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Mechanoluminescnce and photoluminescence in gamma irradiated NaCl:Eu

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Abstract
Rare earth (RE) ions posses unique optical behavior when doped into phosphors. Eu^{2+} activated phosphors find use in many applications. Eu^{2+} emission arises from the lowest band of $4f^6$ 5d configuration to $^8S_{7/2}$ state of $4f^7$. NaCl having different concentrations of Eu were prepared by melt technique. The crystals of small sizes were cleaved from the grown crystal block and crushed to obtain powder or microcrystalline form of NaCl. Annealed samples were exposed to gamma rays at dose level 0.930kGy. Mechanoluminescnce (ML) was excited impulsively by dropping a load of mass 0.4 kg with the impact velocity of 0.6 ms^{-1} on to it. An intense ML peak was observed in its ML glow curve. ML intensity increases with increasing concentration of dopant. ML emission spectrum shows a single peak at 482 nm. Photoluminescence (PL) of the sample has also been recorded and a single peak at 427 nm was observed. Shift in ML and PL emission spectrum was observed.

Keywords: Mechanoluminescnce, photoluminescence, NaCl:Eu

INTRODUCTION

Mechanoluminescence is an interesting luminescence phenomenon whereby light emission in solids is caused by mechanical stimuli such as compressing, stretching, fracture, cutting, cleaving, breaking, grinding, rubbing, scratching, crushing and so on [1–3]. In the recent past, intense ML materials have been prepared whose ML emission can be seen in daylight with naked eye and such materials are finding important applications in novel self-diagnosis systems, optical stress sensors, stress imaging devices [4–6], wireless fracture sensor systems [5–9] and in damage sensors [10–12]. They also find application in fuse system for army warheads [13]. It has been reported that X or γ-irradiated alkali halide crystals [14–16], Mn-doped zinc sulphide [16–18] and a few polymers [19,20] show ML when they are deformed elastically. ML produced by the plastic deformation and fracture of coloured alkali halide crystals has been studied in detail [1–3]. Present paper reports ML and photoluminescence (PL) of gamma irradiated Eu doped NaCl crystals and microcrystalline powder.

EXPERIMENTAL

Single crystals of NaCl doped with different concentrations of Eu were grown by melt method. The crystals of small sizes were cleaved from the grown crystal blocks. To obtain powder of the sample it was crushed and sieved. The crystals so grown and the microcrystalline powder (0.150μm) as obtained were annealed at 4500C for two and half hours and subsequently cooled by quenching to room temperature The irradiation of samples was carried out using 60Co gamma source having exposure rate of 0.930KGy. The ML was excited impulsively by dropping a load of mass 0.2 kg on to the gamma-irradiated sample 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 $v = \sqrt{2gh}$. The ML was monitored by RCA 931 photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope. ML emission was recorded by inserting filters of different wavelength between Lucite plate and photomultiplier tube. Photoluminescence measurements were carried out on undoped and Eu doped NaCl samples prior to gamma irradiation. 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, 1.5 nm).

RESULTS AND DISCUSSION

Figure 1 shows time dependence of ML intensity of gamma irradiated NaCl crystals doped with different concentration of Eu. ML intensity initially increases with time attain optimum value at a particular time then decreases with time and finally disappears. The results obtained were normalized to a fixed volume of doped crystals(1mmx1mmx1mm). Peak ML intensity as well as total ML intensity increases with increasing concentration of dopant without any considerable change in tm i.e. time corresponding to ML peak. Similar results (Fig. 2) are observed when gamma irradiated microcrystalline samples (0.150μm) were recorded. The results were taken for known quantity of microcrystalline powder (1mg) It is also observed that the ML intensity in crystalline form is slightly greater than that of their microcrystalline form, but curves of microcrystalline NaCl:Eu is sharper than the crystalline NaCl:Eu. Figure 3 shows the ML emission spectra of NaCl:Eu(1000ppm) in crystalline and microcrystalline forms. A single peak at 482 nm was observed for both the samples.

Figure 4 shows PL emission spectrum of NaCl:Eu of crystal (a) and microcrystalline (b) samples when it is excited by a electromagnetic radiation having wavelength 243 nm PL peak intensity increases with increasing concentration of Eu in both of the cases. The PL intensity of pure NaCl sample is almost zero. The sharp PL peak at 427nm is obtained in both the cases and this PL peak is the characteristics of the Eu^{2+} emission in the blue region of the spectrum. This peak has been ascribed to the de-excitation of the Eu^{2+} from the lower excited state to $4f^6$ 5d to the ground state $^8S_{7/2}(4f^7)$ [21,22]. Lopez et al in 1980 [21] have studied the fluorescence spectrum of NaCl:Eu^{2+} single crystals excited with a wavelength of 350 nm which consists of four emission bands

peaking at 410, 427, 439, and 485nm. Gracia et al in 1980 [23], Rubio et al.in 1981 [24], Cordero-Borboa et al. in 1986 [25] have confirmed the existence of these bands in terms of the presence of different aggregation-precipitation states of he Eu^{2+} ions in the Nacl matrix as related to many thermal treatment and doping concentrations. Pre-annealing NaCl crystals before irradiation produces

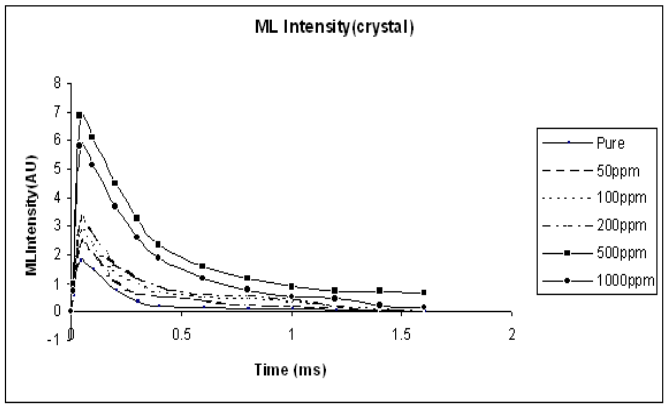

Fig 1. Time dependence of ML intensity of NaCl:Eu crystals.

