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Preparation and Thermoluminescence Properties of Polycrystalline Na_2SO_4/SiO_2 composite

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Astract: A sodium sulphate/silica (Na_2SO_4/SiO_2) composite was prepared by a sol-gel procedure using a geode as the silica source. The prepared sample was characterized by XRD, XRF and IR techniques. The Na_2SO_4/SiO_2 has an orthorhombic phase, and an average crystalline size is about 51 nm. Thermoluminescence characteristics of Na_2SO_4/SiO_2 were studied at different parameters. The glow curve resulting from Na_2SO_4/SiO_2 showed one clear peak between 150 ºC to 200 ºC, depending on the energy. The general peak structure of the TL glow curve remains unchanged as a result of repeated cycles of irradiation at various X–ray energies, and exhibits good linearity over the used exposure. There were no significant changes in the TL reading after ten times of reuse, and the fading was observed at 56% after 15 days of irradiation and after one month about 82.3% of the TL signal was lost, and the value of Z_{eff} of Na_2SO_4/SiO_2 was found to be 13.56.

Keywords: TLD, Geode, Silica.

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Propiedades de preparación y termoluminescencia del compuesto policristalino Na_2SO_4/SiO_2

Resumen: Se preparó un compuesto de sulfato de sodio/silica (Na_2SO_4/SiO_2) mediante un procedimiento sol-gel utilizando un geodo como fuente de silica. La muestra preparada se caracterizó por técnicas XRD, XRF e IR. El Na_2SO_4/SiO_2 tiene una fase ortorhóbica, y un tamaño cristalino promedio es de aproximadamente 51 nm. Se estudiaron las características de termoluminescencia de Na2SO4/SiO2 en diferentes parámetros. La curva de brillo resultante de Na2SO4/SiO2 mostró un pico claro entre 150 ºC y 200 ºC, dependiendo de la energía. La estructura general de pico de la curva de resplandor TL permanece inalterada como resultado de ciclos repetidos de irradiación en diversas energías de rayos X, y muestra buena linealidad sobre la ex-posura utilizada. No hubo cambios significativos en la lectura de TL después de diez veces de reuso, y el desvanecimiento se observó en 56% después de 15 días de irradiación y después de un mes aproximadamente el 82.3% de la señal TL se perdió, y se encontró que el valor de Z_{eff} de Na_2SO_4/SiO_2 era de 13.56.

Palabras clave: TLD, Geode, Silica.

1. INTRODUCTION

Thermoluminescence dosimetry (TLD) is a proper method for assessing ionizing radiation dosage. TLD materials come in a broad range of physical shapes, allowing for evaluating various radiation characteristics at dosage levels ranging from µGy to kGy. The tiny physical size of TL dosimeters and the point that no cables or additional equipment are required during dose measurement are significant benefits. As a result, they are well-suited to many dosimetric applications [1,2,3]. Natural minerals are used for a large variety of purposes in modern science and technology, which enhances human life. Quartz is a typical natural mineral with several benefits in a variety of TL dosimetry applications, such as for determining a substance's radiological history [4,5], monitoring nuclear accidents [6], and food irradiation control [7]. Geodes are discrete bodies of mineral matter with various shapes, but commonly they are globular or ellipsoidal. There are two types of geodes, sedimentary geodes which are formed within sedimentary rock formations and the volcanic geodes that are formed within igneous or volcanic rocks. Geodes commonly have a chalcedony (*cryptocrystalline quartz*) shell lined internally by various minerals, often as crystals, particularly calcite, pyrite, kaolinite, sphalerite, millerite, barite, celestite, dolomite, limonite, smithsonite, opal, chalcedony and macrocrystalline quartz, which is by far the most common and abundant mineral found in geodes. On the other hand, sulphates are attractive materials in the field of thermoluminescence (TL) dosimetry for the measurement of radiation dose, and sodium sulphate, though very simple in chemical composition, has been the subject of various applications. It is used for the production of glasses, paints and for thermal energy storage techniques [8, 9,10]. The current study aims to investigate the capability of using prepared Na_2SO_4/SiO_2 as a thermoluminescent dosimeter material.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Geode is rich in silica : A geode sample is surrounded by a hard material formed from sediment, and inside, the geodes are white in color. In the lab, the samples were washed with distilled water and dried at 100 °C to get rid of dust and dirt. They were then grounded, sifted with a diameter of 0.063µm, and burnt at 500 °C. The chemical extraction process started by mixing 2.5g of the starting material with 150ml of sodium hydroxide in a 250ml beaker equipped with a condenser and stirring at 300rpm for 24 hours to dissolve the silica and form sodium silicate.

