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## Synthesis and Thermoluminescence Properties of Undoped Calcium Fluoride (CaF<sub>2</sub>) Nanoparticles using Co-Precipitation Method

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### ABSTRACT

This study investigated the thermoluminescence properties of undoped CaF<sub>2</sub> nanoparticles synthesized via co-precipitation with ethanol. X-ray diffraction revealed pure CaF<sub>2</sub> 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 °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<sub>2</sub> nanoparticles was determined using initial rise methods of approximately 0.83 eV and 5.99 x 10<sup>-19</sup> 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 techniques that 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<sub>2</sub>:Mg,Ti, CaSO<sub>4</sub>, CaF<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>:C [5]. Among these materials, a TL dosimeter based on calcium fluoride (CaF<sub>2</sub>) is particularly popular due to its chemical stability and overall dose sensitivity [6]. Pure undoped CaF<sub>2</sub> crystals lack structural defects, making them unsuitable for dosimetry purposes. As a result, CaF<sub>2</sub> 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<sub>2</sub> is

prohibitively expensive and may limit the availability of CaF<sub>2</sub>-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<sub>2</sub>-based dosimeters with various dopants [10,11]. Nanoparticles CaF<sub>2</sub>-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<sub>2</sub> nanoparticles is possible due to its high surface defects-to-volume ratio.

Currently, there are no more study on the intrinsic thermoluminescence of undoped CaF<sub>2</sub> nanoparticles. This study aims to study the thermoluminescence properties of undoped CaF<sub>2</sub> nanoparticles. In this study, CaF<sub>2</sub> nanoparticles were synthesized using a co-precipitation method with ethanol as a co-solvent. The activated energy of CaF<sub>2</sub> nanoparticles were 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<sub>2</sub> 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<sub>4</sub>F, with a purity level of 99%), calcium chloride (CaCl<sub>2</sub>, 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<sub>4</sub>F and CaCl<sub>2</sub> also purchased from Sigma Aldrich were used as precursors for the synthesis of CaF<sub>2</sub> nanoparticles, and deionized water served as the solvent for the mixture, while absolute ethanol as a co-solvent for the precursor solution.

### 2.2. Preparation of CaF<sub>2</sub> nanoparticles

CaF<sub>2</sub> nanoparticles were synthesized using co-precipitation method with the ratio of solvent and co-solvent is 4:1 [16]. The synthesis process were based on the following chemical equation (1):



A 1 M calcium chloride (CaCl<sub>2</sub>) solution was prepared by dissolving 11.1 g of CaCl<sub>2</sub> in 100 ml deionized water. A solution of 2 M ammonium fluoride (NH<sub>4</sub>F) was prepared by dissolving 7.4 g of NH<sub>4</sub>F in a mixture of 50 ml deionized water and 50 ml absolute ethanol and stirring for 30 minutes. The NH<sub>4</sub>F solution was added dropwise to the constantly stirred CaCl<sub>2</sub> solution at 400 rpm on magnetic stirrer, forming a white precipitate of CaF<sub>2</sub> suspended in the solvent right after the addition of NH<sub>4</sub>F. The mixture then allowed to settle for 30 minutes. The formed CaF<sub>2</sub> solid then separated from the solvent using a centrifuge and washed several times using ethanol and distilled water to remove any reaction byproduct. The obtained CaF<sub>2</sub> was then dried in an oven at a temperature of 120 °C for 45 minutes until the powder are completely dry.

### 2.3. Characterization

#### 2.3.1. Morphological and crystal structure of CaF<sub>2</sub> nanoparticles

The crystal structure of CaF<sub>2</sub> sample was analyzed by using XRD apparatus PANalytical Table Top Aeris with the Cu-Kα source in scan range used is 2θ = 20 - 90°. 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<sub>2</sub> nanoparticles

Thermoluminescence (TL) glow curves of CaF<sub>2</sub> 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 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 trap are emptied samples then exposed to 7 mGy of 90Sr beta rays and proceed to TL glow curves recording. The sample TL glow curves were recorded twice. The second record was considered as the background emission. The background data obtained in the second recording will then be subtracted from the sample TL glow.

