Journal of Atomic, Molecular, Condensed Matter & Nano Physics
Vol. 9, No. 1, pp. 31–39, 2022
ISSN 2582-8215
Published by RGN Publications
http://www.rgnpublications.com

Special Issue:
Nuclear Track Detectors, Luminescence and Their Applications
Guest Editors: P.D. Sahare, Rajesh Kumar, Ashok Kumar

DOI: 10.26713/jamcnp.v9i1.1957

Research Article

Passive Dosimeter Based on BaBrF:Tm^{3+} Phosphor for γ-ray Dosimetry

Shashank Yadav[1], Manveer Singh*[2], Bhavna Vidhani[3], Ashok Kumar[2] and P.D. Sahare[4]

[1] *Amity Institute of Nanotechnology, Amity University, Noida 201313, Uttar Pradesh India*
[2] *Department of Physics, Ramjas College (University of Delhi), Delhi 110007, India*
[3] *Department of Physics, Hansraj College (University of Delhi), Delhi 110007, India*
[4] *Department of Physics & Astrophysics (University of Delhi), Delhi 110007, India*
***Corresponding author:** manveersingh@ramjas.du.ac.in

Received: November 12, 2021 **Accepted:** May 12, 2022

Communicated by: Rangoli Bhatnagar

Abstract. Thulium (Tm^{3+}) ions doped Barium Bromide Fluoride (BaBrF) samples were synthesized successfully through the solid-state diffusion method. The crystal structure and phase purity of the synthesized sample were examined by Powder X-Ray Diffraction (PXRD) analysis. Dosimetric properties of γ-ray exposed samples of BaBrF:Tm^{3+} investigated. To obtain the maximum Thermoluminescence (TL) sensitivity of the material, the dopant concentration level and annealing temperature were optimized. It is observed that the dopant concentration 2.0 mol% of Tm^{3+} and the annealing at 673 K temperature the phosphor material exhibits maximum TL intensity. The γ-Ray dose-response, fading of the TL signal, and kinetic parameters of the TL glow curve were also investigated. TL sensitivity of the BaBrF:Tm^{3+} phosphor compared to the commercially available $CaSO_4$:Dy (TLD-900) dosimeter used for radiation measurement. On the basis of their promising dosimetric characteristics, it can become a good TL dosimeter for passive dosimetry of high energy γ-ray radiation.

Keywords. TLDs, Thermoluminescence, Dosimetry, Phosphor, Radiation

PACS. 87.53.Bn (Dosimetry/exposure assessment)

1. Introduction

Present and future is the time of development of science and technology. Now-a-days new scientific inventions are taking place in which low energy and height energy (ionizing) radiation are playing an amazing role. Ionizing radiation is being used more and more in various fields such as defense, medical science, industries, remote sensing, food processing, and forensic science in the field of security etc. [5, 7–9, 16, 18], where there are ionizing radiation has a serious effect on human life and flora. Beyond a limit it is a cause of acute health effect such as skin burn, cancer or acute radiation syndrome.

Due to these reasons, along with the utility of ionizing radiation, its monitoring becomes equally important. Many systems of Passive and Active radiation dosimetry being used in radiation measurement have been invented so far. Passive dosimetry is commonly used for personal dosimetry. For this purpose, basically Thermoluminescence (TL), Mechanoluminescence (ML), Optically Stimulated Luminescence (OSL) and similar other techniques are used. Among them TL them is a popular technique for radiation dosimetry. For this purpose a number of Thermoluminescence Dosimeters (TLDs) phosphor materials have been developed [1–3, 6, 14]. There are several commercially available TLD phosphors also such as LiF:Mg,Ti (TLD-100), LiF:Mg,Cu,P (TLD-700), CaF_2:Dy (TLD-200), CaF_2:Tm (TLD-300), CaF_2:Mn (TLD-400), Al_2O_3:C (TLD-500) and $CaSO_4$:Dy (TLD-900) available. However, each phosphor has one or the other limitation(s) [3]). For example, $CaSO_4$:Dy is very sensitive but it is not tissue equivalent and its instability and high fading introduce errors in estimation of dose. There are not many tissue equivalent (low-Z) phosphors and the available ones are also not very perfect. LiF:Mg,Ti, BeO:A (A→Li, Na, K) and LiF:Mg,Cu,P are a few to name. They are also not ideal as the first one is not very sensitive, the second one is highly sensitive but loses reusability if proper care is not taken while readouts, and the third is toxic and need special facilities for synthesis and its use. Hence, a constant efforts are being made either to develop a new phosphor or to improve the existing ones [3, 10, 11, 13, 17].