The solution is filtered using a Whatman 41 filter paper, and washed with distilled water, sodium silicate begins to precipitate when the pH is less than 10. To form silica gel, sulfuric acid was added to the solution to reduce the pH to 7. The formed gel was left at room temperature for 24 hours before being filtered and washed with distilled water to reduce the sulfate salt. The sample was dried at 80 °C for 24 hours. To reduce the dissolved substances, the sample was washed with hydrochloric acid at 110 °C for three hours with continuous stirring. Then it was filtered and washed with water and dried at 110 °C overnight, then the sample was burned at 800 °C for two hours in the oven, then burned again at 1000 °C for half an hour, to obtain a soft, bright white substance.

XRF spectrometer was used to identify the elemental composition of the prepared sample, while XRD was used for crystallographic phase identification. FT-IR Spectrometer was used to measure Fourier transformation infra-red (FTIR) absorption spectra of the prepared sample in the spectral range 400–4000 cm^{-1}. According to a qualitative XRF examination of raw material silicon was the predominant ingredient (97.7%), with lesser amounts of aluminum (1.74%), potassium (0.361%), calcium (0.173%), and a variety of other elements as impurities. After chemical processes, the predominant ingredient was SO_3 (43.8%), then SiO_2 (39.8%), Na_2O (15.1%), and Al_2O_3 (0.495%). The TL reading was carried out in a TLD 3500 Harshaw, during the process a preheating temperature of 50 °C was used, with a heating rate of 25 °C/s until reached a maximum temperature of 400 °C.

3. RESULTS AND DISCUSSIONS

3.1 Structural Analysis (XRD and FTIR)

XRD analysis was carried out and the typical diffraction pattern is shown in Figure 1, from XRD data the SiO_2 has a hexagonal phase and Na_2SO_4/SiO_2 has an orthorhombic phase. The crystalline size is calculated using the Debye-Scherer equation 1, where D is the average crystalline size, K is constant (0.98), λ is the X-rays wavelength (1.54nm), and β is the full width at half maximum (FWHM). The prepared Na_2SO_4/SiO_2 has an average crystalline size of about 51 nm.

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Figure 1 : The XRD pattern of (a) SiO_2 and (b) Na_2SO_4/SiO_2

