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Mechanoluminescence and thermoluminescence studies of gamma irradiated sodium chloride single crystals and microcrystalline powder doped with dysprosium

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Rare earth ions play an important role in modern technology as optically active elements in solid-state luminescent materials. In many of these materials, interactions between the electronic band states of the host crystal and the rare earth ion's localized $4f^N$ and $4f^{N-1}$ 5d states influence the optical properties of materials. This paper reports the mechanoluminescence (ML) induced by impulsive excitation and thermoluminescence (TL) of γ-irradiated dysprosium doped NaCl single crystals and powder. The NaCl crystals having different concentrations of dysprosium were prepared by melt technique (slow cooling).The crystals of small sizes were cleaved from grown crystal block and crushed to obtain microcrystalline powder. The annealed samples were irradiated by gamma source with dose rate of 0.50 kGy/h. Mechanoluminescence is excited impulsively by dropping a load of 0.4 kg with impact velocity 313 cm/s onto it. Two peaks are observed in the ML intensity versus time curves for both single crystals and powder samples. In thermoluminescence of NaCl: Dy crystals and powder samples only one peak is observed in the glow curve at around 210-230°C. In the ML spectra, a broad band with single peak at 482 nm is obtained. The ML and TL intensities of single crystals are compared with the microcrystalline powder of the same mass in the present investigation. The total TL intensity obtained is more in microcrystalline powder than single crystal and reverse intensity yield is obtained in the ML process.

Keywords: Mechanoluminescence, Thermoluminescence, Microcrystalline powder, γ –rays irradiation

1 Introduction

Mechanoluminescence (ML) 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]. The ML intensity depends on a large number of factors, including stress, strain, strain rate, pressing rate, temperature, atmospheric pressure particle/ crystal size, sample mass, dopant type and concentration, annealing temperature etc[3,4]. 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[5-7], wireless fracture sensor systems[8,9] and in damage sensors[10-12]. Some ML materials have been made to visualize the stress distribution in solids and visualization of stress near the tip of a crack[13,14]. It has been reported that X or γ-irradiated alkali halide crystals[15-17], Mn-doped zinc sulphide[18,19] and a few polymers[20] show ML when they are deformed elastically. Thermoluminescence (TL) is the thermally stimulated emission of light from an insulator or a semiconductor following the previous absorption of energy from ionizing radiation. TL of single crystals and microcrystalline powder of alkali halides have been studied by various research groups[21-26]. The behaviour of single crystals of NaCl: Ca^{+2}, Mn^{+2} exposed to gamma rays was studied by Ortiz *et al*[27]. Recently, Bangaru and Muralidharan[28-31] and Bhujbal *et al*[32-34]. also reported the enhanced luminescent properties and TL studies in alkali halides by doping rare earth materials[28-34]. The microcrystalline powders can be thought as made up of two physically interwined sub-systems one of which is the perfect lattice sub-system and another the imperfections made up of dislocations etc. The microcrystalline powder is distinguishable from single crystal, as it has greater surface to volume ratio and reduced stability of excess electron centres in alkali halides. Deshmukh and co-workers[35] have studied the stability of colouration in microcrystalline powders and single crystals of alkali halides and observed several interesting differences in the properties of colour centres in microcrystalline powders as compared with those in single crystals using optical absorption technique. Kalkar[36] has reported that the LL intensity of microcrystalline powder of NaCl increases linearly with increasing mesh size in a very narrow range 50-200 µm. Sahu *et al*[37]. have reported the lyoluminescence (LL) intensity of gamma irradiated KCl:Sr microcrystalline powder of different particle sizes in the mesh range 150-355 µm. The aim of present investigation is to compare the ML and TL intensities of single crystal and microcrystalline powder of different sizes of Dy doped NaCl.