In the present work, a detailed study on synthesis, heat treatment, and TL dosimetry characteristics of BaBrF:Tm^{3+} phosphors have been reported. The literature survey revel that there is no work done to study the TL properties of Tm^{3+} rare-earth ions doped BaBrF phosphor material. Therefore, it encourages us to investigate the effect of Tm^{3+} ions on TL properties of BaBrF materials.

2. Experimental

2.1 Materials and Method

Tm^{3+} doped BaBrF samples ware synthesized through a conventional solid state diffusion method by taking BaF_2 (99.5%) and $BaBr_2$ (99.9%) as the starting materials and $TmCl_3$ (99.5%) as the dopant salt. The mixture of precursors salt was taken in stoichiometric ratio as per the given chemical reaction and then mixed using mortar pestle in the presence of EtOH for better mixing.

$$BaF_2 + BaBr_2 + TmCl_2(\text{x mol\%}) \xrightarrow{\text{Heating}} 2BaBrF : Tm^{3+}$$

The homogeneous mixture of the precursors sintered in an alumina crucible at 1083 K temperature for 12 hours inside a temperature-controlled furnace and then cooled down slowly to room temperature. The grown material was crushed in mortar pestle and obtains fine powder. Proper heat treatment was given to the powder sample before using for further studies.

2.2 Characterization Techniques

The Powder X-Ray Diffraction (PXRD) patterns were recorded using a high-resolution D8 Discover Bruker X-ray Diffractometer, equipped with a point detector (scintillation counter), employing monochromatized Cu Kα1 radiation obtained through a gobel mirror with a scan rate of 1.0 s/step and step size of 0.02 at room temperature.

The SEM micrograph of the sample was recorded on a Hitachi S-3700 M microscope. TL was recorded on a Harshaw TLD Reader 3500 HT immediately after the irradiation by taking about 5mg of sample every time at the linear heating rate of 5 K/s.

3. Results and Discussion

3.1 Crystal Structure and Morphology

Phase formation of the synthesized material BaBrF examined by PXRD characterization. The PXRD pattern of the BaBrF:Tm^{3+} powder is shown in Figure 1. PXRD pattern of the synthesized material were indexed and match with the tetragonal space group P4/nmm of BaBrF (i.e., ICSD file # 98-003-5393) standard data available in the literature. All the diffraction peaks well matched to the standard data and no additional peaks were observed related to the precursors or impurity phase. BaFBr has the matlockite structure, a tetragonal symmetry with layers perpendicular to the c-axis. The average crystallite size calculated using the Debye-Scherer equation $D = K\lambda/\beta\cos\theta$, which was found to be 42.5 nm.