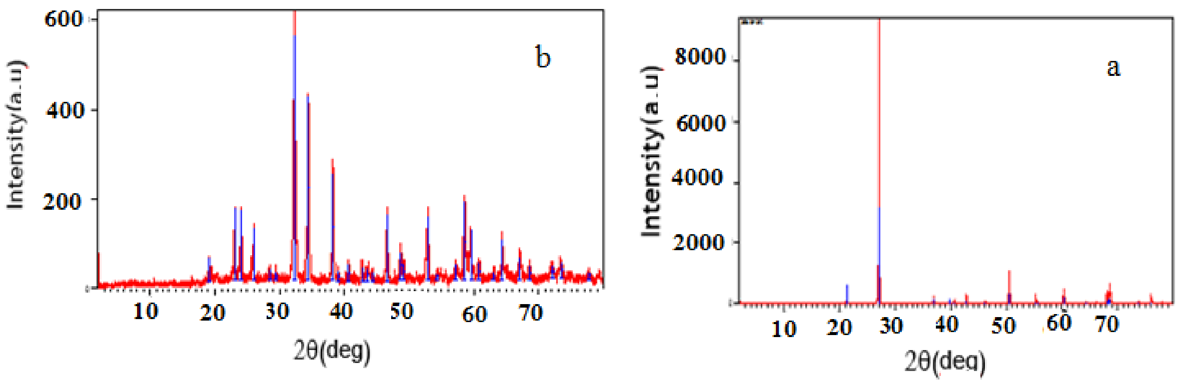
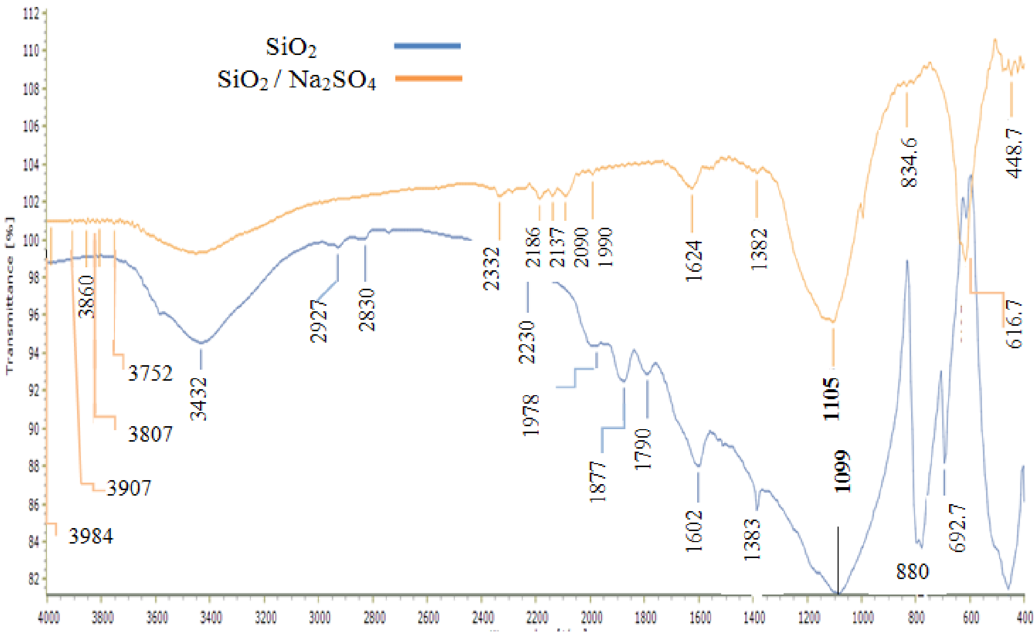


Figure 2 shows the FTIR transmission spectrum of SiO_2 and Na_2SO_4/SiO_2. For SiO_2 the strong bands at 1099 cm^{-1}, 450 cm^{-1}, and 880 cm^{-1} were associated with the asymmetric and symmetric Si-O-Si stretching vibration bondings. The peak at 3432 cm^{-1} is corresponding to the – OH stretching vibration from the Si – OH groups and adsorbed H_2O in the Silica [11]. Similarly, a peak corresponding to vibration bending can be found at 1602 cm^{-1}, which indicates the presence of O-H stretching bond [12]. Characteristic peaks at 1105 cm^{-1}, 834.6 cm^{-1}, 616.7 cm^{-1}, and 448.7 cm^{-1} are found in the IR spectrum of the Na_2SO_4/SiO_2 composite and due to the stretching and bending of S–O bond, the most intense bands are situated at 1105 and 610.7 cm^{-1}, respectively.

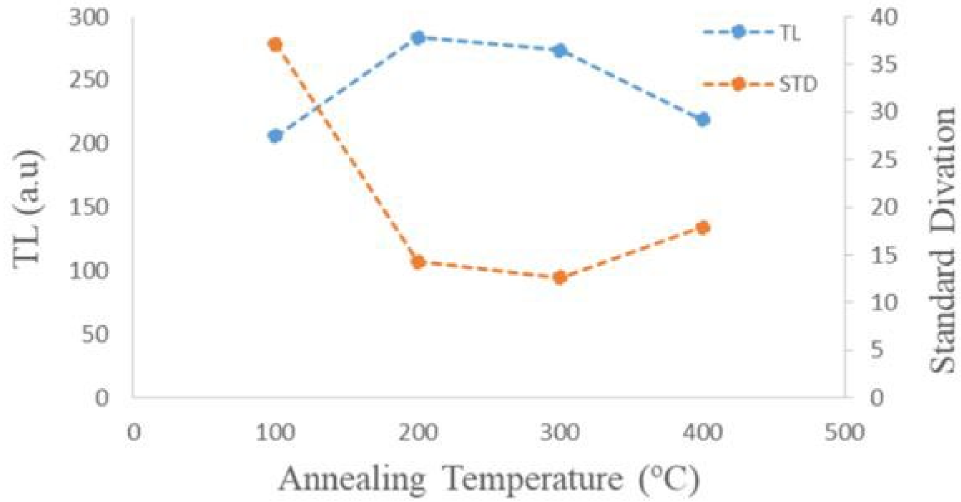
Figure 2: The FTIR transmission spectrum of the Na_2SO_4/SiO_2 and SiO_2.



