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Mechanoluminescence and Thermoluminescence characterization of Tb³⁺ doped CaAl₂O₄: A theoretical and Experimental Study

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Abstract

Mechanoluminescence and thermoluminescence of Tb in CaAl₂O₄ prepared by solution combustion method has been reported. Phase purity, formation of phosphor and surface morphology were confirmed by XRD and SEM techniques. The resulting phosphors were characterized by photoluminescence (PL) to detect incorporation of dopant. When an gamma-irradiated Tb-doped CaAl₂O₄ crystal is impulsively deformed, two peaks appear in the ML intensity versus time curve, whereby the first ML peak is found in the deformation region and the second in the post deformation region of the crystals. The energy levels and hence trapping and detrapping mechanism of charge carriers can be explained using ML. Tb-doped CaAl₂O₄ phosphor can be used in the dosimetric applications for ionizing radiation. The TL characteristics of CaAl₂O₄ may be useful for high radiation doses. Thermoluminescence (TL) materials have wide applications in the dosimetry of ionizing radiation, scintillators, X-ray laser materials, etc. The samples were irradiated using a ⁶⁰Co gamma-ray source at a dose of 0.930 kGy/hour and the heating rate used for TL measurements was 5°C/s. The samples show good TL peaks for 0.2mol% (urea), 0.2mol% (hydrazine) and 0.2 mol% (carbohydrazide) doping concentrations of Tb³⁺ ions. We also report a more detailed theoretical understanding of the mechanism of TL and ML. All TL glow curves obey the second-order kinetics with a single glow peak, which reveals that only one set of trapping parameter is set for a particular temperature. The TL sensitivity was found to depend upon the annealing temperature and Tb³⁺ doping concentration. The prepared sample may be useful in TL dosimetry.

Introduction

Inorganic phosphors are widely used in luminescent devices. Stability of trivalent state rare earth ions have been found to be the most stable [1–3]. Because the phosphor is crystalline in nature, excitation of the particles creates defects in the phosphor material [4–5]. In recent decades the long afterglow phosphor CaAl₂O₄ has been used in many fields, because of its characteristics of high luminescent brightness at an approximate wavelength of 440nm, long afterglow time good chemical stability and low toxicity [6–7].

Mechanoluminescence (ML), occurs due to deformation and fractures of solids and light emitted as a result of the mechanical energy of solids. It offers a number of applications such as detection of cracks in solids, mechanical activation and sensors. Mechanoluminescence phenomenon occurs in the solid state, which is useful to develop a suitable technique for the explanation

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of mechanical, optical, structural and electrical properties of solids. In the study of luminescence induced by elastic deformation suggested that the expressions explored for the dependence of ML intensity on several parameters may be useful in tailoring the suitable nanomaterials capable of exhibiting ML during their elastic deformation [8-9]. The ML is excited during the mechanical deformation of a solid, and a correlation between ML intensity and the deformation of a solid is anticipated. There are some prominent reasons for the ML excitation, as the ML does not appear in all solid materials [10-11]. A large number of inorganic and organic solids exhibit the phenomenon of ML, which has also been observed in insulators and semiconductors as well as in certain conductors. An alternative mode of light emission at room temperature is to release the stored energy in the irradiated material by dissolving it in an appropriate solvent. This phenomenon has attracted many researchers from various disciplines such as radiation physics, radiation chemistry and physical chemistry [12].

When an insulator subjected to ionizing radiation is heated the energy stored in the crystal or phosphor as a result of the radiation process, liberates in the form of visible light in addition to the normal thermal radiation. Heating the crystal, immediately after it, gives rise to only the thermal emission. The additional visible light emitted during, first heating is called thermoluminescence (TL). A material that emits light even after removal of the excitation source is known as a TL glow phosphor. Many TL-sensitive phosphors have been developed for environmental radiation dosimetry [13–15]. In Thermoluminescence (TL), a material is initially heated for a sufficiently long time until all traps are emptied. The material is subsequently cooled and completely excited by a light source for some time [16-17]. It is customary to also measure the temperature dependence of the fluorescence (by repeating the measurement under constant excitation), in order to compensate for temperature quenching effects. For nearly all materials, the glow curve shows one or more broad, often asymmetrical peaks. Each peak is observed to be originating from a separate trap. The study of shape and location of these peaks provide insight in the different depths and distributions of the traps present in the sample. These studies are very useful in the field of geology (dating technique) [18] and radiation dosimetry [19].