2 Experimental Details

Single crystals of NaCl doped with different concentrations of Dy were grown by melt method. Analar grade chemicals were used in the present investigation. The single crystals of small sizes (1×1×1, 2×1×1, 2×2×1, 1×2×3 mm^3 etc.) were cleaved from the grown crystal blocks. Microcrystalline powders were prepared by crushing some of the grown crystal blocks. Test sieves of known dimensions were used to separate the microcrystalline powders of different grain sizes.The crystals so grown and the microcrystalline powder (120-150 µm) as obtained were annealed at 450°C for two and half hour and subsequently cooled to room temperature. The irradiation of samples was carried out using ^{60}Co gamma source having exposure rate of 0.50 kGy/h. The ML was excited impulsively by dropping a load of mass 0.4 kg on to the gamma-irradiated sample placed on the Lucite plate from the height of 50 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 (Scientific SM-340). ML emission was recorded by inserting filters of different wavelength between lucite plate and photomultiplier tube. Thermoluminescence measurements were carried out of undoped and Dy doped NaCl single crystals and powder samples using a PC based TLD reader (Nucleonix Model 10091).The TL measurements were taken after 24 h of irradiation, whereas the ML measurements were taken after two days of irradiation. For the measurement of TL intensity of single crystals of known mass of different sizes (reading normalized to same mass) and microcrystalline powder of mass 2 mg of gamma irradiated phosphor were heated every time in a temperature range 10–300°C with a constant rate of 5°C/s. For each measurement at least three observations were taken.

3 Results and Discussion

Figures 1 shows time dependence of ML intensity of gamma irradiated NaCl single crystals doped with different concentration of Dy. Where, two peaks are observed in the ML intensity versus time curve. The ML intensity of first and second peak as well as total ML intensity (area below the curve) increase with increasing concentration of dopant up to 500 ppm without any considerable change in t_m i.e. time corresponding to ML peaks. Thereafter, the ML intensity decreases with further increase in concentration of dopant. Similar results are observed for NaCl: Dy powder samples (Fig. 2); however, the ML intensity of powder sample (120-150 µm) is less (about1/6) as compared with crystal sample (of the same mass). The ML intensity gets saturated at 500 ppm of Dy doped in the NaCl material due to concentration quenching and the ML intensity decreases above 500 ppm due to aggregation of

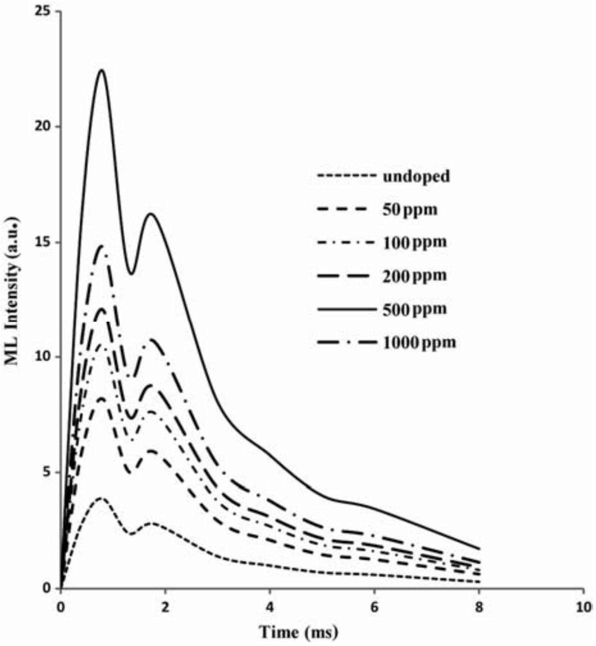

Fig. 1 — Time dependence of ML intensity of NaCl: Dy single crystals (dose: 0.50 kGy).

impurity ions. Figures 3 shows the time dependence of ML intensity of gamma irradiated NaCl: Dy (500 ppm) microcrystalline powder of different sizes. The ML intensity increases with the increase in the particle size.

This is because, when alkali halide crystal is exposed to high energy radiation like γ-rays or X-rays, excitation of electrons of halides atoms from valence band to conduction band takes place. Some of the excited electrons return immediately from the conduction band to the valence band; however, some of the electrons in the conduction band get trapped in the negative ion vacancies during their movement and consequently, the formation of colour centres takes place. Initially the number of colour centres increases with the radiation doses given to the crystals and thereby, the ML intensity increases with the radiation dose. However for long duration of the irradiation of the crystals the recombination between electrons and holes takes place and consequently the density of colour centres in the crystals attains a saturation value. As a matter of fact, the luminescence intensity attains a saturation value for high radiation doses given to the crystallites[38].

