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Al_2O_3:Tb – Phosphor For Mechanoluminescence Dosimetry

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Abstract

Tb activated Al_2O_3 phosphors were synthesized by combustion technique using hydrazine as a reductive non-carbonaceous fuel. X-ray diffraction (XRD) patterns of the samples were recorded to confirm the formation of the sample. Scanning electron microscope (SEM) images were taken to observe the surface morphology. The photoluminescence (PL) and mechanoluminescence (ML) properties of the γ-ray irradiated samples were studied. In the PL spectra the $^5D_4 \rightarrow {}^7F_5$ line at 544 nm in the green region, which is the strongest in Al_2O_3 system. ML was excited by applying gradually varying pressure on the sample using pressure device. Number of peaks is observed, when continuously increasing pressure applied on to the sample; however less number of ML peaks is observed when continuously decreasing pressure applied on to the sample. ML intensity increases with activator concentration. Optimum PL/ML was observed for the sample having 0.5mol% of Tb ions. Total ML intensity increases almost linearly with gamma dose in the dose range 0.15 kGy to 1.4 kGy. It is suggested that recombination of the de-trapping of trapped charge carriers followed by recombination is responsible for ML in this system.

Keywords: Phosphors, mechanoluminescence, photoluminescence, X-ray diffraction

Introduction: The effects of ionizing radiation in qualitative and quantitative terms has become very important in the present day context due to the influence of nuclear technology in various areas that include radiation medicine, radiotherapy, food processing, radiation based polymerization and nondestructive testing techniques using radiography.

With the ever increasing importance of radiation, both natural and manmade in almost all departments of human activity e.g. medicine, industry, research and agriculture, food safety; there is continuous need to update the existing technique and to develop new ones for the detection and measurement of radiation. Dependable radiation dosimetric procedures need to be developed over wide range of dose levels [1].

Mechanoluminescence (ML) is an interesting phenomenon, which is a light emission caused by mechanical stimuli such as cutting, grinding, striking friction etc[2]. Aluminum oxide is a material of technological importance because it offers a large transparent window for UV to near infrared, excellent mechanical properties and good chemical stability. Therefore, it is a good candidate to be used as a host material of the rare earth ions[3]. In the present investigation we have studied the ML of Al_2O_3:Tb phosphor, excited by applying continuously varying pressure on to the sample Photoluminescence (PL) has also been recorded for better understanding of ML excitation.

Experimental: The microcrystalline Al_2O_3:Tb (0.1, 0.2, 0.5 and 1.0 mol%) phosphor samples were synthesized by low cost combustion technique as reported by Mackitrick[4] using hydrazine as a fuel. Hydrazine was used as a reductive no-carbonaceous fuel that prevents carbon contamination. The starting materials taken were $Al(NO_3)_3.9H_2O$, $Tb(NO_3)_3.6H_2O$ compounds of ultra high purity (99.9%). All of them were acquired from Alfa Aesar Lancaster, USA. The crystalline structure and particle morphology of the resulting samples were investigated by X-ray diffraction analysis (XRD model D8 Advance Bruker AXS) using Cu Kα radiation (λ = 1.5418 Å). Data have been collected by step scanning 2θ from 20^0 to 70^0 and 9.6 sec swept time at each step at room temperature. In order to study the surface morphology of phosphor prepared by combustion synthesis, scanning electron microscopy (model LEO 0435 VP) has been carried out. All characterization was performed at Institute Instrumentation Centre, IIT Roorkee, Uttranchal, India. Gamma irradiation was carried out using a ^{60}Co source having exposure rate 0.930 kGy/h. ML is excited by applying continuously varying pressure on to the sample using pressure device[5] Figure (1).

Results and Discussion: Figure (2) shows the XRD pattern of Al_2O_3:Tb phosphor. The small amount of doped Tb ions has virtually no effect on the phase structures. The observed XRD pattern was found to match well with the standard JCPDs[6] data of the compound Al_2O_3 (file no. 00-001-1243).

Figure (3) shows the surface morphology of the microcrystalline powder sample. The microstructure of the sample reflects the inherent nature of the combustion process. The non-uniform and irregular shapes of the particles as shown can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.