It is well known that Tb^{3+} ions present stronger absorption around 380 nm. When the host compound is doped by Tb^{3+} ion, the sub lattice structure around luminescent center ions will be somewhat distorted so, the spectral lines of rare earth ions are expected to be broadened. Aluminates are good candidate as phosphor host materials and are widely applied because of their high quantum efficiency, good stability, high quenching temperature, anti-radiation, being of low cost, pollution-free, nontoxic etc. [20]. Tb^{3+} doped composite calcium aluminate phosphors have rarely been investigated are usually prepared by a traditional solid-state reactive method, whose synthesis temperature is high. On the other hand, the crystal shapes of the phosphor particles are seriously damaged and the luminescent intensity obviously reduced. Whereas, the combustion synthesis technique possesses a fast reaction, at a low temperature, saving energy. [21-23]. In particular, the products present loose powders, with small particle sizes, large specific surface areas, effective crystallization and easy crushing's. The aluminates have been the center of attention in persistent luminescent research. The alkaline earth aluminates MAI_2O_4 ($M=Ca, Sr, Ba$) are by far the most studied family of persistent luminescent materials [24-26]. It has been proved that

the combustion technique is regarded as one of the most promising synthesis methods. In this study, we report the theoretical and experimental approach of the luminescence properties of Tb^{3+} doped $CaAl_2O_4$ phosphor.

Experiment

Phosphors were prepared by the combustion technique using urea, hydrazine and carbonylhydrazide as a fuel. The starting materials taken were $Ca(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$ compounds of ultra high purity (99.9%). Stoichiometric amount of all material were taken in a glass beaker and dissolved in distilled water. The beaker was kept in a furnace set at 300°C. The reaction is self-propagating and is able to sustain this high temperature long enough. The entire combustion process was over in about 5 min. This technique can produce a homogeneous product in a short amount of time without the use of an expensive high-temperature furnace. Formations of the samples were confirmed by XRD pattern recorded by X-ray diffractometer (PW-1710). The gamma-ray-irradiation was carried out using ^{60}Co source. ML was excited impulsively by dropping a load on the sample placed on a Lucite plate with different impact velocities. The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). All ML measurements were carried out after gamma irradiation. To confirm the presence of rare earth ions in aluminate based phosphors photoluminescence (PL) of the samples have been recorded by Spectrofluorophotometer. A PC based thermo luminescence analyser system (TL-10091) was used for recording TL of gamma irradiated sample.

Result & discussion

XRD Study

Figure 1 shows the XRD pattern of $CaAl_2O_4$. The diffraction peaks represent to all the planes of the pure monoclinic phase for $CaAl_2O_4$. It has been observed that the XRD pattern matched perfectly with reported for the JCPDS card No. 83-2025 of $CaAl_2O_4$. No peak of any other phase has been observed in the XRD pattern.

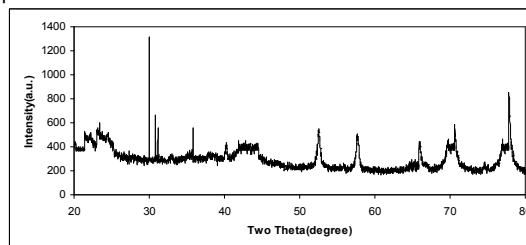


FIG.1. XRD pattern of $CaAl_2O_4:Tb$.

SEM characterization

An SEM study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The synthesis was carried out at 500°C by a combustion reaction. This shows that the combustion reactions of the mixtures took place well. The typical morphological image represented in fig. 2 shows representative SEM micrographs taken for $CaAl_2O_4$ phosphor materials. The surface of the powder shows a lot of voids and pores, which may be formed by the evolved gases during combustion.