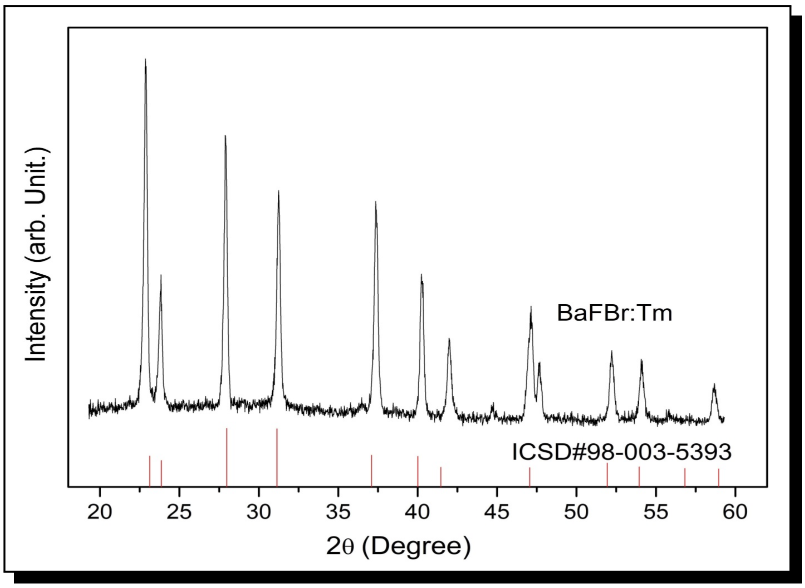

Figure 1. PXRD pattern of BaBrF:Tm^{3+} phosphor sample. The stick pattern of the available data in the literature (ICSD file # 98-003-5393) has also been given for comparison

A typical SEM image shows the morphology of synthesized material. Irregular particle shapes and sizes were observed in the range of 50 nm - 2.0 μm which could be clearly seen in SEM micrograph Figure 2. The wide range distribution of particle size is observed since the material synthesized by solid state diffusion method.

