SRI VENKATESWARA INTERNSHIP PROGRAM FOR RESEARCH IN ACADEMICS (SRI-VIPRA)

Project Report of 2022: SVP- 2238

"To study the thermoluminescence properties of nanophosphors for radiation dosimetry"

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SRIVIPRA PROJECT 2022

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Title: To study the thermoluminescence properties of nanophosphors for radiation dosimetry

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Certificate

This is to certify that the aforementioned students from Sri Venkateswara College have participated in the summer project SVP-2238 titled "**To study the thermoluminescence properties of nanophosphors for radiation dosimetry".** The participants have carried out the research project work under my guidance and supervision from 21st June 2022 to 25th September 2022. The work carried out is original and carried out in offline mode.

Signature of Mentor

Acknowledgements

We would like to acknowledge and deeply thank our mentor, Prof. Anant Pandey, without who's support, this work wouldn't have been possible. His valuable advice and guidance at every stage of this project helped us perform to the best of our potential and we are grateful for it. We would also like to express our gratitude to Sri Venkateswara College for providing us with this incredible research internship opportunity under the SRIVIPRA initiative.

We would also like to extend special thanks to our parents who provided us with endless support and encouragement at all times that constantly motivated us to give our best and push ourselves towards fulfilling our goal.

Contents

Abstract

Thermoluminescence is a form of luminescence that is exhibited by certain crystalline materials, such as some minerals, when previously absorbed energy from electromagnetic radiation or other ionizing radiation is re-emitted as light upon heating of the material.It has wide range of applications in medical, archaeology, geology, meteorology and also in space dosimetry or in industries to maintain the quality of products. For this project, we synthesize a nanophosphor $CaNa_2(SO_4)_2$ and $CaNa_2(SO_4)_2$ doped with 0.1 mol% Europium was synthesized by co-precipitation method.The samples were annealed using a muffle furnace at Inter University Accelerator Centre (IUAC). The thermoluminescent properties of this sample were then investigated by irradiating it with ^{60}Co gamma rays at 50Gy and 100Gy and obtaining TL Glow curves. The intensity of TL glow curves with the concentration of dopant was investigated.

1 Introduction

Proton beam radiation therapy centres are emerging around the world with specific treatment plans and beam shaping technologies. The properties of protons differ impressively from that of photons which poses a huge advantage in their usage in radiation therapy. The chief objective of radiotherapy is to maximize effects of radiation on tumour cells while keeping the damage done to healthy cells at a minimum. Therefore, studies predominantly focus on two aspects: developing new treatment planning systems to deliver higher doses of radiation to defined target volumes and searching for new forms of radiation therapy to improve the therapeutic ratio. The fact that proton beams can theoretically produce excellent dose localization is described in the paper. Hence, dose escalation can be easily performed while mitigating radiation toxicity in surrounding normal tissues. Most importantly, to come up with an efficient treatment plan which is patient specific, it is fundamentally important to study the modes of dose calculation and choose the most efficient approach amongst others for a particular treatment case.

1.1 Thermoluminescense

Thermoluminescence[1][6] is a form of luminescence that is exhibited by certain crystalline materials, such as some minerals, when previously absorbed energy from electromagnetic radiation or other ionizing radiation is re-emitted as light upon heating of the material. Thermoluminescence can be used to date materials containing crystalline minerals to a specific heating event. This is useful for ceramics, as it determines the date of firing, as well as for lava, or even sediments that were exposed to substantial sunlight. These crystalline solids are constantly subjected to ionizing radiation from their environment, which causes some energized electrons to become trapped in defects in the molecular crystal structure. An input of energy, such as heat, is required to free these trapped electrons. The accumulation of trapped electrons, and the gaps left behind in the spaces they vacated, occurs at a measurable rate proportional to the radiation received from a specimen's immediate environment. When a specimen is reheated, the trapped energy is released in the form of light (thermoluminescence) as the electrons escape. The amount of light produced is a specific and measurable phenomenon. TL is a wide spread phenomenon and is exhibited by most of minerals, inorganic crystals, glasses and ceramics, organic compounds such as polymers including polyethylene and Teflon, certain biochemical materials etc. but amongst them the most sensitive are the dielectric solids. TL has also been observed in mixed sulphates.[2]