Figure (4) shows the PL excitation (wavelength 240 nm) and emission spectrum of the Al_2O_3:Tb phosphor. The 4f-4f emissions from $^5D_4 \rightarrow {}^7F_j$ (j = 6, 5, 4, 3) states of Tb^{3+} are found at 490 nm, 544 nm, 588 nm and 590 nm respectively. There are two additional emissions at 424 nm and 441 nm corresponding to the Tb^{3+} transitions from the $^5D_3 \rightarrow {}^7F_5$ state and $^5D_3 \rightarrow {}^7F_4$ state[7]. The $^5D_4 \rightarrow {}^7F_5$ line at 544 nm is the strongest in nearly all the host samples. The reason is that this transition has the largest probability for both the electric and magnetic dipole induced transition[8].

Figure (5) shows the time dependence of ML intensity of γ-ray irradiated Al_2O_3:Tb (1.0 mol%) phosphor. ML intensity was measured by applying continuously varying pressure on the sample using pressure device. When ML is excited by applying

continuously increasing/decreasing pressure (@9.1 x 10^3 N/m^2 sec^{-1}). Number of ML peaks is observed in the ML intensity versus time curve, when increasing pressure applied on to the sample; however less number of peaks is observed when the pressure was released from the sample. In general the peak intensity during the release in pressure is less as compared with those observed during application of pressure. Similar pattern was observed for all the samples; however peak intensity and the time corresponding to peak is slightly changed.

Figure (6) shows the dependence of total ML intensity of Al_2O_3: Tb on dopant concentration. The ML intensity increases with increasing Tb concentration attains a optimum value (0.5 mol% Tb) and decreases with further increase in dopant concentration.

Figure (7) shows the dependence of ML intensity on gamma doses given to the sample. The ML intensity increases almost linearly with gamma dose given to the sample, in the dose range (0.15 – 1.4) kGy. The total ML intensity i.e. area below time versus ML intensity curve is calculated using MATLAB software. The optimum PL/ML intensity observed for the sample having concentration of 0.5 mol% of Tb.

Akiyama et al [9, 10 ,11, 12] observed that the photoluminescence spectrum of RE doped oxides is very much similar to their mechanoluminescence spectrum. On the basis of spectral analysis they concluded that doped RE^{3+} ions act as a luminescence centre and same luminescence centre are responsible for PL/ML emission.

The ML of oxides phosphors are extensively studied by various workers[13, 14, 15, 16, 17, 18] and they concluded that the ML phenomenon is related to the movement of dislocation and the recombination of activated electrons and holes in the doped RE^{3+} ions. 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. Figure (8) shows the schematic graph of the mechanism of ML emission. The ML process can be explained by the following process:

During the gamma irradiation of the sample

Gamma rradiation $\rightarrow$ e^- (electron) + $hole^+$

$RE^{3+} + e^- \rightarrow RE^{2+}$

During the deformation

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

Released holes + $RE^{2+} \rightarrow (RE^{3+})^*$

$(RE^{3+})^* \rightarrow RE^{3+} + h\nu$

The time duration of ML pulse due to the action of single cracks is in the microsecond range, which is the order of the time needed for crack to move through the crystal. However, the time duration of a continuous ML pulse produced during the impact of a load on the crystal is of the order of milliseconds and depends on the strain rate. The continuous ML signal produced during the impact should be the superposition of the individual ML pulses produced during the motion of many cracks in the crystal. In the present investigation the number of ML pulse is observed because the electrons are released from different trap depth at different time with increasing pressure applied on to the sample.

In the present investigation ML is also observed when pressure is released from the sample after applying maximum pressure. The dislocation in dense bends exerts force on each other, which would be expected to cause some loops to shrink and disappear upon the release of the applied pressure [19]. Many of the luminescence centers in the vicinity of the dislocations might have ionized during their creation and further some of the dislocation loops may not sweep through a virgin area of the crystal during the shrinking of the dislocation loops.

It has been reported that, when the pressure is released from the crystal the dislocations together with redistribution by diffusion of vacancy clouds of ions may take place. This process produces electric charge on the surface of the crystals [20].

The ML emission during the application of decreasing pressure may mainly be due to the diffusion and electric charge produced during the relaxation of the dislocation. The dislocation moving in backward direction may excite the luminescence centers by similar mechanism as that were described for the dislocation moving in the forward direction. The increasing number of defects with increasing applied pressure increases the probability of retrapping. These retrapped electrons during the application of pressure are also responsible for the ML emission during the application of decreasing pressure.