3.2 Optimum Temperature

In order to prepare a thermoluminescent material to be used for dosimetric applications, it is necessary to perform a thermal treatment process, usually called annealing. This process is carried out in an oven, where the TL samples are heated up to a certain temperature and kept at this temperature for a given period of time. The samples are then cooled down to the room temperature [13]. This process has two main goals : (i) to find a good combination of annealing temperature and time to stabilize the trap structure; (ii) to produce the lowest intrinsic background and to obtain the highest reproducibility of TL response. Figure 3 shows the TL intensity and its standard deviation (STD) value of Na_2SO_4/SiO_2 along with annealing temperature between 100° and 400 °C. Each data point is an average of five samples. The highest TL response with the lowest STD was found at 200 °C after 2h, and this temperature was chosen as optimized temperature.

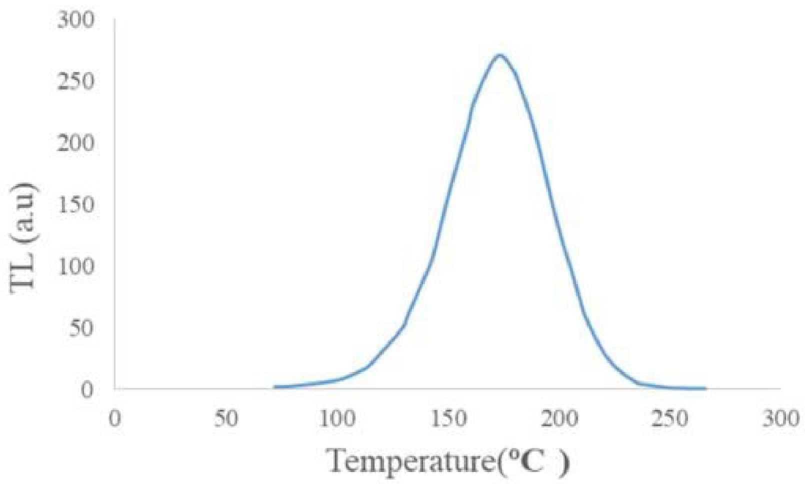
Figure 3: The TL response of Na_2SO_4/SiO_2 as function of annealing temperature at 2h annealing time.



3.3 Glow Curve

When irradiated thermoluminescent material with a crystal structure is heated under control, the glow curve shows several peaks. According to band theory these peaks correspond to the different traps in the forbidden band gap of the crystal. An important physical factor in determining the stability of a given TL material for medical applications is the temperature at which the peak of the glow curve occurs. Figure 4 shows the glow curve of Na_2SO_4/SiO_2, it is clear that the material has only one glow peak which appears between 150 °C to 200 °C, depending on the energy and indicating that the only unit set of trap states is being activated within the particular temperature range with its own value of activation energy (Eg) and frequency factor (s). It is slightly shifted towards higher temperature side as the X-rays dose increases accompanied by the intensification of the peak. The increase in the intensities of the glow peaks with an increase of radiation dose can be understood by the fact that more and more traps are responsible for these glow peaks and were getting filled with the increase of irradiation dose and subsequently these traps release the charge carriers on thermal stimulation to finally recombine with their counterparts, thus giving rise to intense glow peaks.