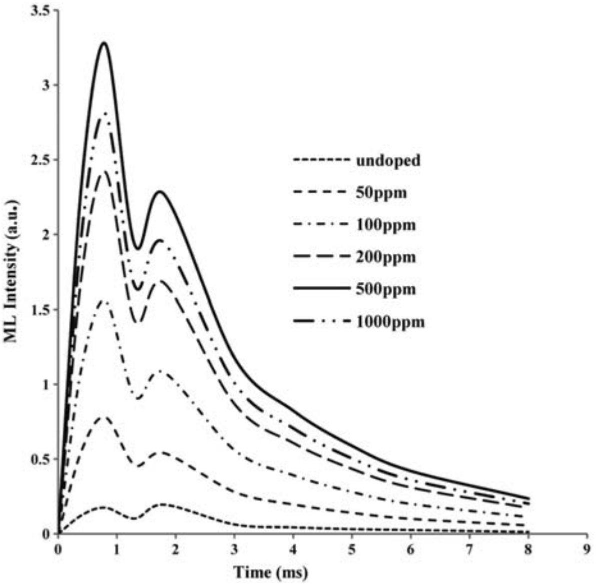

Fig. 2 — Time dependence of ML intensity of NaCl: Dy powder (120-150 μm) (dose: 0.50 kGy)

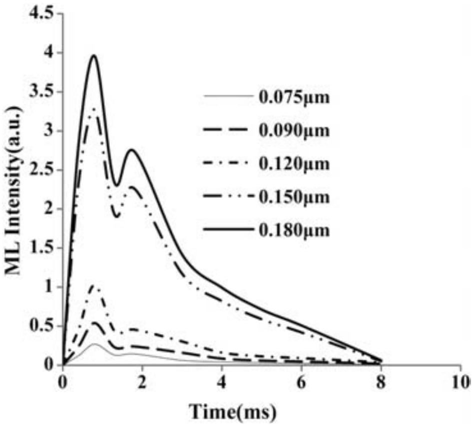

Fig. 3 — Time dependence of ML intensity of NaCl: Dy powder (500 ppm) with different sizes (γ-dose: 0.50 kGy)

In alkali halide crystals, the electron dislocation band lies just above the F-centre level where the energy gap between the bottom of the dislocation band and ground state of an F-centre is of the order[39,40] of 0.10 eV. Near an edge dislocation, some of F-centres lie in the compression region and some of them lie in the expansion region. As the energy gap between two levels in alkali halide crystals decreases with decrease in the local density of crystals, the energy gap between dislocation band and ground state of F-centre may increase in the compression region due to the increase in local density of the crystals. The electrons captured by a dislocation have a finite lifetime. If the moving dislocation containing electrons encounters the defect centres containing holes, the dislocation electrons may be captured by these centres and luminescence may arise due to the radiative recombination of electrons from F-centres with the hole in V_2 centres. Schematically, the ML process can be described by the following equations:

$$F + D \rightarrow e_d + [-]$$

$$V_2(= X^- + X^- + X^0) + e_d \rightarrow V_2^-(= 3X^-) + D + h\nu$$

where F and D represent the F-centre and dislocation, respectively, e_d is the dislocation electron i.e. the electron captured by a dislocation, (–) is the negative ion vacancy, X^- is the halogen ion, X^0 is the self trapped hole and V_2^- is the V_2 centre with captured electron[1,41].

