s. TL glow curves were recorded on a Harshaw TLD reader (Model 3500) fitted with 931B photomultiplier tube (PMT) by taking 5 mg of sample each time. The measurements were recorded in nitrogen atmosphere at a heating rate of 5 K s^{-1}. The phase transition was investigated using Shimadzu DSC-60. The calorimetric sensitivity is ±10 μW with a temperature accuracy of ±0.1 K. Typically, 5 mg of sample in powder form was sealed in standard pans and heated at a heating rate of 10 K/min under dry nitrogen supplied at the rate of 35 mL/min. Photoluminescence excitation and emission spectra were recorded at room temperature using Fluorescence Spectrofluorophotometer, model RF-5301 PC, Shimadzu, Japan. Small quantity of the nanomaterial was dispersed in ethanol (5 mg in 5 mL) and is used for recording PL.

3. Results

3.1. X-ray diffraction

Fig. 1 shows the XRD diffraction patterns with hkl values for the synthesized ZrO_2 powder. The diffracted peaks show a major tetragonal phase, which is confirmed by the presence of a high intensity peak at $2\theta=30$ (Aruna and Rajam, 2004; Scholz and Kaskel, 2008). Small portion of the produced nanomaterial has a monoclinic phase (Scholz and Kaskel, 2008). The figure shows a clear broadening of the diffracted peaks, which is due to the reduction in the particle size (Aruna and Rajam, 2004). The crystallite sizes calculated with the Scherrer formula are between 20 and 30 nm.

3.2. Particle shape and size

The shape and size of the prepared nanocrystalline were determined by scanning electron microscope (SEM). Fig. 2a and b shows SEM images of ZrO_2 nanoparticles produced by the chemical combustion technique. The particles are of spherical shapes with diameters in the range of 25–35 nm. This result is close to that obtained using the Scherrer formula on the XRD peaks. It is also

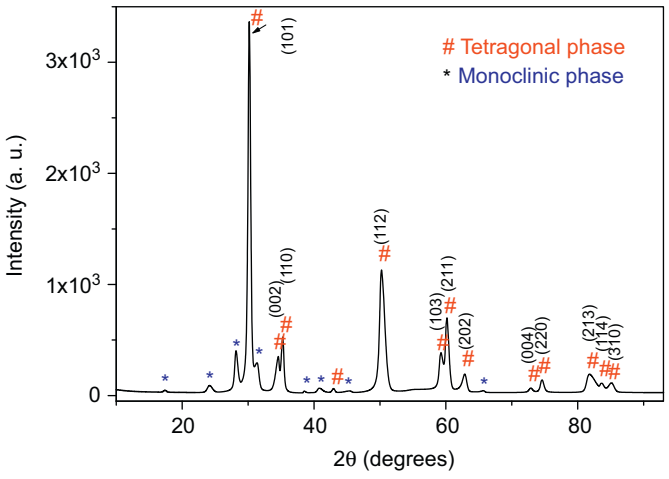

Fig. 1. XRD pattern of ZrO_2 nanocrystalline powder (two phases are observed).