Figure 4: Glow curve of Na_2SO_4/SiO_2 exposed to X-rays (150 kV_p , 40mAs)

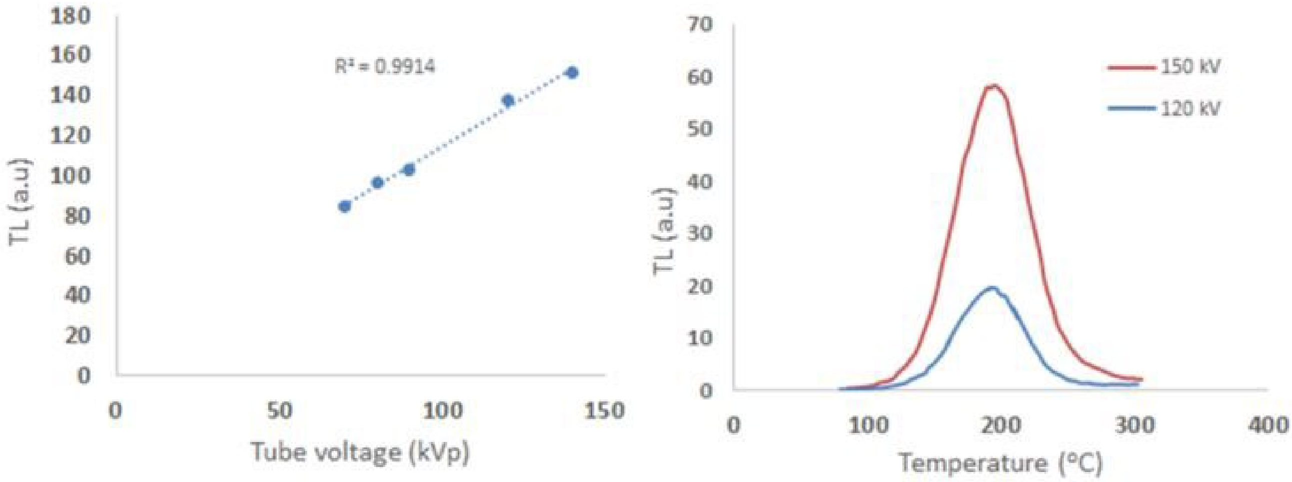


3.4 Linear Dose-Response

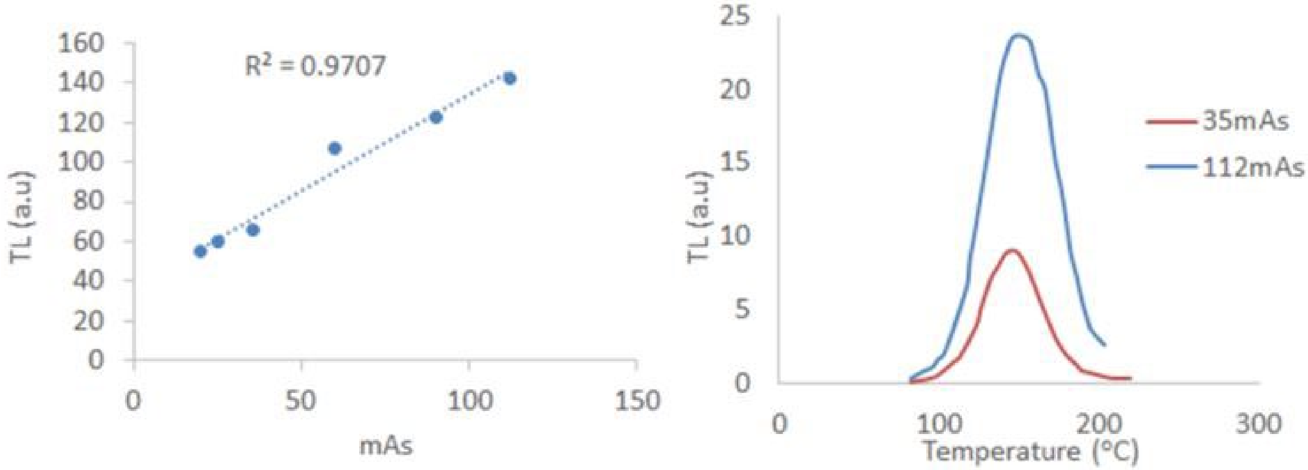
The linearity of response of the dosimeters is an essential factor to evaluate their performance. Materials that have to be used as TLDs should have a linear dose response over a long range of doses [14]. The Na_2SO_4/SiO_2 sample was exposed to X-rays of 70 kV_p 80, 90, 120, 140, and 150 kV_P , at 40 mAs and SSD was 3°Cm. Figure 5a presents the overall TL glow curves of Na_2SO_4/SiO_2 for 120 kv_p and 150 kV_p , which indicate that the TL emission intensity increased with the increasing X-ray energy filling more and more traps with increasing energy amount. Figure 5b shows the effect of changing mAs as a function of kV_p, the amount of TL response increases as the mAs increases which results in more radiation. The presence of a linear relationship between the X-ray energy and TL response of the Na_2SO_4/SiO_2 and the maximum peak intensity justifies their use in radiation dosimetry.