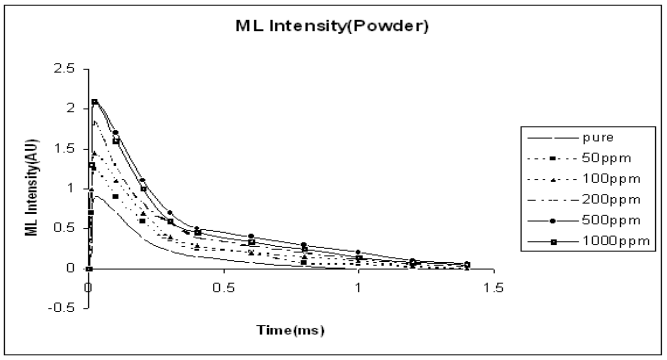

Fig 2. Time dependence of ML intensity of NaCl:Eu microcrystalline powder.

Significant effects in the emission spectra. The mechanism of ML is not well established but is accepted that the ML is associated with the release of trapped carriers from electronic defects by the movement of dislocations set in the motion by applied motion. Is observed that ML intensity increases with increasing Eu concentration it seems that electronic defect population increases with increasing Eu concentration undoped and non-irradiated samples show poor ML. Sodium chloride is an important member of alkali halide family. The deformation of alkali halide crystals is known to result in the colour centre destruction. During the deformation of gamma irradiated NaCl:Eu, the dislocation interact mechanically with colour centers and subsequently capture electrons from those nearby[24]. The captured electrons move with dislocations and they also move freely along the dislocation line at the same time. The dislocation electrons have a finite life time t_d. At $t > t_d$, they either recombine with the holes or are captured by other shallow traps in the sample if the moving dislocations containing hole, the dislocation electrons may be captured by these centers and luminescence may arise.

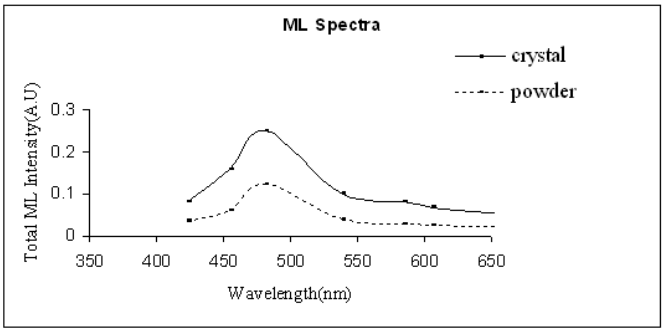

Fig 3. ML emission spectra of NaCl:Eu(1000ppm) crystal and microcrystalline samples(0.150μm).

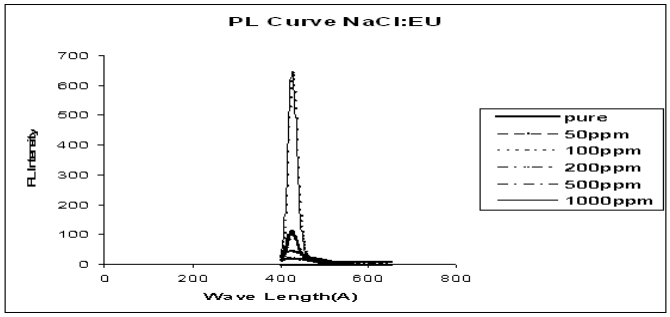

Fig 4(a). PL emission spectra of NaCl:Eu crystal samples excitation wavelength 243 nm

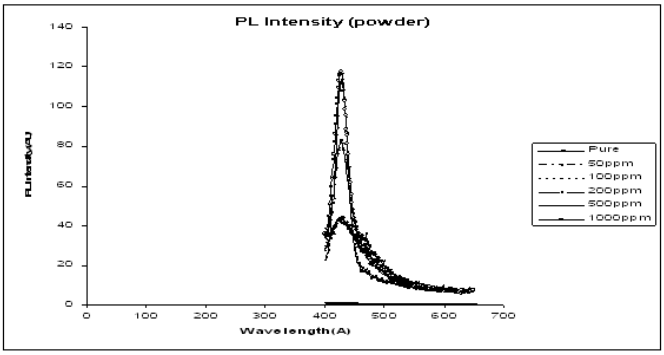

Fig 4(b). PL emission spectra of NaCl:Eu Microcrystalline powder samples excitation wavelength 243 nm

On the basis of ML, thermoluminescence and lyoluminescence spectra of coloured alkali halide crystals, Atari [26] and Chandra [27] proposed that the ML emission in X and γ-irradiated alkali halide crystal is due to the recombination of F-centre electrons with V_2 centre. Thus, the energy corresponding to peak of ML spectra should reflect the energy difference between the bottom of conduction band E_C and energy level of the V_2 centre E_{V2}. The calculated value of wavelength [λ_m=ch/(E_C–E_{V2})] corresponding to peak ML spectra of pure NaCl is 451 nm. However, in present investigation, one sharp peak around 482 nm is observed in ML spectra. In PL emission spectra a single peak around 427 nm is observed for all the samples. It seems that incorporation of Eu ions enhances the ML peak intensity. The shift obtained in ML and PL emission spectra may due to different devices used for recording the same.

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