In the present investigation, it was observed that the ML intensity of γ-irradiated Al_2O_3:Tb phosphor increases with increasing dopant concentration attains an optimum value at particular concentration then decreases with further increase in concentration of dopant. It has been found that ML intensity is maximum for a particular concentration of the activator in the phosphor. When the activator concentration is increased, initially the number of luminescent centers increases; hence the ML intensity also increases. Later on, when the activator concentration increases beyond a particular level, the concentration quenching starts and the efficiency of radiative transition decreases. As matter of fact, the ML intensity is maximum for a particular concentration of the activator in the phosphor. It may be possible that too much traps capture the free charge carriers released by the loaded stress and resulted in the ML quenching.

It was also observed that the ML intensity of Al_2O_3:Tb phosphor initially, increases linearly with gamma dose, attains an optimum value and seems to saturate for higher gamma doses given to the sample. Initially the defect centers increases with increasing gamma doses given to the sample. Therefore the moving dislocation may interact with more defect centers and consequently there may be more ML emission from the crystals having larger density of the defect centers. However for longer duration of γ-irradiation, the recombination of electron and holes takes place and the density of luminescent centers attain a saturation value; hence the ML intensity also attains a saturation value for higher γ-doses given to the sample.

Conclusions: The polycrystalline Al_2O_3:Tb (0.1, 0.2, 0.5 and 1.0 mol %) phosphors were successfully synthesize by combustion technique at an initiating temperature of ~300°C and its luminescence properties were investigated for ML dosimetric application. ML intensity, initially increases with Tb concentration approaches to optimum value for 0.5 mol % of Tb and then decreases with further increase in Tb concentration.

Al_2O_3:Tb shows the characteristic emission of Tb^{3+} ions and the principal emission was observed in green region, which is

suitable for commonly used photomultiplier tubes. Since the mechanical energy can not be supplied directly to the trapped charge carriers, deformation induced intermediate processes are responsible for the detrapping of charge carriers.

The occurrence of PL emission in the green region (544 nm) and enhancement of total ML intensity with gamma dose in the dose range 0.15 kGy to 1.4 kGy suggested that Al_2O_3:Tb phosphor is a suitable candidate for ML dosimetry.

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Figure and Figure Caption

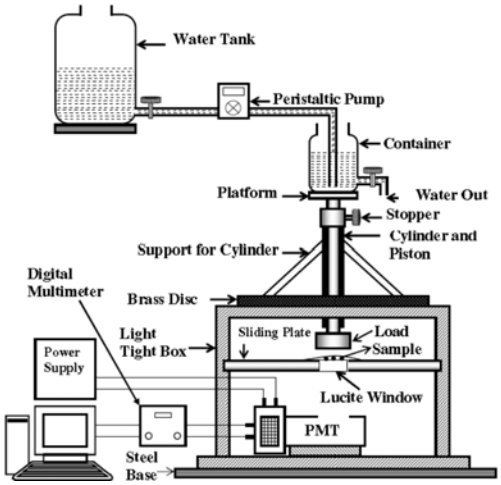

Fig.1 Schematic diagram of experimental set-up used for deforming the sample and measuring the ML.