Figure 5: Dose - response curve of Na_2SO_4/SiO_2 exposed to X – rays (a) different kV_p at 40 mAs. (b) 75 kV_p and different mAs

(a)



(b)



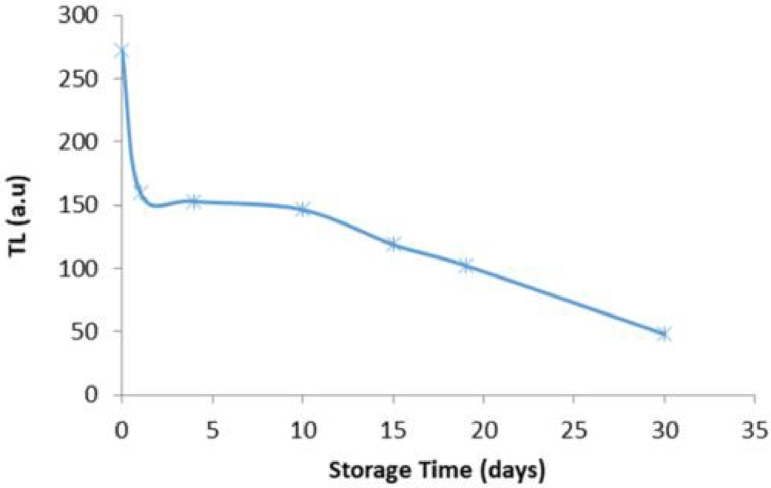
3.5 Fading Effect

Fading is the unintentional loss of the TL signal and may be caused by optical stimulation. Thermal fading originates from the fact that even at room temperature there is a certain probability of charge carriers escaping from their trapping centres. The trapping parameters affecting this process are the frequency factor (s) and activation energy (E) [15]. Other types of fading, which are not temperature dependent, are caused by quantum mechanical tunneling of the trapped charge to the recombination sites and the transitions between localized states, that is, transitions that do not take place via the delocalized bands [16]. The minimum loss in the stored radiation energy of any TLD phosphor makes a phosphor more suitable for radiation dosimetry. The percentage amount loss of TL signals can be calculated from Equation 2.

$$\%\, loss\ of\ TL\ signal = \frac{TL\ reading\ at\ 1^{st}\ day\ -\ TL\ reading\ at\ last\ day}{TL\ reading\ at\ \ 1^{st}\ day} x100 \qquad (2)$$

In the present work, the fading of Na_2SO_4/SiO_2 was observed over a period of one month as shown in Figure 6. The samples were exposed to 110 kVp, 60 mAs and the SSD was 3°Cm. The samples were stored at room temperature (20–25 °C) in a black box to prevent trapped electrons from being thermally stimulated and released. The data were recorded immediately after the exposure and 24 hours, 4, 10, 15, 19, and 30 days. The percentage amount loss during 19 days was found 62.4% and after one month about 82.3% of the TL signal was lost, the quick fading may be related to the peak temperature. Generally fading occurs due to the recombination of shallow traps responsible for low temperature peaks, and the retrapping of the deep traps in their places could be responsible for further fading of low as well as high temperature peaks.

