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Synthesis and Thermoluminescence Properties of Undoped Calcium Fluoride (CaF_2) Nanoparticles using Co-Precipitation Method

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ABSTRACT

This study investigated the thermoluminescence properties of undoped CaF_2 nanoparticles synthesized via co-precipitation with ethanol. X-ray diffraction revealed pure CaF_2 nanoparticles with a complete cubic structure and an average crystallite size of 36.5 nm. Scanning electron microscopy confirmed the nanoscale size, averaging 51.23 nm. Electron dispersive spectroscopy analysis showed that the sample mainly consists of Ca and F, with oxygen potentially introducing defects in the crystal structure. Synthesized nanoparticles TL glow curves exposed to 7 mGy of 90Sr beta rays exhibited a prominent peak at 205 ^{o}C in thermoluminescence glow curves, likely due to oxygen-induced defects that act as thermoluminescence activators. The thermoluminescence activating energy and the frequency factor of the CaF_2 nanoparticles were determined using initial rise methods of approximately 0.83 eV and 5.99 x 10^{-19}, respectively.

Keywords: *Calcium fluoride, co-precipitation, nanoparticles, phosphor, thermoluminescence*

1. INTRODUCTION

Radiation monitoring is crucial for activities involving ionizing radiation. Several dosimetry techniques have been developed for this purpose, including film, thermoluminescence, and electronic dosimetry [1–3]. Among these techniques, thermoluminescence dosimetry is one of the simplest and most commonly used for radiation monitoring and safety. This method works by measuring the thermoluminescence (TL) emission of irradiated phosphor materials when heated, with the intensity of the emission directly correlated to the radiation dose. Therefore, the radiation doses can be approximated by measuring the intensity of the TL emissions [4].

Various phosphor materials have been utilized as TL dosimeter materials over the years, and many are commercially available under their respective trade names. Some commonly used materials include LiF_2:Mg,Ti, $CaSO_4$, CaF_2, and Al_2O_3:C [5]. Among these materials, a TL dosimeter based on calcium fluoride (CaF_2) is particularly popular due to its chemical stability and overall dose sensitivity [6]. Pure undoped CaF_2 crystals lack structural defects, making them unsuitable for dosimetry purposes. As a result, CaF_2 is typically doped with rare earth metals such as Dy, Eu, or Tm to enhance its thermoluminescence properties [7–9]. However, using rare earth metals as dopants to introduce structural defects in CaF_2 is prohibitively expensive and may limit the availability of CaF_2-based dosimeter applications.

In recent years, there has been growing interest in researching nanoparticles as materials for thermoluminescence dosimetry. Several studies in the last decade have extensively investigated the thermoluminescence properties of CaF_2-based dosimeters with various dopants [10,11]. Nanoparticles CaF_2-based TL dosimeter was found to have better sensitivity when measuring higher radiation doses and a lesser fading rate [12,13]. These properties may occur due to the effect of quantum confinement and their high surface area-to-volume ratio, which can significantly alter their thermoluminescence properties [14]. The high surface area of nanoparticles can also increase the likelihood of surface defects or impurities appearing, resulting in a thermoluminescence effect [15]. Based on this, thermoluminescence emission from undoped CaF_2 nanoparticles is possible due to their high surface defects-to-volume ratio.

Currently, there are no more studies on the intrinsic thermoluminescence of undoped CaF_2 nanoparticles [16]. This study aims to study the thermoluminescence properties of undoped CaF_2 nanoparticles. In this study, CaF_2 nanoparticles were synthesized using a co-precipitation method with ethanol as a co-solvent. The activated energy of CaF_2 nanoparticles was determined from thermoluminescence spectra using initial rise methods based on the TL glow curve data. This analysis will provide valuable insights into the thermoluminescence properties of undoped CaF_2 nanoparticles, contributing to their potential use in radiation dosimetry and other applications.

2. MATERIALS AND METHODS

2.1. Materials

The chemicals used in this study were of analytical grade; all chemicals were used as received without undergoing any additional purification. These included ammonium fluoride (NH_4F, with a purity level of 99%), calcium chloride ($CaCl_2$, with a purity level of 99%), and absolute ethanol (with a purity level of 99.8%), all of purchased from Sigma Aldrich. Besides that, NH_4F and $CaCl_2$ also purchased from Sigma Aldrich, were used as precursors for the synthesis of CaF_2 nanoparticles, and deionized water served as the solvent for the mixture, while absolute ethanol was used as a co-solvent for the precursor solution.