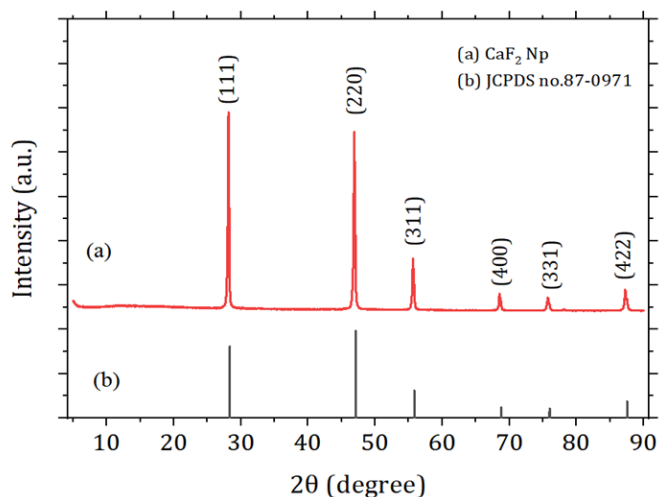
## 3. RESULTS AND DISCUSSION

### 3.1. Crystal structure, morphology and chemical composition of CaF<sub>2</sub> nanoparticles

The XRD pattern of the synthesized CaF<sub>2</sub> nanoparticles is shown in Figure 1. The XRD pattern of the sample found to exhibits a close match to the JCPDS reference card no. 87-0971 for pure CaF<sub>2</sub> crystal, confirming the presence of a complete cubic structure [11,18]. Assuming the samples are not subject to thermal or mechanical stress, the average crystallite size of the synthesized CaF<sub>2</sub> nanoparticles was calculated using Scherrer's-Debye's formula (equations (2)).

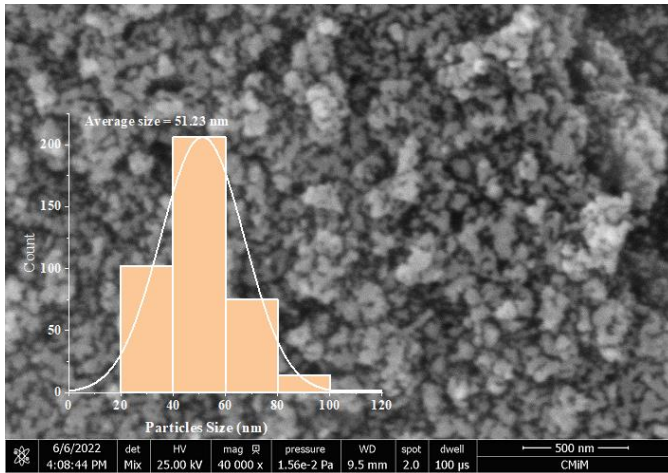
$$D = k\lambda / \beta \cos\theta \quad (2)$$

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<sub>2</sub> sample is 36.5 nm, which indicates the most likely smallest single crystalline size of CaF<sub>2</sub> 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<sub>2</sub> nanoparticles [10,11,13].



**Figure 1.** XRD pattern of synthesized CaF<sub>2</sub> nanoparticles

The SEM image and size distribution of the synthesized CaF<sub>2</sub> nanoparticles are shown in Figure 2. The particle size distribution was obtained using SEM image and analyzed by using FIJI image software [17]. 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<sub>2</sub> is smaller than 100 nm so that 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, this indicates that the CaF<sub>2</sub> particles consist of several individual crystallites.

**Figure 2.** SEM image and particles size distributions of CaF<sub>2</sub> nanoparticles

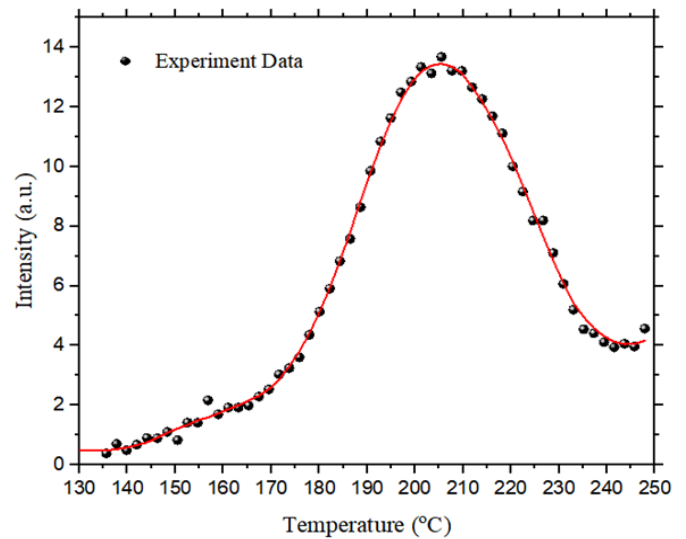
The energy-dispersive X-ray spectroscopy (EDS) analysis of the synthesized CaF<sub>2</sub> nanoparticles was done in this research to study the chemical composition of the sample. Table 1 shows the result of EDS analysis. The chemical composition of the sample was found to majorly consist of Ca and F. A small amount of oxygen also observed in the EDS analysis. A small amount of O may indicate a CaO that may form due to the heating in the synthesis process. The presence of O may introduce a defect on the synthesized nanoparticles CaF<sub>2</sub> which can create TL trapping centers in the sample [18].