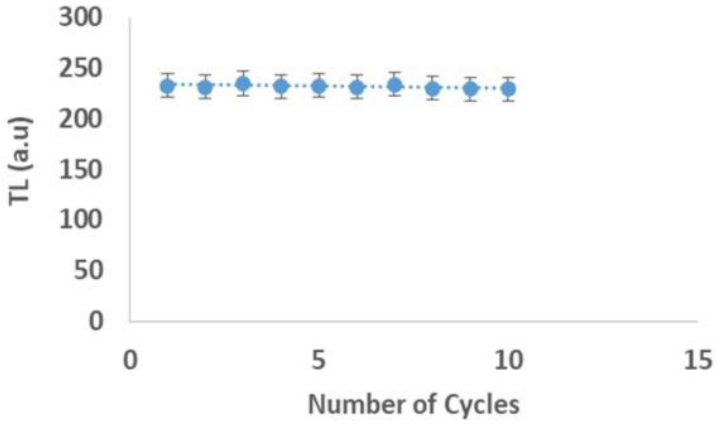
Figure 6: Thermal fading of Na_2SO_4/SiO_2 after exposed to X-rays beam



3.6 Reproducibility

Reproducibility is one of the most important properties of TL qualities to determine the reusability of the samples [17]. In other words, the TL intensity signal of a given dosage should be about the same after several measurements. There should be no change in the physicochemical properties of materials that have been repeatedly irradiated, readout, and annealed [18]. To conduct the reproducibility test for Na_2SO_4/SiO_2 five samples were exposed to X–ray radiation "150 kV_P, 40 mAs, SSD 3°Cm", and then irradiated again ten times under the same conditions. Figure 7 shows that the Na_2SO_4/SiO_2 material has acceptable reusability, with roughly 1% variance in successive measurements, and there is no change in the intensity of the peak.

Figure 7: Reproducibility characteristics of the Na_2SO_4/SiO_2 after exposed to X–ray



3.7 Effective Atomic Number

The effective atomic number Z_{eff} is an important parameter to characterize the TLD materials and can be used to describe the interaction of ionizing radiation with multi – element materials. The Z_{eff} depends on the energy and chemical composition of the corresponding material and provides information on how radiation interacts with the materials at different energies and widely used in medical physics. Equation 3 was used to calculate the Z_{eff} for Na_2SO_4/SiO_2 compound, and the value of Z_{eff} of Na_2SO_4/SiO_2 was found to be 13.56 as shown in Table 1.

$$\bar{z}_{eff} = \sqrt[x]{a_1 z_1^x + a_2 z_2^x + a_3 z_3^x + \cdots} \quad (3)$$

Table 1. Physical parameters for calculation of effective atomic number for Na_2SO_4/SiO_2

ELEMENTS	Z	AVOGADRO NUMBER	n_i	a_i	z^x	$a_i .z^x$	Z_{eff}
Si	*14*	6.022×10^{23}	8.43×10^{24}	*0.2859*	*2342.1*	*6.6690*	13.5
O	*8*	6.022×10^{23}	4.81×10^{24}	0.1628	451.9	73.569	
Na	*11*	6.022×10^{23}	6.62×10^{24}	0.2245	1152.6	258.76	
S	*16*	6.022×10^{23}	9.66×10^{24}	0.3272	3468.2	1134.79	

Where x is the power dependency of the photoelectric interaction, 2.94 being typically adopted, a_i *is* the fractional contents of electrons belonging to element Z_i, *and* n_i is the number of electrons, in one mole, belonging to each element Z_i [19].

4. CONCLUSIONS

Na_2SO_4/SiO_2 phosphor has been prepared at RT by sol – Gel method. The Na_2SO_4/SiO_2 sample is shaped into small disks to be used as a thermoluminescence dosimeter. The most effective temperature and period for annealing was 200˚C and 2h. The Na_2SO_4/SiO_2 sample shows one glow peak between 150 ℃ to 200 ℃ depending on X-ray energy and the material showed linear TL dose response with a correlation of 0.9914 which is a good characteristic for the development of material for radiation dosimeter in the range of used kV_p and mAs. After two weeks, the fading rate decreased dramatically and about 56% of the original was lost, this instability is attributed to the presence of shallow traps more than deep traps which are involved in the TL process. Reasonable repeatability of about 1% variation in successive measurements is noted. These characteristics may qualify Na_2SO_4/SiO_2 as the sustainable natural material used in this study for a variety of applications involving radiation dose assessment.

CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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