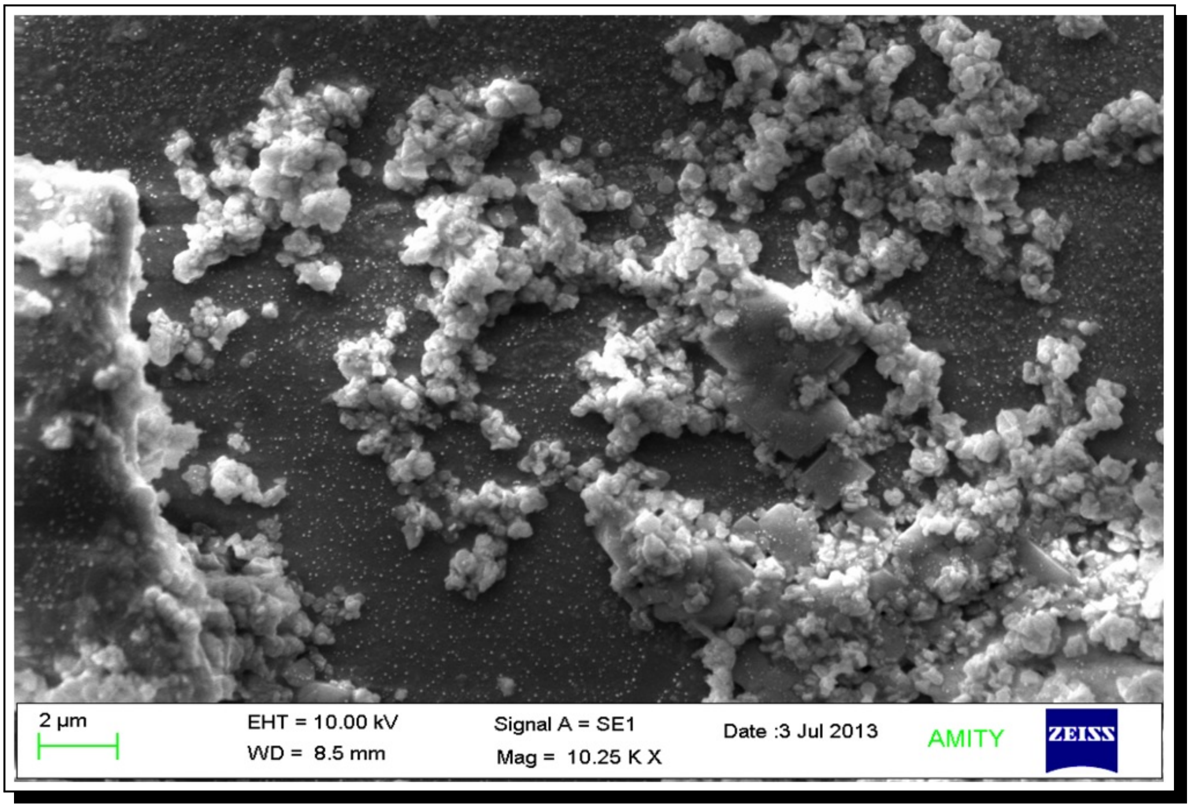

Figure 2. SEM image of Tm^{3+} doped crystalline BaFBr material

3.2 Thermoluminescence (TL) Characteristics

3.2.1 Optimization of the Dopant (Tm^{3+}) Concentration and Annealing Temperature

Shape and sensitivity of the TL glow curve of a TLD phosphor material depend on the dopant concentrations as well as its ionic state in the host matrix. In the present study, the material was doped for different impurity concentrations in the range of 0.1 - 3.0 mol% of Tm^{3+} ions. Samples of different concentration of dopant annealed at 673 K, irradiated at 10 Gy from the ^{137}Cs source and the TL was taken. The TL sensitivity of the exposed samples increased with the increases in the impurity concentration up to 2.0 mol% and then started decreasing as shown in Figure 3. The TL glow curve is simple (single glow curve) and peak centred at around 425 K. The TL glow curve structure is found to change a bit with the impurity concentration as the intensity of the satellite peaks change. Apparently, peak position of the glow curve slightly changes with the dopant concentration. At higher concentrations >2.0 mol% of dopant, the TL intensity start to decrease. It has also been found to decrease due to non-radiative crossover transitions between Tm^{3+} ions on increasing the doping concentration (concentration quenching) as they come closer than the critical separations [4].

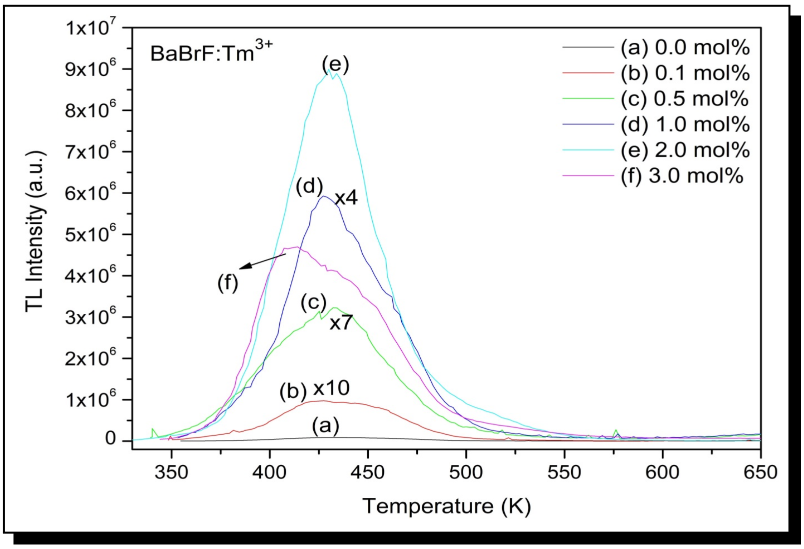

Figure 3. Glow curves of the BaBrF:Tm^{3+} samples with different impurity concentrations (0.1 - 0.3 mol%). The ordinate is to be multiplied by the numbers near the curves to get the relative intensities