**Table 1.** Element composition of synthesized CaF<sub>2</sub> 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<sub>2</sub> nanoparticles

Thermoluminescence glow curves of the synthesized CaF<sub>2</sub> nanocrystal exposed to 7 mGy 90Sr Beta ray is shown in Figure 3. The glow curve of the sample showing only one prominent peak around 205 °C. Based on the result of the EDS analysis (Table 1), it was found that the presence of oxygen in CaF<sub>2</sub> crystals. The presence of oxygen could act as a crystal defect that allowed the formation of a metastable state in CaF<sub>2</sub> crystals. The oxygen-induced defects in CaF<sub>2</sub> crystals can be attributed to the observed thermoluminescence emission in the sample light curve, showing one prominent peak around 205 °C. This oxygen-induced defect acts as an activator, which induces a thermoluminescence effect on CaF<sub>2</sub> nanocrystals [19, 20].

**Figure 3.** Thermoluminescence glow curve of synthesized CaF<sub>2</sub> nanoparticles exposed to 7 mGy of 90Sr beta ray

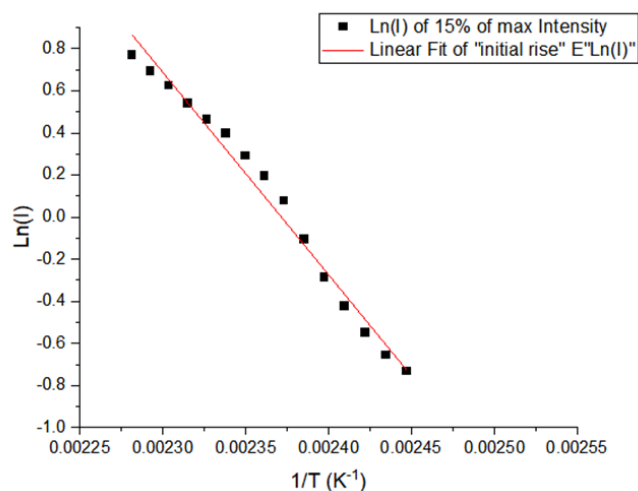
To further analyze the TL glow curve of the synthesized CaF<sub>2</sub> nanoparticles, initial rise (IR) method analysis was conducted. The IR method is the most straightforward experimental procedure to obtain the trap depth and is nearly independent of the frequency factor  $s$ . In the initial rise tail of the peak, the amount of trapped electron can be assumed to be constant and the dependence of the temperature being negligible. Due to that, the initial part of TL curves is exponentially dependent on the temperature according to Equation (2). 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 3). The activation energy ( $E$ ) can be easily approximated without knowing the frequency factor  $s$  [21]. The frequency factor  $s$  of the synthesized CaF<sub>2</sub> nanoparticles can be obtained using Equation (4) [22]. With  $\beta$  is heating rate,  $E$  is activating energy,  $k$  is Boltzmann's constant, and  $T_m$  is peak temperature.

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

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

$$s = \beta E k T m \cdot 2 \exp(E k T m) \quad (5)$$

Figure 4 shows the initial rise plot of the CaF<sub>2</sub> nanoparticles TL glow curve. Using Equation (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<sub>2</sub> nanoparticles is approximately 0.83 eV. The frequency factor  $s$  using Equation (4) is determined to be  $5.99 \times 10^{-16} \text{ s}^{-1}$ . From this result, the activation energy and the frequency factor  $s$  of the TL sample are indicating the probability of low thermoluminescence fading rate [23].



**Figure 4.** Initial rise plot of 15% peak intensity CaF<sub>2</sub> nanoparticles glow curve

#### 4. CONCLUSION

Undoped CaF<sub>2</sub> 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<sub>2</sub> nanoparticles was calculated from the XRD data to be 36.5 nm, which confirming the sample is a nanocrystalline. The SEM images showed that the particles are 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<sub>2</sub> crystal. The thermoluminescence properties of the synthesized CaF<sub>2</sub> 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<sub>2</sub> crystal. The activating energy and the frequency factor of the CaF<sub>2</sub> nanoparticles was found to be approximately 0.83 eV and  $5.99 \times 10^{-14} \text{ s}^{-1}$  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<sub>2</sub> nanoparticles.

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