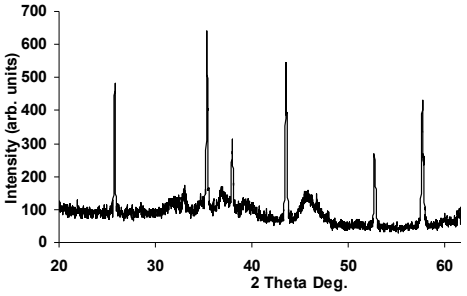

Fig. 2 XRD pattern of Al_2O_3:Tb (0.1 mol %) phosphor

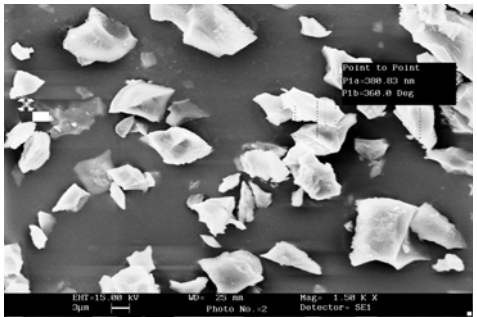

Fig. 3 SEM photograph of Al_2O_3:Tb (0.1) phosphor

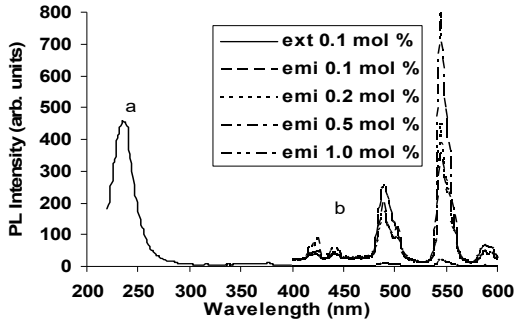

Fig. 4 (a) Excitation (b) emission spectra of Al_2O_3:Tb phosphor having different concentration of Tb.

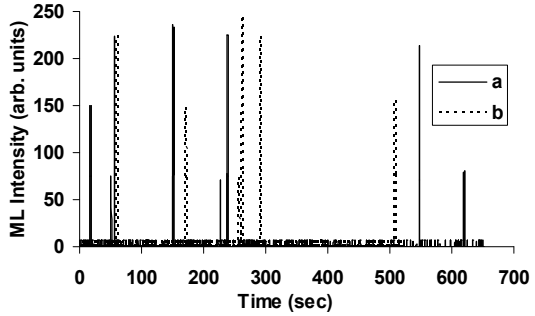

Fig. 5 Time dependence of ML of Al_2O_3:Tb (1.0 mol%) during (a) increasing (b) decreasing pressure (Gamma dose 1.86kGy and rate of pressure @ $9.1x10^3$ N/m^2-sec^{-1})

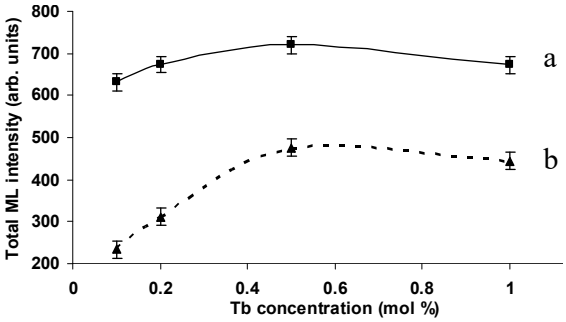

Fig. 6 Dependence of total ML intensity on Tb concentration of Al_2O_3:Tb during (a) increasing (b) decreasing pressure. (Gamma dose 1.86 kGy, rate of pressure $9.1x10^3$ N/m^2-sec^{-1})

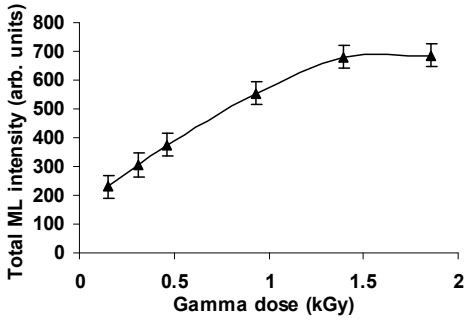

Fig. 7 Dependence of total ML intensity ofAl_2O_3:Tb (0.1 mol %) on gamma dose (Increase in pressure @ 9.1 x 10^3 N/m^2 sec^{-1})

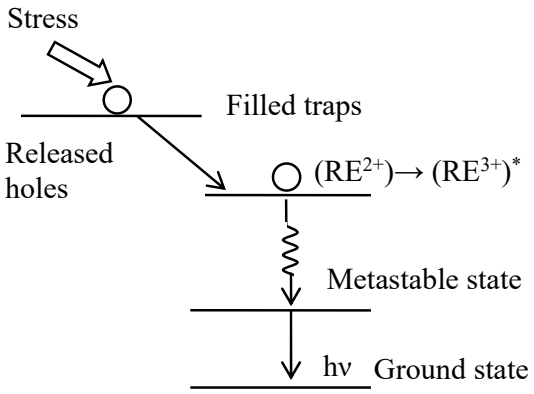

Fig. 8 Schematic graph of the mechanism of ML excitation for Al_2O_3:Tb phosphor