Mechanoluminescence and Thermoluminescence of γ-irradiated Eu Doped BaWO₄ Phosphors

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Abstract: Europium (Eu) doped BaWO₄ phosphor has been prepared by solid state diffusion technique and the formation of compound was confirmed by taking XRD pattern. Photoluminescence (PL) emission spectrum of the BaWO₄:Eu shows that Eu enters in both Eu²⁺ and Eu³⁺ ionic states in to the lattice. Samples were irradiated with gamma rays using ⁶⁰Co source. Mechanoluminescence (ML) and thermoluminescence (TL) of gamma irradiated BaWO₄:Eu(0.1mol%) phosphors have been studied. A single peak has been observed in ML intensity versus time curve. However, two distinct peaks were observed in ML glow curves of the phosphors irradiated with higher gamma doses. Similarly in TL glow curve a single peak around 122 °C was observed for the samples exposed to gamma dose 232.5 Gy. Shoulder appears in the TL glow curve if sample irradiated with higher values of gamma dose.

Key words: Thermoluminescence, BaWO₄

1. Introduction

Mechanoluminescence (ML) or sometimes deformation, tribo or piezoluminescence are terms commonly applied to the emission of light by the process of mechanical deformation by rubbing, cutting, compressing, and shaking or by impulsive deformation of a solid substance. Many organic and inorganic crystals, polymers, ceramics and glasses exhibit the phenomenon of ML. The phenomenon of ML links the mechanical, electrical, spectroscopic and structural properties of solids. This technique offers a number of interesting possibilities such as detection of cracks in the solids and for mechanical activation of various traps present in the solids. In general all the thermo-luminescent materials also show ML during or following their deformation. Tungstates are known to be good materials for radiation dosimetry. BaWO₄: Dy is one of the phosphor that is increasingly utilized in thermoluminescence (TL) radiation dosimetry. In recent years a series of magnesium tungstate phosphors have been prepared and their TL characteristics studied and it was proposed that in these phosphors large defect complexes are produced which include intrinsic imperfections and dopants, and these complexes could be regarded as basic elements in TL multistage process. In the present investigation the ML of γ-irradiated BaWO₄:Eu phosphors have been studied and an attempt has been made to understand the mechanism of ML in this system using their TL and photoluminescence (PL) properties.

2. Materials and Methods

BaWO₄ phosphors containing different concentrations of Eu (0.05-1.0 mole%) were prepared by solid-state diffusion method. BaWO₄ and Eu₂O₃ were mixed as per the concentration of Eu ion in BaWO₄ and crushed for 1 h, then heated at 400 °C for 2 h. The mixture was again crushed for 1 h and fired at 800 °C for 24 h, then slowly cooled to room temperature. All the chemicals used in the present investigation were of AR grade.

The XRD pattern of prepared material is shown in Fig. 1. XRD data of prepared BaWO₄:Eu phosphor matched well with standard data of JCPDs (File no. 01-072-1259). The prepared phosphors were used for further study. The samples were exposed to γ-rays using

Fig.1 XRD pattern of BaWO₄:Eu(0.1mol%)
60Co source having dose rate of 930 Gyh⁻¹. The ML was exited impulsively by dropping a load of 0.4 kg onto 1 mg gamma-irradiated phosphor placed on the Lucite plate from the height of 20 cm using a guiding cylinder. The impact velocity of the load is determined by the relation \( v = \sqrt{\frac{2gh}{m}} \). The ML was monitored by RCA 931 photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope. For TL measurements a routine TL set-up (Indothem) was used and glow curves were recorded by heating the sample with 90 °C/min. The PL emission spectra of the samples were recorded by using fluorescence spectrophotometer (Shimatzu RF-530 XPC). Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3. Results and discussion

Figure 2 shows PL emission spectrum of BaWO₄:Eu(0.1mol%) phosphors in the dose range 232.5 to 1395 Gy. A band around 500 nm was observed. The emissions from 360-440 nm in Eu doped tungstate based phsphors are due to 4F⁵⁵D→4F⁷ transition of Eu²⁺ ions. It has been reported that the Legand field of host affects the Eu²⁺ emission as well as peak position. The emission around 589 nm and 620 nm in Eu doped phosphors are due to ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ transition of Eu³⁺ ions.

Figure 3 shows the TL glow curves of gamma irradiated BaWO₄:Eu(0.1mol%) phosphors for different gamma doses given to the samples. A single peak is observed in ML intensity versus time curve at gamma dose level 232.5 Gy. For higher gamma doses two distinct peaks were observed. ML emission spectrum has also been recorded (Fig. 5) and it is found that the ML emission is characteristics of Eu²⁺ and Eu³⁺ ions. It has also been observed that the peak intensity of the first and second peaks increases with increasing the gamma dose without any considerable change in peak time.
Zhang et al. reported that the main glow peak of BaWO$_4$:Eu phosphors are characteristics of Eu$^{2+}$ ions, however, higher temperature peaks are characteristics of Eu$^{3+}$ ions. In phosphor preparation Eu$_2$O$_3$ was taken for doping Eu in to the lattice. During firing phosphors at 800 °C in air some of the Eu$^{3+}$ ions may become Eu$^{2+}$ due to reduction or electron capture. Therefore characteristics of both Eu$^{2+}$ and Eu$^{3+}$ ions are observed in PL emission spectrum. When the tungstate based phosphors are exposed to ionizing radiation the defect centers like cation vacancies and tungstate radicals are created. On increasing the γ dose, the defect centers increases and thereby the peak TL and ML intensity increases. When the phosphors are heated holes are released and they may recombine with trapped electrons at Eu$^{2+}$ sites subsequent radiation may excite the Eu$^{2+}$ and Eu$^{3+}$ ions present into the lattice and de-excitation of these ions give rise the characteristic emission of Eu$^{2+}$ and Eu$^{3+}$. Similar to TL mechanism release of holes/electrons from the defect centers might be responsible for ML emission as described elswhere.

4. Conclusions

Eu ions act as luminescence centre in BaWO$_4$:Eu phosphors. TL glow curve is complex in nature. Complexity increases with gamma doses. Results indicate correlation between TL and ML.

5. References