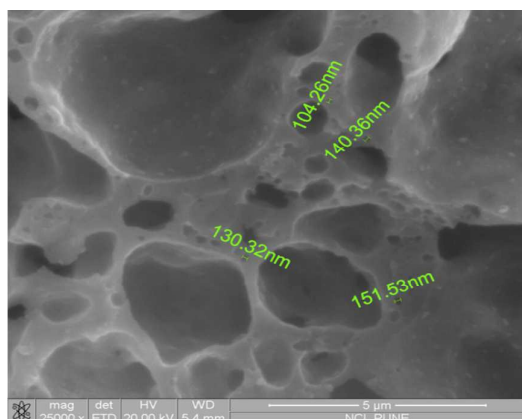
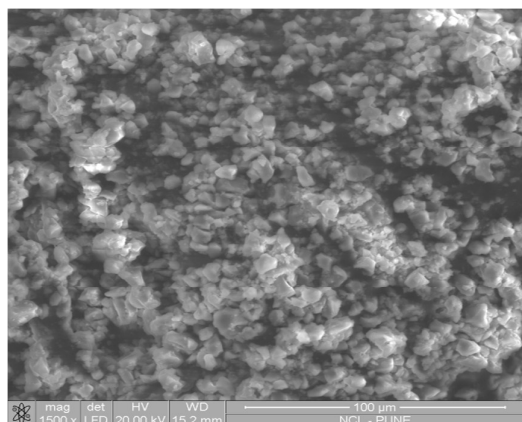


FIG. 2 SEM images of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphor.

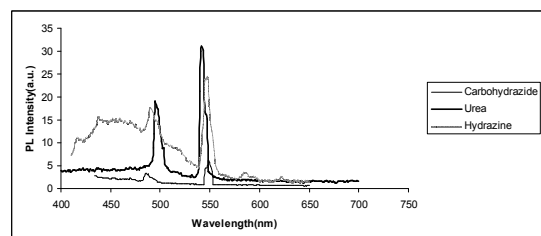


FIG. 3. PL emission spectra of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphors for different fuels.

Figure 3 shows PL emission spectra of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphors for different fuel. Tb^{3+} doped γ -irradiated CaAl_2O_4 phosphor show two prominent peaks one at around 495 nm and another at around 550 nm corresponding to transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$. Peak around 550 nm is greater than the 495 nm peak.

Mechanoluminescence of $\text{CaAl}_2\text{O}_4:\text{Tb}$

Figure 4 shows the ML intensity versus time curve of gamma ray irradiated $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphors. Two distinct peaks were observed when ML was excited by dropping a load on to it. ML intensity increases linearly with increasing the impact velocity of the piston dropped on to the sample. ML intensity initially increased with time

attained an optimum value for a particular time then decreased again increases to a value then decreases and finally disappeared.

Figure 5 shows the total ML intensity as a function of the dopant concentrations. It is clear that in all the samples ML intensity initially increased with increasing the dopant concentration attained an optimum value for a particular concentration of dopant then decreased with further increase in the dopant concentration. Optimum ML is found for 0.2 mol% dopant.

Figure 6 shows the dependence of ML intensity on γ -ray dose of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphors. ML intensity increased almost linearly with γ -ray doses given to the samples. On increasing the γ -dose, the density of defect centres increases and when a sample of a given mass is deformed at a given impact velocity, I_m and I_T should increase with the density of defect centres.

Figure 7 shows low fading of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphor within 15 days of its irradiation with gamma ray dose. Figure shows only 25-30% fading within observed time.

Figure 8 shows that ML intensity increased almost linearly with increasing the mass of the sample deformed for recording ML, in the range (0.5 to 2.5 mg) investigated. When we increase the mass of the sample, the number of crystallites in the sample increases and thereby the ML intensity and the total ML intensity increase.