2.2. Preparation of CaF_2 nanoparticles

CaF_2 nanoparticles were synthesized using the co-precipitation method with the ratio of solvent and co-solvent is 4:1 [17]. The synthesized process was based on the following chemical equation (1):

$$CaCl_2 + 2NH_4F \rightarrow CaF_2 + 2NH_4Cl \quad (1)$$

A 1 M calcium chloride ($CaCl_2$) solution was prepared by dissolving 11.1 g of $CaCl_2$ in 100 ml of deionized water. A solution of 2 M ammonium fluoride (NH_4F) was prepared by dissolving 7.4 g of NH_4F in a mixture of 50 ml deionized water and 50 ml absolute ethanol and stirring for 30 minutes. The NH_4F solution was added dropwise to the constantly stirred $CaCl_2$ solution at 400 rpm on a magnetic stirrer, forming a white precipitate of CaF_2 suspended in the solvent right after the addition of NH_4F. The mixture was then allowed to settle for 30 minutes. The formed CaF_2 solid was then separated from the solvent using a centrifuge and washed several times using ethanol and distilled water to remove any reaction byproducts. The obtained CaF_2 was then dried in an oven at a temperature of 120 °C for 45 minutes until the powder was completely dry.

2.3. Characterization

2.3.1. Morphological and crystal structure of CaF_2 nanoparticles

The crystal structure of the CaF_2 sample was analyzed using the XRD apparatus PANanalytical Table Top Aeris with the Cu-Kα source in the scan range used is $2\theta = 20 - 90^o$. Morphological nature of the sample was recorded on scanning electron microscope (SEM) FEI Quanta 650 equipped with Energy Disperse X-Ray spectroscopy.

2.3.2. Thermoluminescence properties of CaF_2 nanoparticles

Thermoluminescence (TL) glow curves of CaF_2 nanoparticles were recorded using a Harshaw TLD-reader model 3500. The recording was conducted under a nitrogen atmosphere with a temperature range of 50–300 °C and a heating rate of 10 °C/s. Before the recording process, 5 mg of the sample were first heated at 350 °C for 30 min and rapidly cooled to room temperature. The heating process is carried out to ensure all TL traps are empty before radiation exposure. After all the traps are emptied, samples are then exposed to 7 mGy of 90Sr beta rays and proceed to TL glow curve recording. The sample TL glow curves were recorded twice. The second record was considered the background emission. The background data obtained in the second recording will then be subtracted from the sample TL glow.

3. RESULTS AND DISCUSSION

3.1. Crystal structure, morphology and chemical composition of CaF_2 nanoparticles

The XRD pattern of the synthesized CaF_2 nanoparticles is shown in Figure 1. The XRD pattern of the sample found to exhibit a close match to the JCPDS reference card no. 87-0971 for pure CaF_2 crystal, confirming the presence of a complete cubic structure [11]. Assuming the samples are not subject to thermal or mechanical stress, the average crystallite size of the synthesized CaF_2 nanoparticles was calculated using Scherrer's-Debye's formula (equation (2)).

$$D=k\lambda/\beta \cos\theta \quad (2)$$

where D is the crystallite size, k is the Scherer's constant (0.89), λ is the wavelength of the X-ray source, β is the FWHM of the peaks, and θ is the Bragg's angle. Based on the results of calculations with the Scherer formula, the estimated crystallite size of the CaF_2 sample is 36.5 nm, which indicates the most likely smallest single crystalline size of CaF_2 nanoparticles. This result is not much different from previous studies, which also used the precipitation method, which is in the range of around 30 nm for CaF_2 nanoparticles [10,11,13].

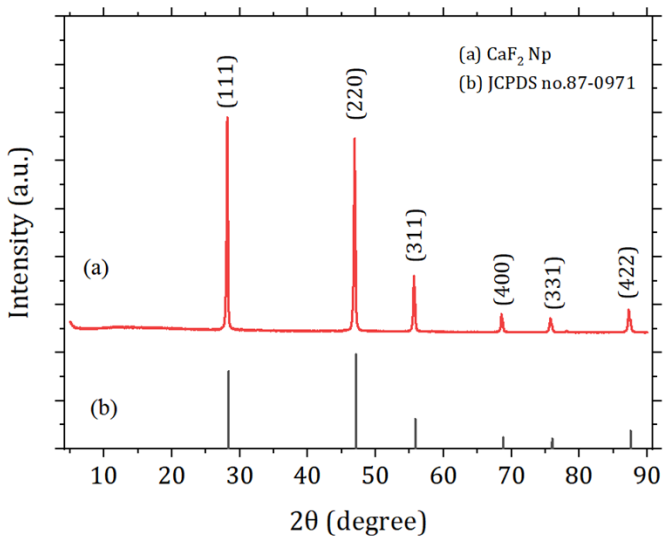

Figure 1. XRD pattern of synthesized CaF_2 nanoparticles

The SEM image and size distribution of the synthesized CaF_2 nanoparticles are shown in Figure 2. The particle size distribution was obtained using an SEM image and analyzed using FIIJI image software [18]. The particle size represents the diameter of discrete pieces of material with