The doping of trivalent ions in alkali halides requires charge compensation and it directly involves several lattice sites, and the resulting distortions encompass even larger volumes of the lattice and as a result trapping and recombination sites interact. The doping of Dy^{3+} lead to charge compensating vacancies in NaCl, which increases the probability of formation of colour centres. The trivalent impurity ion Dy^{3+} enters the crystal lattice replacing Na^+ ions. During γ-irradiation, electron hole pairs are created as expected hole is captured by host related centres and released electrons are captured by the impurity Dy^{3+} ions reducing these to Dy^{2+} ions. So γ-irradiated rare earth doped alkali halide crystals, rare earth ions enhance the relative density of defects. That is why the ML intensity increases with dopant concentration. Initially, the number of luminescence centers and defect centers increases with increasing concentration of dopant, which causes increase in ML intensity with increasing dopant concentration. For the higher values of dopant concentration, concentration quenching of luminescence centers may take place and therefore, the ML intensity decreases with further increasing in concentration of the dopant. As the matter of the fact, the ML intensity is optimum for a particular concentration[42] 500 ppm of Dy (dopant).

In most of the crystals, only one peak (in the deformation region) is observed in the ML intensity versus time curve and ML emission stops as soon as the deformation is interrupted. In the previous studies of NaCl: Dy Bhujbal *et al*[32]. prepare powder by wet chemical method. They observed only one peak in their ML glow curve. However, in the present study, the samples were prepared by melt method (slow cooling) and it is observed that the ML emission occurs even after the deformation and in addition to the first peak, a second peak is observed in the ML intensity versus time curve. These differences may be speculated due to the different physical conditions of the samples during crystallization. Further, the occurrence of second peak can be explained by considering that some of the defect centres are excited during mechanical deformation where the dislocation-trapped electrons recombine with the holes. However, when the dislocation trapped electrons meet the deep traps, then the energy release causes auger process in which the electrons from dislocations band or other centres reach the conduction band and subsequently some of them recombine with the holes or some of them may be trapped in the shallow trap near the conduction band. The thermal vibrations of lattice may release later the electrons from the shallow trap and their recombination with the holes may cause luminescence. Thus, the second peak (in the post deformation region) may be due to thermally stimulated emission from shallow traps[43].

Figure 4 shows the ML spectra of single crystals of NaCl: Dy. The ML spectra consist of a broad band with single peak at 482 nm for doped crystals. The effect of incorporation of impurity is the overall intensity enhancement in the host emission from 423 to 580 nm i.e. impurities improve the luminescence property of the host material. It may either be due to the overlapping of the emissions of host and impurity or due to the emission of host which is being enhanced by the impurity.

In the TL studies, a single glow peak for undoped and doped samples are obtained at around 210-230°C for single crystals and powder samples (Figs 5 and 6).

TL glow curve shows a single isolated peak due to the formation of only one type of luminescence centre created due to high energy irradiation. In the glow curves for single crystals and microcrystalline powder, it is noticed that the total TL intensity (area