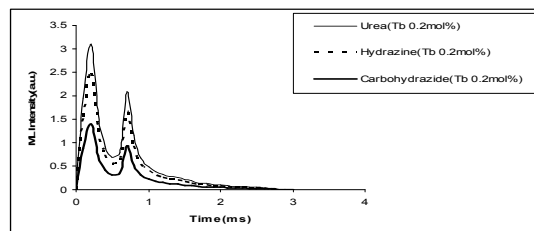


FIG. 4. Time dependence of ML intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphors (γ -ray dose 1.1 kGy, mass of the sample 1 mg, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1})

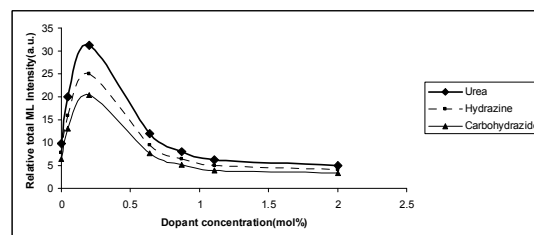


FIG. 5. Total ML intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of dopant concentration (mass of the sample 1mg, γ -ray dose 1.1 kGy, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1}).

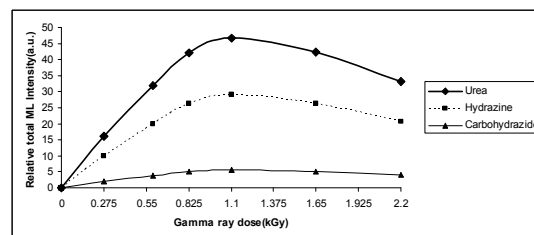


FIG.6. Relative total ML intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of gamma ray dose (mass of the sample 1mg, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1}).

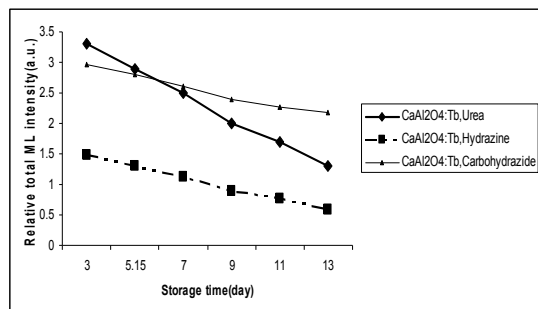


FIG.7. Relative total ML intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of storage time (mass of the sample 1mg, mass of the piston 0.7 kg, γ -ray dose 1.1 kGy, impact velocity 2.83 ms^{-1}).

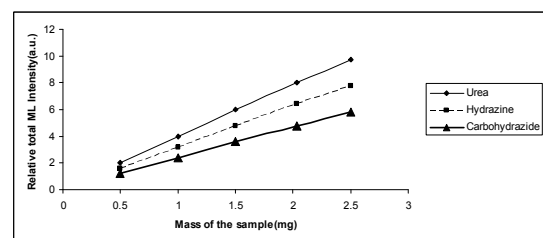


FIG.8. Total ML intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of mass of the sample (mass of the piston 0.7 kg, γ -ray dose 1.1 kGy, impact velocity 2.83 ms^{-1}).

Thermoluminescence of $\text{CaAl}_2\text{O}_4:\text{Tb}$

Figure 9 shows the TL glow curves of $\text{CaAl}_2\text{O}_4:\text{Tb}^{3+}$ powders at 1.1 kGy of gamma ray dose. It shows a significant thermoluminescence glow peak at around 110°C . The peak indicates the existence of electron and/or hole trapping sites at that temperature in the crystal.

Figure 10 shows the relative total TL intensity as a function of dopant concentration. It is observed that the total TL intensity initially increased with increasing dopant concentration attained an optimum value for a particular concentration of dopant and then decreased with further increase in dopant concentration.

Figure 11 shows total TL yields as a function of γ -ray doses given to the rare earth doped aluminate based phosphors. It is found that TL intensity increases with increasing the γ -ray doses given to the samples and seem to saturate for higher values of gamma doses.

Figure 12 shows fading of TL over 15 days from gamma-ray irradiation of rare earth doped aluminate based phosphors.

Maximum 8% reduction in TL yield was observed.