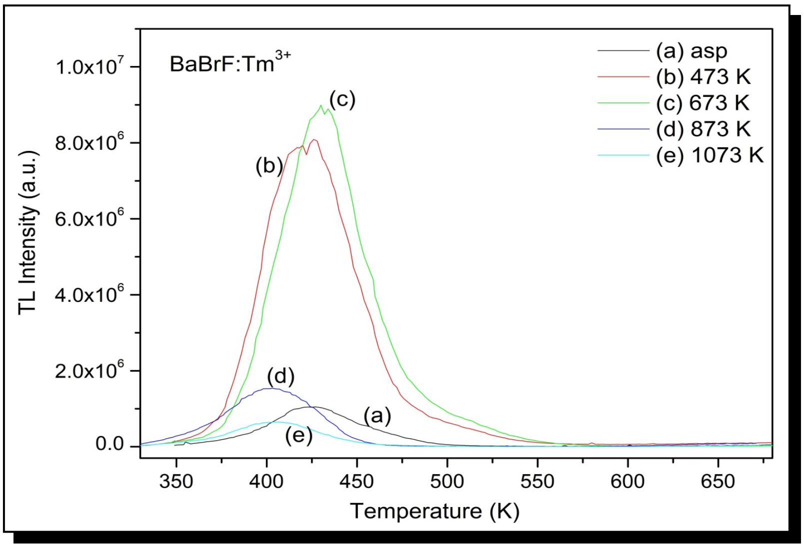

Figure 4. Glow curves of the BaBrF:Tm^{3+} phosphor material annealed at different temperatures for 1 h and quenching to room temperature t. The maximum TL intensity was observed for 673 K

The samples were annealed at different temperatures (473 to 1073 K) to study the effect of annealing on the shape and TL sensitivity of the material. The variation of TL sensitivity with annealing temperatures is shown in Figure 4. It is observed that samples annealed at 673 K for 1 h show the highest TL sensitivity. There is not much change observed in the TL glow curve structure on annealing except a little change in the peak position. Initially, the TL intensity increases with the corresponding annealing temperature up to 673 K but for annealing at higher, temperatures the TL intensity decreases. The increase in the TL intensity can be attributed to the more dispersion of the impurity ions, however, further decrease at higher temperatures (beyond 673 K) may be due to formation of more complex defects on diffusion of atmospheric oxygen [11, 12, 15].

3.2.2 γ-ray Dose Response

As mentioned in Section 3.2.1, samples doped with 2.0 mol% of Tm^{3+} ions and annealed at 673 K, were used for further dosimetric studies. The samples were exposed to the different doses (in the range of 0.1 Gy to 10 kGy) of γ-rays from the ^{137}Cs source and TL was taken. The TL glow curves for different radiation doses of the samples are shown in Figure 5. Simple TL glow curve consisting of apparently a single peak centred at around 425 K was observed. An appreciable change in the peak position (peak temperature) has also been observed and varies from 415 to 436 K in the given dose range. The γ-ray dose response is shown in Figure 6, it is observed that sub-linear up to 10 Gy after that it become nearly linear before the saturation.

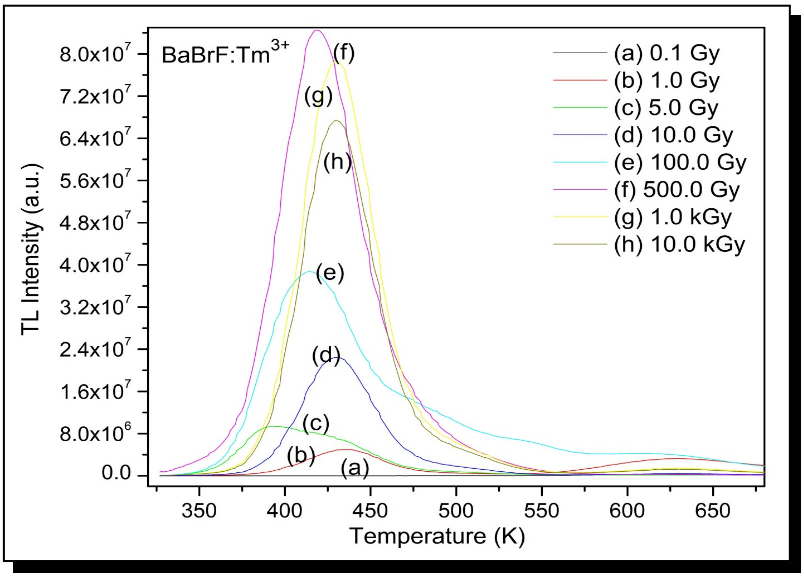

Figure 5. TL glow curves of BaBrF:Tm^{3+} TLD phosphor exposed to different doses of γ-rays from a ^{137}Cs source