1.2 Application of thermoluminescence: Radiation dosimetry

Thermoluminescence has wide range of applications in medical, archaeology, geology, meteorology and in other applications like space dosimetry or in industries to maintain the quality of products.[4][5] Before ion beams, medicine had very few options to treat malignant tissues. X-rays were discovered by Rontgen in 1885 followed soon by Becquerel's radioactivity phenomenon in 1896 and radium was discovered by curie in 1898. These discoveries developed the field of ionizing radiations.When X-rays and Gamma rays are irradiated to the affected body part, it penetrates through the tissues.The detection and measurement of absorbed radiation was one among the first suggested uses of TL. The possibility of TL use in radiation dosimetry is what has sparked the majority of interest in it. Programs for nuclear and medical research use radiation as a key instrument. Given the dangers of radiation, it is important to keep an eye on the dose given to program participants.[7] The radiation dosage can be measured using a wide variety of equipment. One of them is the thermoluminescence dosimeter. It is cheap and highly radiation-sensitive. The main component of this device is a TL phosphor, typically one of the LiF:Mg,Ti, LiF:Mg,Cu,P, or $CaSO_4 : Dy$ phosphors. To fit the needs of the customer, TLDs are offered in a variety of forms, including micro-crystalline powder, chips, sintered discs, and micro-rods. The measurement effectiveness of the system is unaffected by the shape of the TLDs. These TLDs will be heated on a TL reading device after being exposed to them in the field in order to measure the thermoluminescence signal. The radiation dose that the TL experienced from the fields is reflected in its output signal. These TLDs

can be used multiple times without the TL efficiency diminishing. They are calibrated with a known dose after being used in the field, and the field exposure is assessed.An ideal dosimeter is desired to have some basic characteristics-: a simple glow curve structure with single glow curve peak, high sensitivity to various ionizing radiations, linear TL response curve, energy independence for different energies of ionizing radiations.

1.3 What are nanophosphors?

The general function of any phosphor is to convert a certain kind of external energy into visible light. This conversion process can serve different purposes and, from this point of view, all practical applications of phosphors can be classified into several main groups: Light sources (fluorescent lamps, backlights of liquid crystal displays (LCDs), light-emitting diodes (LEDs) including phosphor-converted white LEDs (pc-WLEDs), etc.).Information displays (plasma display panels (PDPs), field emission displays (FEDs), cathode-ray tubes (CRTs), etc.).[3] Radiation converters (X-ray intensifying screens and other image intensifiers, spectral converters for solar cells, down-converters for excimer laser beam profilers and photolithography mask inspection tools, viewing screens for electron microscopy, etc.). Fluorescent pigments and tracers (non-destructive testing, bio-labeling, security labeling, leisure goods, etc.). The size of phosphor particles is one of the main parameters affecting the performance of phosphor screens. Phosphors produced by conventional methods usually consist of particles with the sizes ranging from several micrometers to several tens of micrometers, i.e. significantly larger than the wavelengths of light they emit. The reduction of phosphor particle size into the sub-wavelength regime could be advantageous in many applications provided that the luminescent properties of the chosen material are still appropriate and the technological route is economical. Nanophosphors can be defined as nanoparticles of transparent dielectrics (hosts) doped with optically active ions (activators), so that the emission of light happens due to the electronic transitions between the levels of the impurity ions inside the band-gap of the host (characteristic luminescence).

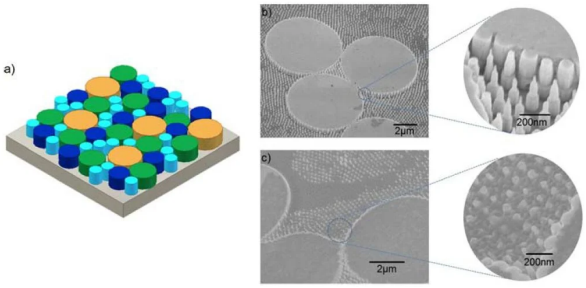

Figure 1: micro and nano phosphors

2 Synthesis and Characterisation

2.1 Methods for synthesis of material

2.1.1 Co-precipitation Method

co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed.