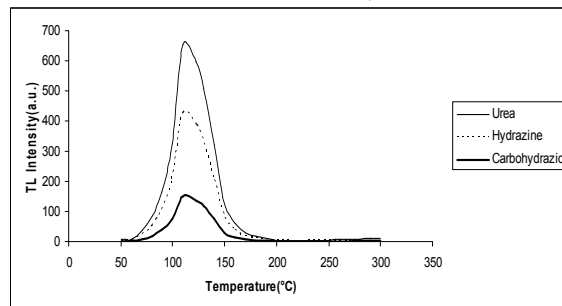


FIG.9. TL glow curve of Tb doped CaAl_2O_4 phosphors for the fuels urea, hydrazine and carbohydrazide (γ -ray dose 1.1 kGy; Heating rate $5^\circ\text{C}/\text{second}$)

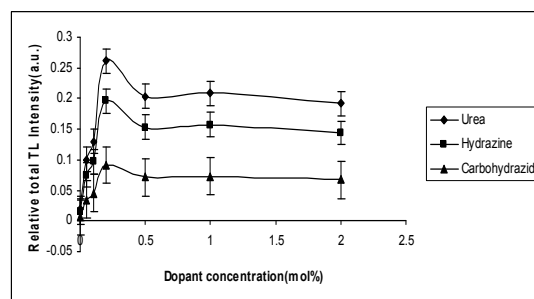


FIG.10. Relative total TL intensity as a function of dopant concentration of γ -ray irradiated Tb doped CaAl_2O_4 phosphors for the fuels urea, hydrazine and carbohydrazide (γ -ray dose 1.1 kGy, mass of the sample 1mg, heating rate 5°Csec^{-1}).

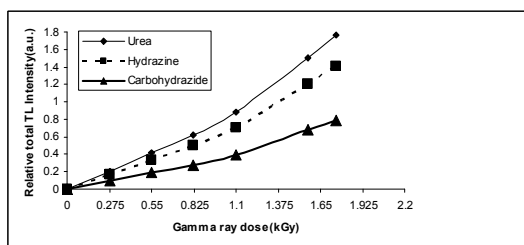


FIG.11. Relative total TL intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of gamma ray dose (γ -ray dose 1.1 kGy, mass of the sample 1mg, heating rate 5°Csec^{-1}).

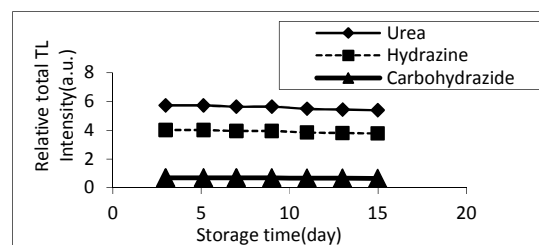


FIG.12. Relative total TL intensity of $\text{CaAl}_2\text{O}_4:\text{Tb}$ as function of storage time (γ -ray dose 1.1 kGy, mass of the sample 1mg, heating rate 5°Csec^{-1}).

Theoretical discussion

Mechanoluminescence

In the study of Mechanoluminescence the principal objective is to understand the origin of ML. Since the mechanical energy cannot populate directly the excited states of the molecules comprising the sample, some alternative process should be responsible for the ML excitation [27-29].

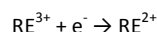
There are many speculations as:

- i The mechanical energy added to the atoms of the solid by modified lattice vibration should excite the atoms to luminescence. In fact, the mechanical energy is rather transferred into other form of energy, which then constitutes the last state of excitation. Thus in reality, it seems that the ML is mechano-induced luminescence.
- ii Charging of the newly created surfaces of crystals take place due to the asymmetric movement of the charge dislocation towards the surface or due to the baro-diffusion of defects.
- iii The electrification produced due to the charged surfaces may be sufficient to cause the dielectric breakdown of intervening gases, as well as, the dielectric breakdown of the crystals. If the surface charge is primarily neutralized by the charge carriers and ions produced due to the dielectric breakdown of surrounding gases, then only the gas discharged emission will be observed.
- iv On the other hand, if the fracture induced surface charge is neutralized primarily by the charge carriers produced due to the breakdown of the crystals, then only the ML emission resembling the solid state luminescence like photoluminescence will be observed.
- v The piezo-electrification caused by elastic deformation may give rise to the light emission in non-centrosymmetric crystal.

The mechanism of ML emission can be explained as follows.