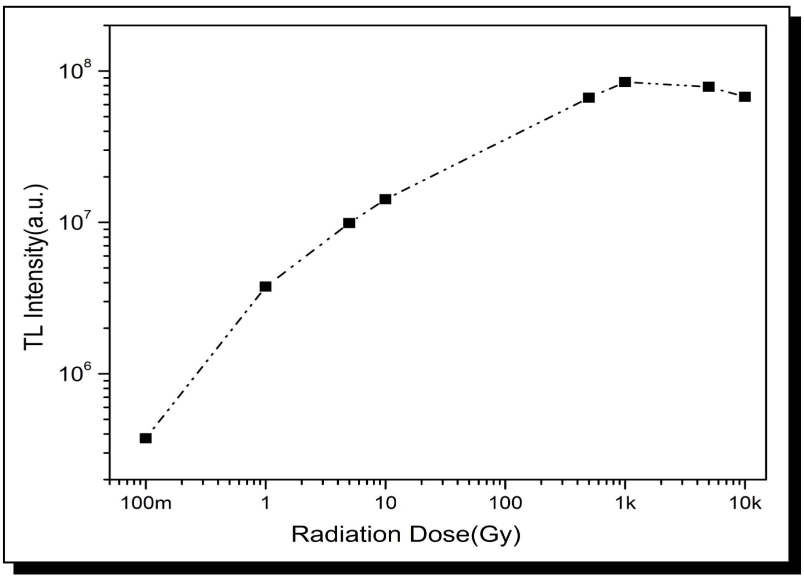

Figure 6. TL dose response of BaBrF:Tm^{3+} TLD phosphor

The TL sensitivity of the synthesized Tm^{3+} doped BaFBr phosphor material was also compared with the commercially available TLD-900 phosphor. The results are shown in Figure 7. It was found that the Tm^{3+} doped BaFBr phosphor is nearly equally sensitive to TLD-900.

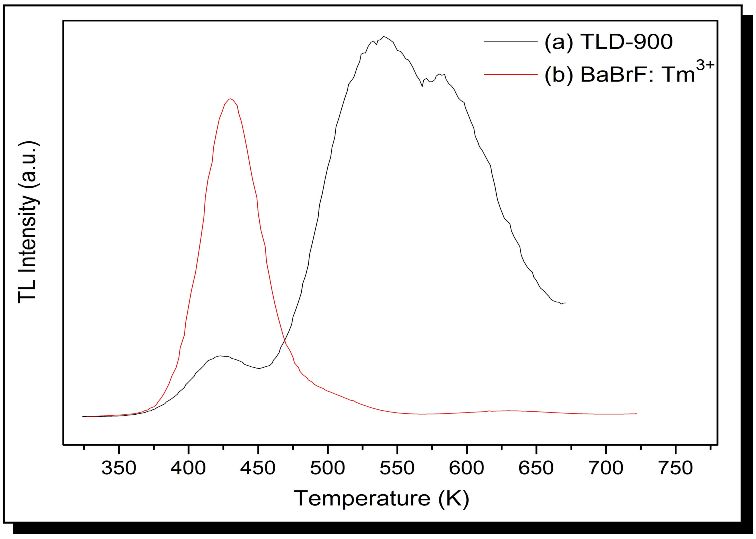

Figure 7. Comparison of the TL sensitivity of the BaBrF:Tm^{3+} (0.2 mol%) phosphor material with that of other commercially available phosphors, i.e. $CaSO_4$:Dy (TLD-900)

3.2.3 Fading

Loss of TL signal intensity with time after the exposure express by a dosimetric characteristic term called fading. Fading is an important characteristic from the dosimetric application point of view. TLD phosphors who exhibit low TL signal loss with the storage time are assumed best for radiation dosimetry. BaBrF:Tm^{3+} TLD phosphor was tested for its fading characteristics. Several pallets of BaBrF:Tm^{3+} phosphor were exposed (10 Gy) to the γ-rays from ^{137}Cs source, stored at room temperature. TL of the stored samples were taken after 3 h, 2, 7, 14, 21, 28 and 35 days. The fading pattern of the TLD phosphor is shown in Figure 8.