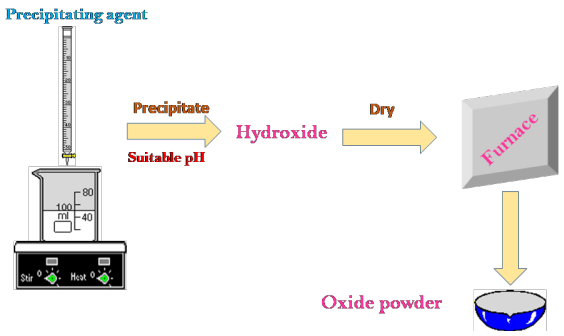

Figure 2: co-precipitation method

2.1.2 Solid State Diffusion Method

Diffusion in solid state materials is a process whereby a liquid, a gas, or another solid can mix together with the host solid on the atomic level. For diffusion to occur, there must be a concentration gradient present.

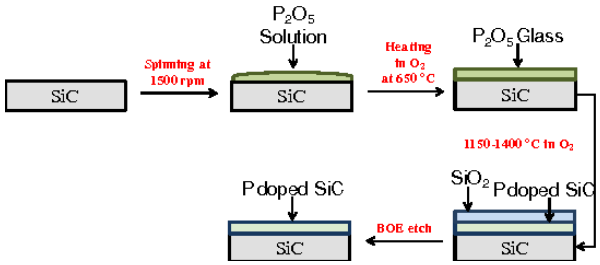

Figure 3: solid state diffusion method

2.1.3 Combustion Method

The mechanism involved in the reaction is very complicated. The factors which is significant during the reaction are; the type of fuel, fuel-to-oxidizer ratio, quantity of water in the precursor mixture and ignition temperature etc.

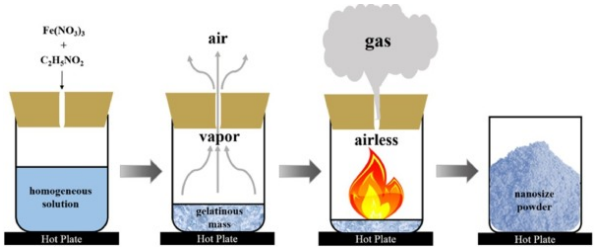

Figure 4: combustion method

2.2 Annealing

Annealing refers to thermal treatment required to remove any irradiation memory from the thermoluminescent material. High Temperature annealing was performed to clear the dosimetric traps and to avoid unwanted background reading while using dosimeter. This in turn stabilize the traps and enhance the sensitivity of dosimeter. Annealing is performed by heating the phosphor to a predetermined temperature, followed by keeping it to the constant temperature for a certain duration and then finally cooling it to room temperature. Effect of annealing temperature on the TL glow curve structure of the samples annealed at different temperature ranging from 700°C to 1100°C.

2.3 Analysis of surface structure of synthesized sample

Surface morphology on our sample is done which gives an advanced form of high spatial resolution image of the surface of our sample. Surface Morphology is a subset of Analytical Imaging, that uses sophisticated microscopes to produce high resolution images of products, samples and objects that cannot be seen with the naked eye. Such images originates from the exposed surface of the sample or product. Generally TEM and SEM are used for this purpose.

2.3.1 Transmission Electron Microscope

Transmission electron microscopes (TEM) are microscopes that use a particle beam of electrons to visualize specimens and generate a highly-magnified image. TEMs can magnify objects up to 2 million times. TEMs employ a high voltage electron beam in order to create an image. An electron gun at the top of a TEM emits electrons that travel through the microscope's vacuum tube. Rather than having a glass lens focusing the light (as in the case of light microscopes), the TEM employs an electromagnetic lens which focuses the electrons into a very fine beam. This beam then passes through the specimen, which is very thin, and the electrons either scatter or hit a fluorescent screen at the bottom of the microscope. An image of the specimen with its assorted parts shown in different shades according to its density appears on the screen. This image can be then studied directly within the TEM or photographed.