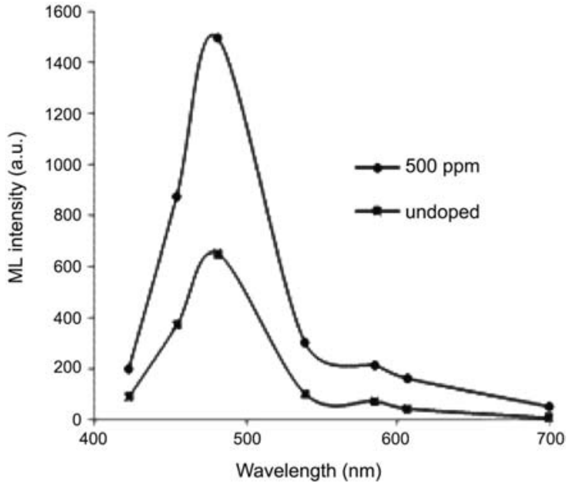

Fig. 4 — ML spectra of γ –rays irradiated NaCl: Dy (500 ppm) crystal

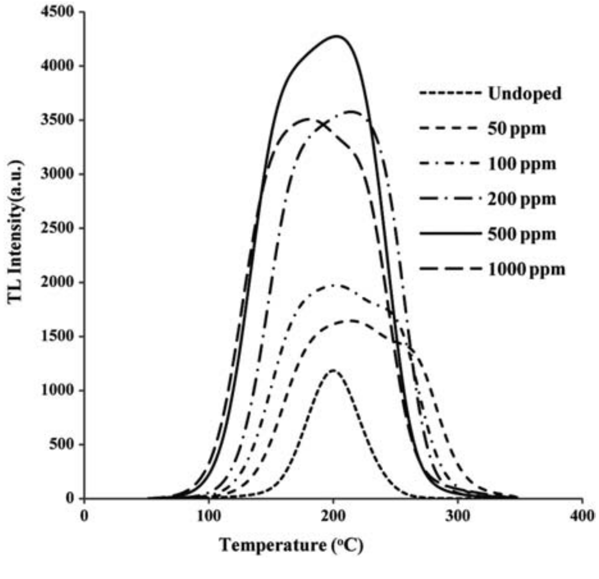

Fig. 5 — Thermoluminescence glow curve of undoped and Dy doped NaCl crystal (dose: 0.50 kGy)

below the curve) increases with concentration of dysprosium up to 500 ppm and thereafter, the TL intensity decreases with further increase of concentration of dysprosium. TL intensity of the samples also increases with the particle size. The TL intensity of microcrystalline powder of NaCl: Dy (200 ppm) (75-90 μm) is greater than the TL intensity of corresponding single crystal of same mass. The TL intensity increases with the increase in particle size without any appreciable change in the peak temperature (Fig. 7).

It is suggested that the recombination centers associated with the glow at the temperature interval (210-230°C) arise from the presence of liberated pairs, which are probably the result from the thermal release of holes from different kinds of traps, and recombine at F-centres. The TL glow curves of microcrystalline powder are flattening; this may be due to newly formed defect centres during crushing of single crystal.

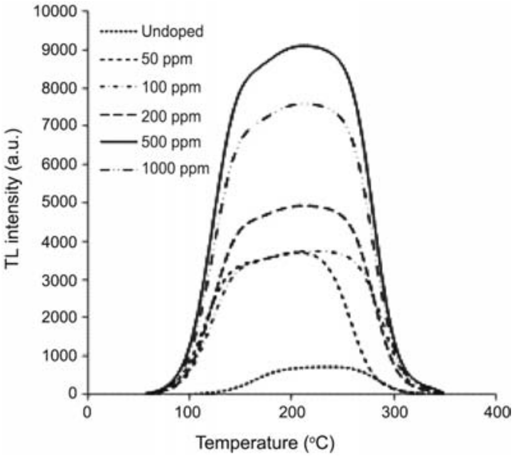

Fig. 6 — Thermoluminescence glow curve of undoped and Dy doped NaCl microcrystalline powder of different concentrations (120-150 μm) (Dose 0.50 kGy).

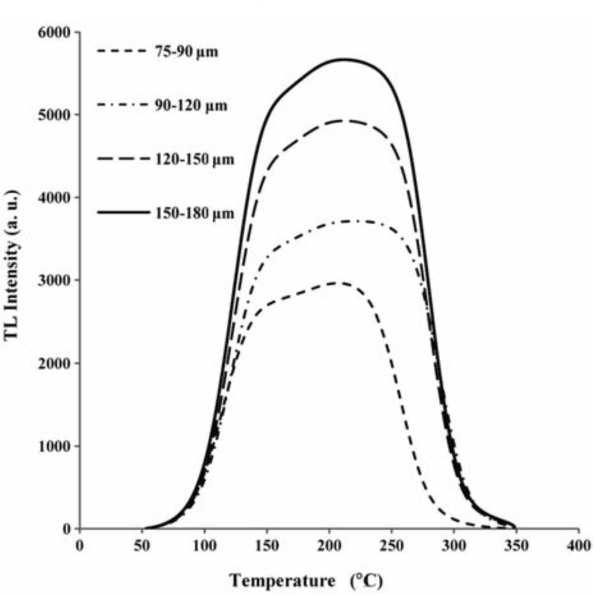

Fig. 7 — TL glow curve of NaCl: Dy (200 ppm) microcrystalline powder of different sizes gamma dose 0.50 kGy

Figure 8 shows the dependence of total ML and TL intensity of γ-irradiated NaCl crystals with different concentrations of Dy (Dose: 0.50 kGy). It is noticed that both the total ML intensity and TL intensity initially increase with increasing concentration up to 500 ppm thereafter, concentration quenching takes place and intensity decreases with further increase of concentration. When the concentration of dysprosium is increased in the sample, initially the number of luminescent centres increases, thereby increasing the ML and TL intensities. However, the intensity cannot be expected to increase indefinitely with concentration since the rate of formation of active luminescent centres by capturing the holes during irradiation might be fading rapidly and concentration quenching occurs.