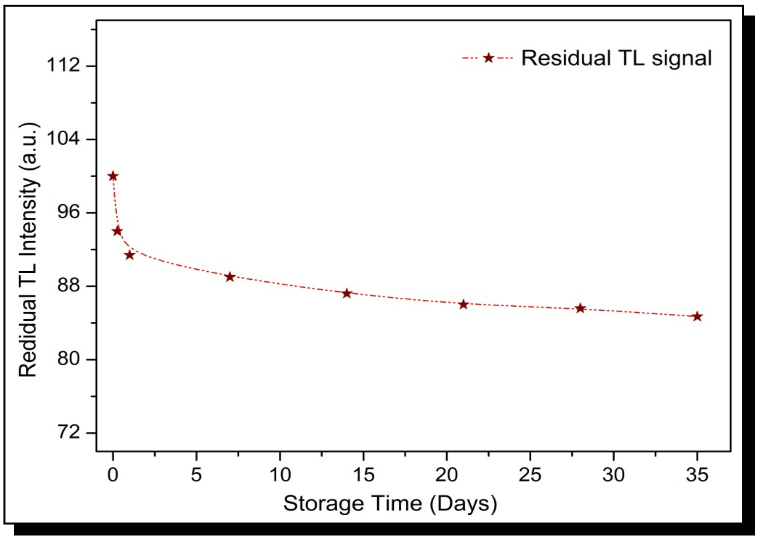

Figure 8. TL signal fading of BaBrF:Tm^{3+}(0.2 mol%) exposed to 10Gy of γ-ray from ^{137}Cs source on storing in dark at room temperature

It can be seen that fading of the TL signal after one week is about 8% and after 5 weeks the fading was found to be around 15% which is considered to be low for the dosimetry purposes.

4. Conclusions

Rare earth Tm^{3+} ions doped BaBrF phosphor samples were synthesized through the conventional solid state diffusion method. BaBrF:Tm^{3+} phosphor material annealed at 673 K and 2 mol% doped with Tm^{3+} ions exhibit the maximum TL sensitivity. Simple TL glow curve was found centred at around 425 K that is sufficiently above the room temperature. By this cause BaBrF:Tm^{3+} phosphor material shows considerably low fading 15% during the 5 weeks. The dose response of the synthesized phosphor shows sub-linear up to 10 Gy after that it becomes nearly linear before the saturation. The sensitivity was found nearly equal to the standard commercially available TLD-900 phosphor. Low cost and simple method of preparation, simple glow curve structure and wide range of dose response, low fading make it a suitable candidate for the radiation monitoring using TL technique.

Acknowledgement

We are thankful to the Inter University Acceleration Centre (IUAC), New Delhi and the University of Delhi for providing all facilities by which this research work could be completed.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

[1] M.J. Aitken, *Thermoluminescence Dating*, Academic Press, London, 351 pp. (1985).

[2] F.H. Attix, *Introduction to Radiological Physics and Radiation Dosimetry*, John Wiley & Sons, New York, 628 pp. (1986), URL: https://www.wiley.com/en-us/Introduction+to+Radiological+Physics+and+Radiation+Dosimetry-p-9783527617135.

[3] J. Azorín, C. Furetta and A. Scacco, *Preparation and properties of thermoluminescent materials*, *Physica Status Solidi (A)* **138** (1993), 9 – 46, DOI: 10.1002/pssa.2211380102.

[4] G. Blasse, New luminescent materials, *Chemistry of Materials* **1** (1989), 294 – 301, DOI: 10.1021/cm00003a005.

[5] B.B. Boltwood, Ultimate disintegration products of the radioactive elements; Part II, Disintegration products of uranium, *American Journal of Science* **s4-23**(134) (1907), 77 – 88, DOI: 10.2475/ajs.s4-23.134.78.