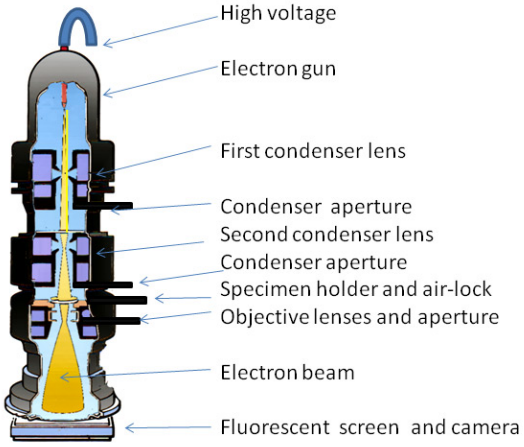

Figure 5: Transmission Electron Microscope

2.3.2 Scanning Electron Microscopy

To overcome the problem with TEMs, the inventor of the TEM invented another type of electron microscope, the SEM. Rather than passing an electron beam through the sample, an SEM focuses a thin electron beam on the sample directly which scans the entire sample in a raster fashion.[8] The high energy electrons hit the sample and emit electrons, photons, and irradiations. The most important are Secondary Electrons and Back-scattered Electrons. BSEs and SEs contain different types of information. BSEs originate from deeper areas of the sample, whereas SEs come from surface regions. Both of these electrons are measured by different detectors. These detectors use this data to form a clear magnified image of the object

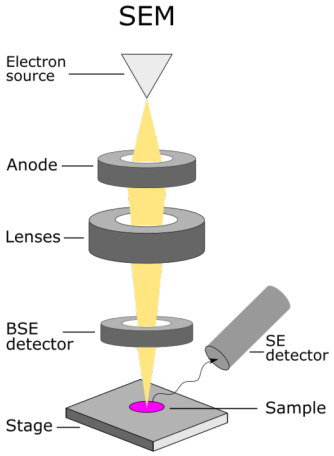

Figure 6: Scanning Electron Microscope

2.4 Characterization

2.4.1 X-Ray Diffraction

To confirm the preparation of our phosphor as well as to determine the grain size, Powder X-ray diffraction (XRD) pattern is obtained. If the size of the crystal is less than 100 nm then an appreciable broadening is seen in XRD patterns. The average grain size of nanoparticles is determined by firstly obtaining the XRD pattern from a diffractometer having some specific energy and wavelength with some particular applied voltage and current. Usually, broadening of the peaks is observed for nanocrystalline materials and to calculate the average grain size for the nanocrystalline sample, we take into account the most prominent peak and use the Scherrer's Formula-:

$$D = \frac{0.9\lambda}{\cos\theta}$$

Where,
D - the average grain size of the crystallites,
θ - Bragg angle
λ - the incident wavelength and
β - the diffracted full width at half maximum in radians caused by the crystallites

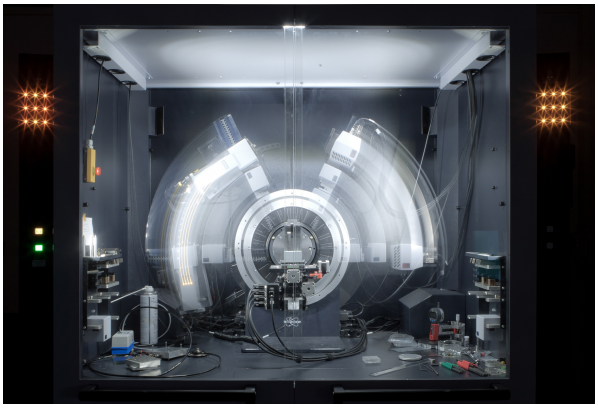

Figure 7: X-Ray diffraction machine

2.4.2 TL Study by irradiation of samples

Using Co60 gamma ray source
As we know, an ideal dosimeter is desired to have some basic characteristics-: a simple glow curve structure with single glow curve peak, high sensitivity to various ionizing radiations, linear TL response curve, energy independence for different energies of ionizing radiations. Thus, we explore above mentioned TL characteristics for nanocrystalline $CaNa_2(SO_4)_2 : Eu$ by irradiating the nanophosphor with various doses of gamma radiation. Firstly the dopant concentration of is optimized by exposing the different prepared samples of $CaNa_2(SO_4)_2 : Eu$ to gamma radiation.
Then to study TL properties, irradiated sample is heated upto a high temperature i.e. $400°C$ at some constant rate and then the TL signal emitted from sample is recorded as function of temperature. Emitted TL signal is recorded in terms of intensity and is plotted against temperature and this plot is called - **TL glow curve**.
And then for a range of dose of gamma radiation, the **TL dose response curve** is plotted.
And hence the different TL characteristics that we get for our sample is further analysed.