a specific crystal orientation. The particles were observed to agglomerate, forming clumps, and their sizes ranged from 20 nm to 120 nm, with an average particle size of 51.23 nm. The particle size of CaF_2 is smaller than 100 nm, so it can be indicated as a nanoparticle [11]. However, the particle size observed by SEM is larger than the crystallite size based on X-ray diffraction analysis, which indicates that the CaF_2 particles consist of several individual crystallites.

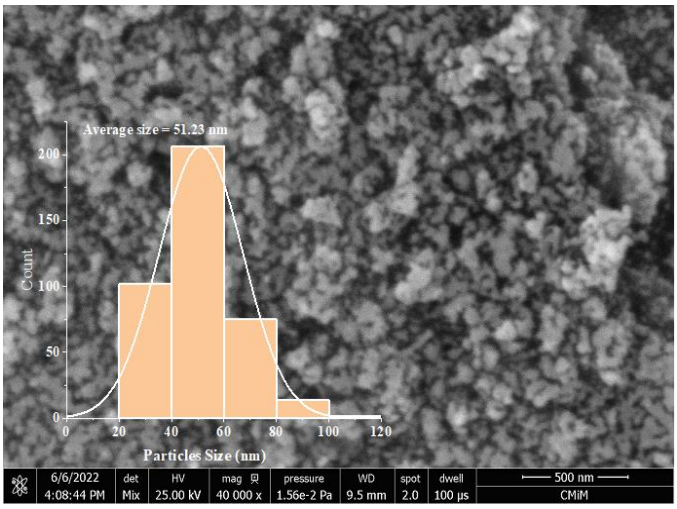

Figure 2. SEM image and particles size distributions of CaF_2 nanoparticles

The energy-dispersive X-ray spectroscopy (EDS) analysis of the synthesized CaF_2 nanoparticles was done in this research to study the chemical composition of the sample. Table 1 shows the result of the EDS analysis. The chemical composition of the sample was found to consist mainly of Ca and F. A small amount of oxygen was also observed in the EDS analysis. A small amount of O may indicate a CaO that may form due to the heating in the synthesize process. The presence of O may introduce a defect in the synthesized nanoparticles CaF_2, which can created TL trapping center in the sample [19].

Table 1. Element composition of synthesized CaF_2 nanoparticles from EDS analysis

Element	Weight %	Atomic %
O	02.43	0.19
F	51.29	69.91
Ca	46.29	29.90
Total	100	100

3.2. Thermoluminescence properties of undoped CaF_2 nanoparticles

Thermoluminescence glow curves of the synthesized CaF_2 nanocrystal exposed to 7 mGy 90Sr Beta ray are shown in Figure 3. The glow curve of the sample shows only one prominent peak around 205 ^oC. Based on the result of the EDS analysis (Table 1), it was found that the presence of oxygen in CaF_2 crystals. The presence of oxygen could act as a crystal defect that allowed the formation of a metastable state in CaF_2 crystals. The oxygen-induced defects in CaF_2 crystals can be attributed to the observed thermoluminescence emission in the sample light curve, which shows one prominent peak around 205 °C. This oxygen-induced defect acts as an activator, which induces a thermoluminescence effect on CaF_2 nanocrystals [20, 21].

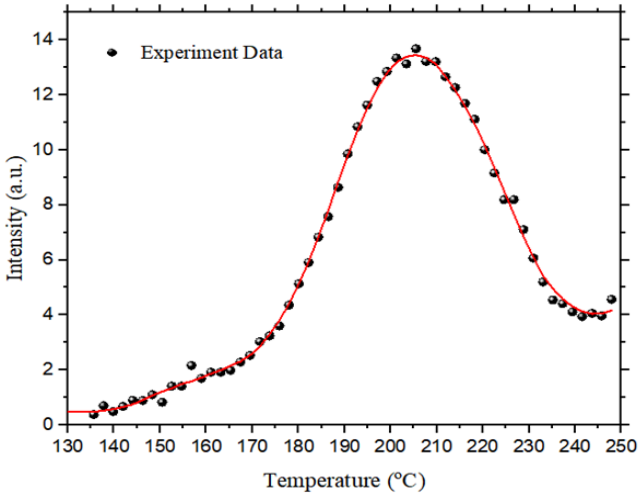

Figure 3. Thermoluminescence glow curve of synthesized CaF_2 nanoparticles exposed to 7 mGy of 90Sr beta ray