[6] R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes*, Pergamon Press, New York (1981).

[7] P.R. Hussain, P.P. Suradkar, A.M. Wani and M.A. Dar, Retention of storage quality and post-refrigeration shelf-life extension of plum (*Prunus domestica L.*) cv. Santa Rosa using combination of carboxymethyl cellulose (CMC) coating and gamma irradiation, *Radiation Physics and Chemistry* **107** (2015), 136 – 148, DOI: 10.1016/j.radphyschem.2014.10.007.

[8] J. Jang, S.E. Jung, W.K. Jeong, Y.S. Lim, J.-I. Choi, M.Y. Park, Y. Kim, S.-K. Lee, J.-J. Chung, H. Eo, H.S. Yong and S.S. Hwang, Radiation doses of various CT protocols: A multicenter longitudinal observation study, *Journal of Korean Medical Science* **31** (Suppl. 1) (2016), S24 – 31, DOI: 10.3346/jkms.2016.31.S1.S24.

[9] A.J.T. Jull, C.L. Pearson, R.E. Taylor, J.R. Southon, G.M. Santos, C.P. Kohl, I. Hajdas, M. Molnar, C. Baisan, T.E. Lange, R. Cruz, R. Janovics and I. Major, Radiocarbon dating and intercomparison of some early historical radiocarbon samples, *Radiocarbon* **60**(2) (2018), 535 – 548, DOI: 10.1017/RDC.2018.18.

[10] G. Kitis, J.M. Gomez-Ros and J.W.N. Tuyn, Thermoluminescence glow-curve deconvolution functions for first, second and general orders of kinetics, *Journal of Physics D: Applied Physics* **31** (1998), 2636 – 2641, DOI: 10.1088/0022-3727/31/19/037.

[11] A.R. Lakshmanan, M.T. Jose, V. Ponnusamy and K.P.R. Vivek, A.R. Lakshmanan, M.T. Jose, V. Ponnusamy and P.R.V. Kumar, Luminescence in $CaSO_4$:Dy phosphor - dependence on grain agglomeration, sintering temperature, sieving and washing, *Journal of Physics D: Applied Physics* **35** (2002), 386 – 396, DOI: 10.1088/0022-3727/35/4/315.

[12] F.M.-T. Lay and A.W. Nolle, Paramagnetic resonance and relaxation and dielectric loss in Ca F_2 crystals containing Mn^{2+}, OH^-, and oxygen, *Physical Review Journals Archive* **163** (1967), 266 – 275, DOI: 10.1103/PhysRev.163.266.

[13] U. Madhusoodanan, M.T. Jose, A. Tomita, W. Hoffmann, and A.R. Lakshmanan, A new thermostimulated luminescence phosphor based on $CaSO_4$:Ag,Tm for applications in radiation dosimetry, *Journal of Luminescence* **82** (1999), 221 – 232, DOI: 10.1016/S0022-2313(99)00044-7.

[14] S.W.S. McKeever, *Thermoluminescence of Solids*, Cambridge Solid State Science Series, Cambridge University Press, London (1985).

[15] R. Nakata, K. Kohnom, M. Sumita and E. Higuchi, ESR study of Manganese complexes in 19heavily doped CaF_2 crystals, *Journal of the Physical Society of Japan* **41** (1976), 470 – 474, DOI: 10.1143/JPSJ.41.470.

[16] A.M. Pollard and C. Heron, *Archaeological Chemistry*, Royal Society of Chemistry, Cambridge (1996), DOI: 10.1039/9781847550156.

[17] P.D. Sahare and S.V. Moharil, A new high-sensitivity phosphor for thermoluminescence dosimetry, *Journal of Physics D: Applied Physics* **23** (1990), 567 – 570, DOI: 10.1088/0022-3727/23/5/015.

[18] B.A. Schueler, The AAPM/RSNA physics tutorial for residents: General overview of fluoroscopic imaging, *RadioGraphics* **20**(4) (2000), 1115 – 1126, DOI: 10.1148/radiographics.20.4.g00jl301115.