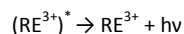
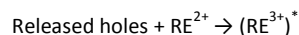
Under the exposure to γ - ray, electron hole pairs are created, some of the released electrons are captured by the impurity RE^{3+} ions reducing these to RE^{2+} and some of the free holes are captured by the trap levels. When the excitation source is removed, the trapped holes are released thermally to the valence band and migrate to recombine with the metastable state. Therefore, if the stress is loaded the movement of dislocation set in the motion by applied pressure. Some of the filled traps can released the captured holes and then the released holes can recombine with metastable (RE^{2+}), transfer as to another metastable (RE^{3+}) form, finally relax and return to the ground state accompanying the luminescence. Thus the, ML intensity should be influenced by the amount of filled traps and the depth of the trap levels. The origin of ML may be caused by the holes released due to the movement of dislocation set in motion by the stress on the phosphors. The ML process can be explained by the following process:

During the gamma irradiation of the sample $\rightarrow e^-$ (electron) + hole⁺



During the deformation

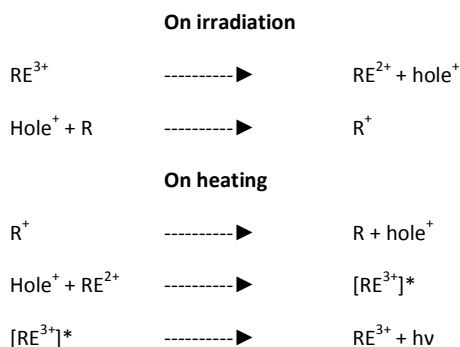
Stress + Filled traps (holes) \rightarrow Vacant traps + Released holes



Thermoluminescence

Researcher have reported that EPR spectra of irradiated aluminate revealed the formation of V and F trap centre. It was observed that the main radicals(R) in aluminate based phosphors are AlO_2^- , Al_2O_2^- , Al_2O_5^- , Al_2O_4^- , Al_2O_3^- etc., which indicate that TL in these phosphors are characteristic emission of RE ions. [30-31]. In present investigation we found that TL of aluminate is characteristics of RE ions incorporated.

On the basis of the above we proposed the following mechanism: TL is a phenomenon occurs due to the imperfections. Incorporation of rare earth impurity increases the population of defects present in the host lattice. When the samples were exposed to gamma rays it induces radicals as AlO_2^- , Al_2O_2^- , Al_2O_4^- , Al_2O_3^- , Al_2O_5^- etc along with conversion of RE^{3+} into RE^{2+} . When sample is heated release of electron from traps may take place. The subsequent electron hole recombination may release energy. This energy may non-radiatively transfers to RE^{3+} ions causing their excitation and subsequent de-excitation of excited RE^{3+} ion may give rise to the characteristic luminescence as shown:



Where, R indicates the radicals such as AlO_2^- , Al_2O_2^- , Al_2O_5^- , Al_2O_4^- , Al_2O_3^- etc. * indicates an activated species and hv indicates the TL photon.

The increase in TL intensity with increasing γ -dose may be due to increase in number of active luminescent centres with γ -irradiation and subsequent emission of TL due conversion of $\text{RE}^{2+} \leftrightarrow \text{RE}^{3+}$ during heating.

With increase in the concentration of rare earth ions, more luminescence centers can be created and hence TL intensity is increased. However, the glow intensity cannot be expected to increase indefinitely with concentration, since the rate of formation

of active luminescent centers by capturing the holes during irradiation might be fading rapidly and concentration quenching is occurred.

Conclusions

[1] When $\text{CaAl}_2\text{O}_4:\text{Tb}$ phosphor sample is subjected to elastic deformation by dropping a small load from a low height, the ML intensity initially increases with the height from which the load is dropped on to the samples. The ML study of the phosphor show low fading, linear response so it can be used in the dosimetric applications.

[2] In the TL glow curve of Tb doped CaAl_2O_4 phosphors, a peak at around 110°C was observed for all the fuels which clearly indicates a kind of defect centres present there in gamma irradiated phosphor sample. The TL study of the phosphor show low fading, linear response so it can be used in the dosimetric applications.

[3] The energy levels and hence trapping and detrapping of charge carriers in the material can be studied using ML and TL.

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