To further analyze the TL glow curve of the synthesized CaF_2 nanoparticles, initial rise (IR) method analysis was conducted. The IR method is the most straightforward experimental procedure to obtain the trap depth and is nearly independent of the frequency factor s. In the initial rise tail of the peak, the amounts of trapped electrons can be assumed to be constant, and the dependence of the temperature is negligible. Due to that, the initial part of the TL, curves are exponentially dependent on the temperature, according to Equation (3). Plotting Ln(I) versus 1/T over this initial rise region (usually 10-15% of maximum intensity) results in a linear area with the slope (-E/k) (Equation 4). The activation energy (E) can be easily approximated without knowing the frequency factor s [22]. The frequency factor s of the synthesized CaF_2 nanoparticles can be obtained using Equation (5) [23], where β is the heating rate, E is activating energy, k is Boltzmann's constant, and Tm is the peak temperature.

$$I(T) = \text{constant} \times \exp(-E/kT) \quad (3)$$

$$\ln(I) \approx -E/k \times 1/T \quad (4)$$

$$s=\beta E/kT_m^2(1/(1+\Delta_m)) \exp(Ek/Tm) \quad (5)$$

Figure 4 shows the initial rise plot of the CaF_2 nanoparticles TL glow curve. Using Equations (3) and (4), from the initial rise method, the activating energy and the frequency factor s can be approximated. The activation energy of the CaF_2 nanoparticles is approximately 0.83 eV. The frequency factor s using Equation (4) is determined to be 5,99 x 10^{-16} s^{-1}. From this result, the activation energy and the frequency factor s of the TL sample are indicated the probability of a low thermoluminescence fading rate [24].

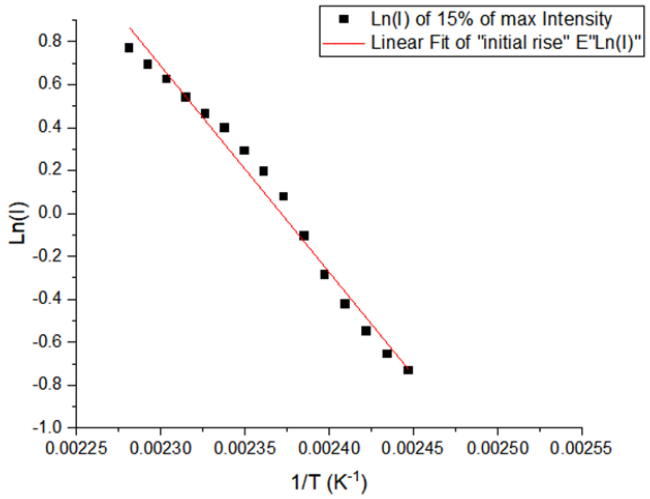

Figure 4. Initial rise plot of 15% peak intensity CaF_2 nanoparticles glow curve

4. CONCLUSION

Undoped CaF_2 nanoparticles were successfully synthesized using a co-precipitation method with ethanol as a co-solvent. The synthesized nanoparticles were characterized using XRD, SEM, and EDS analyses. The average crystallite size of the synthesized CaF_2 nanoparticles was calculated from the XRD data to be 36.5 nm, confirming the sample is nanocrystalline. The SEM images showed that the particles were in the nanometer size range and agglomerated to form a clump. The EDS analysis revealed that the sample consisted of Ca and F with a small amount of oxygen, which may indicate the presence of CaO and could introduce defects in the CaF_2 crystal. The thermoluminescence properties of the synthesized CaF_2 nanoparticles were analyzed using initial rise methods based on the TL glow curve data. The thermoluminescence emission was observed at around 205 °C. This TL emission may be caused by the oxygen-induced defects in the CaF_2 crystal. The activating energy and the frequency factor of the CaF_2 nanoparticles were found to be approximately 0.83 eV and 5.99 x 10^{-14} s^{-1}, respectively, using the initial rise method. Further studies can be conducted to investigate the effects of varying synthesis parameters on the properties of the CaF_2 nanoparticles.

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