2.4.3 FTIR(Fourier Transform Infrared Spectroscopy)

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range.
The goal of absorption spectroscopy techniques (FTIR, ultraviolet-visible spectroscopy, etc.) is to measure how much light a sample absorbs at each wavelength.
In Fourier transform spectroscopy rather than shining a monochromatic beam of light (as in other methods) at the sample, this technique shines a beam containing many frequencies of light at once and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is rapidly repeated many times over a short time span. Afterwards, a computer takes all this data and works backward to infer what the absorption is at each wavelength
And hence performing FTIR spectroscopy helps in identifying the functional groups in our synthesized sample.

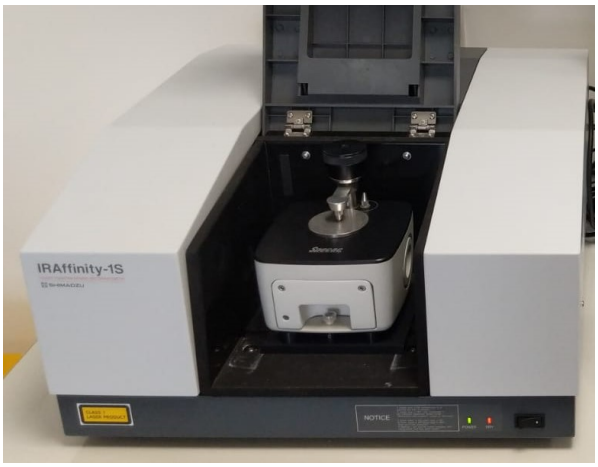

Figure 8: FTIR

3 Experiment

For this project $CaNa_2(SO_4)_2$ and $CaNa_2(SO_4)_2$ doped with 0.1 mole% Europium was synthesized using chemical co-precipitation method to check for its Thermoluminescence dose response.

3.1 Synthesis of $CaNa_2(SO_4)_2$ (pure)

$CaNa_2SO_4$ was prepared by chemical co-precipitation method using the following chemical reaction.

$$2\,NaCl + CaCl_2 + 2\,(NH_4)_2SO_4 \longrightarrow CaNa_2(SO_4)_2 + 4\,NH_4Cl$$

To synthesize $CaNa_2(SO_4)_2$ 14.702g of $CaCl_2$ and 11.688g of NaCl was added to 100ml of double-distilled water in a beaker and stirred continuously with a magnetic stirrer. Simultaneously a solution of 26.426g of $(NH_4)_2SO_4$ in 100ml double distilled water was prepared and added drop wise to the previous solution using a burette while being continuously stirred using a magnetic stirrer.A milky white precipitate was observed to be forming at the bottom of the beaker.

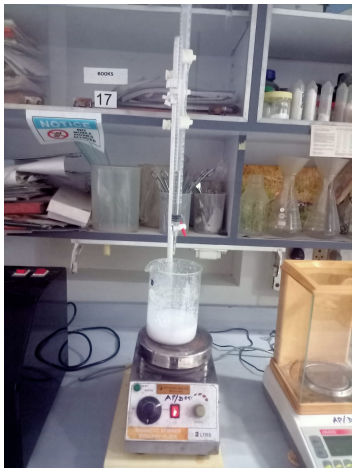

Figure 9: Formation of precipitate due to drop-wise addition of $(NH_4)_2SO_4$ to the solution

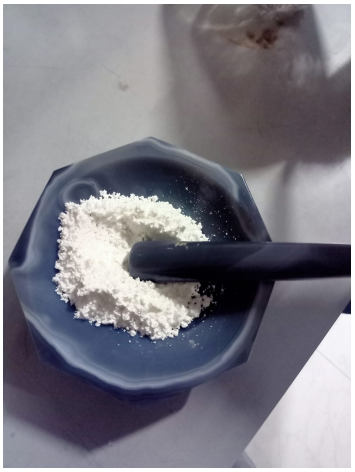

Figure 10: Sample grounded to a fine powder

The solution along with precipitate was then centrifuged 3-4 times using a centrifuge and the precipitate thus obtained was separated and placed on a heating mantle at 40°C for 2 hours and then the temperature was increased to 60°C for the next 5 hours while finally increasing temperature to 80°C and heating the sample for 1 hour. The sample was then let to cool down to room temperature and then grounded into a fine powder using a mortar and pestle. The sample was then stored in a centrifuge tube to be tested for its thermoluminescence properties.

3.2 Synthesis of $CaNa_2(SO_4)_2$:Eu (0.1 mol%)

$CaNa_2SO_4$ doped with 0.1 mole % Europium was prepared by chemical co-precipitation method using the following chemical reaction.

$$2\,NaCl + CaCl_2 + 2\,(NH_4)_2SO_4 \xrightarrow{EuCl_3 \cdot 6\,H_2O} CaNa_2(SO_4)_2 + 4\,NH_4Cl$$

In a beaker with 100ml double distilled water 14.702g of $CaCl_2$ and 11.676g of NaCl was added and stirred continuously with a magnetic stirrer. 0.0368g of $EuCl_3.6H_2O$ was then added to the above solution and stirred continuously for 15 minutes. A solution of 26.426g of $(NH_4)_2SO_4$ in 100ml double distilled water was prepared and added drop wise to the above solution using a burette while being continuously stirred using a magnetic stirrer over a period of 3 hours.A milky white precipitate was observed to be forming at the bottom of the beaker. The solution along with precipitate was then centrifuged 3-4 times using a centrifuge.

Figure 11: Centrifuging the sample

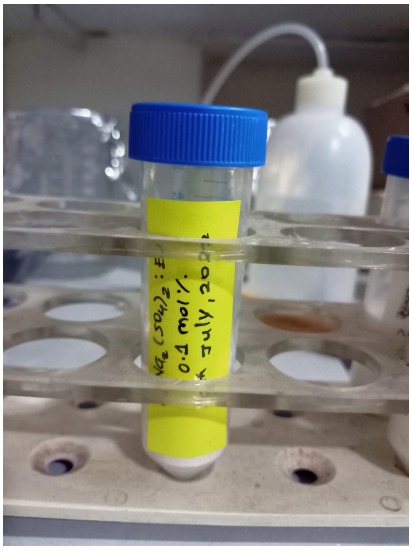

Figure 12: Final sample

The precipitate thus obtained was separated and placed on a heating mantle at 40°C for 2 hours and then the temperature was increased to 60°C for the next 5 hours while finally increasing temperature to 80°C and heating the sample for 1 hour. The sample was then let to cool down to room temperature and then grounded into a fine powder using a mortar and pestle.Approximately 22g of powdered sample was obtained using this method. The sample was then stored in a centrifuge tube to be tested for its thermoluminescence properties.

Figure 13: Sample being prepared for annealing

Figure 14: Muffle Furnace for annealing the sample

3.3 Gamma Ray Irradiation

Both the above samples were then taken to Inter University Accelerator Centre (IUAC) where it annealed at constant temp of 400 C in a muffle furnace for 2 hours and then bought back to room temperature to remove any previous radiation. The samples were then irradiated with Gamma rays using $^{6}0Co$ source first with a dose of 5Gy and then 10Gy. After irradiation, the glow curves(TL GLOW CURVES) were recorded utilizing Harshaw TLD reader by heating the sample from 50°C to 400°C at a continuous heating rate of 5°C/s.

Figure 15: Gamma Ray irradiation chamber

Figure 16: Harshaw TLD reader

4 Results

4.1 TL Glow Curves

The Thermoluminescence Glow curves (TL Glow Curves) obtained using Harshaw TLD Reader 3500 by heating the samples from $50°C$ to $400°C$ at a heating rate of $5°C/s$ for both samples after being irradiated with gamma rays at 50 Gy and 100Gy are shown here:

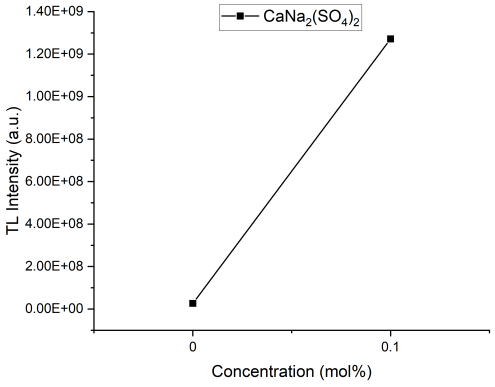

Figure 17: Intensity vs dopant concentration for 50Gy gamma radiation

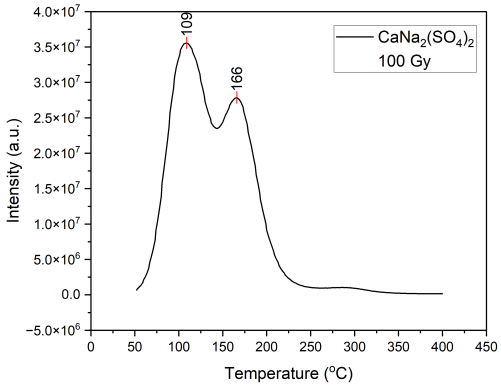

Figure 18: TL glow curve of $CaNa_2(SO_4)_2$ for 100 Gy gamma radiation

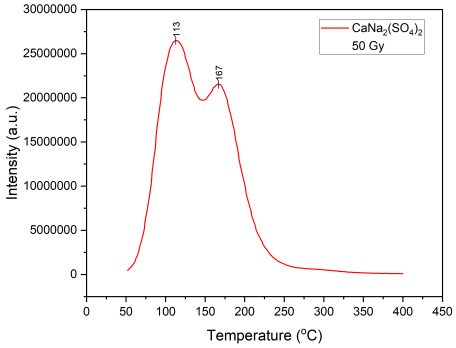

Figure 19: TL glow curve of $CaNa_2(SO_4)_2$ for 50 Gy gamma radiation

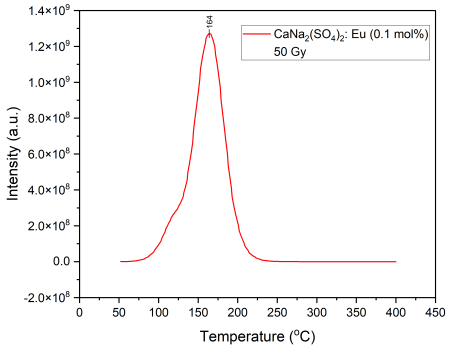

Figure 20: TL glow curve of $CaNa_2(SO_4)_2 : Eu(0.1mol\%)$ for50 Gy gamma radiation

4.2 Analysis

We have synthesized two concentrations of $CaNa_2(SO_4)_2$ doped with Europium (pure and 0.1 mol%). At IUAC, the samples were irradiated in a gamma chamber with 50 Gy and 100 Gy dose of gamma rays. The TL glow curves were recorded using Harshaw TLD Reader 3500 after heating the samples from $50°C$ to $400°C$ at a heating rate of $5°C/s$.

Another study that we undertook is comparison of intensity of TL with the concentration of dopant. As can be seen, with addition of dopant, the glow curves come close to having a single peak as compared to pure sample. Also the thermoluminescence intensity for doped sample is more compared to that of the pure sample. However, conclusive evidence cannot be provided as only one concentration of doped sample was synthesized and further analysis is required.

Conclusion

$CaNa_2(SO_4)_2$ and $CaNa_2(SO_4)_2$ doped with 0.1 mol% Europium was synthesized by co-precipitation method. The thermoluminescent properties of this sample was investigated by irradiating it with ^{60}Co gamma rays at 50Gy and 100Gy.The TL glow curve of $CaNa_2(SO_4)_2$ shows 2 peaks at around $113°C$ and $167°C$ for 50 Gy dose and at around $109°C$ and $166°C$ for 100Gy dose. The sample of $CaNa_2(SO_4)_2 : Eu(0.1mol\%)$ shows a very high intensity single TL glow peak at around $164°C$. This shows that the addition of dopant enhances the thermoluminescent properties of $CaNa_2(SO_4)_2$. Further analysis with different dopant concentrations is required to study the application of $CaNa_2(SO_4)_2$ as an efficient thermoluminescent dosimeter.

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