Figure 9 shows the dependence of total ML and TL intensities of NaCl: Dy crystals on various doses. It is noticed that both the total ML intensity and total TL intensity initially increase with increasing irradiation dose, and then attain saturation values around 1250Gy. The increase in ML and TL intensities may

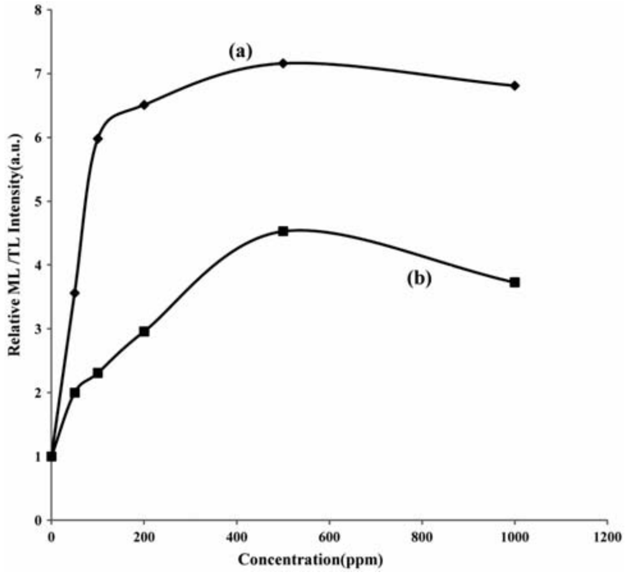

Fig. 8 — Dependence of total ML intensity (a) and total TL intensity (b) of gamma irradiated NaCl: Dy crystals with different concentrations of Dy (Dose 0.50 kGy)

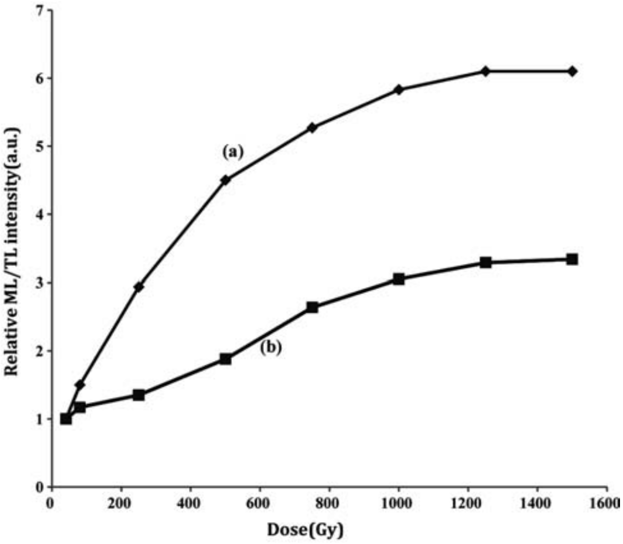

Fig. 9 — Dependence of total ML intensity (a) and total TL intensity (b) of γ –rays irradiated NaCl: Dy crystals (500 ppm) with different dose

be due to increase in the density of defect centres. The saturation of the intensity can be explained on the assumption that only limited numbers of Dy^{3+} ions are available for charge reduction with increasing gamma dose.

The total TL intensity (area below the curve) of microcrystalline powders is more than for crystals. The reasons for the observed differences in the intensities for crystals and microcrystalline powders might result from the fact that in powder, one expects formation of large number of grosser defects such as dislocations, grain boundaries, surface etc during crushing. These dislocations (defects) may increase the diffusion which again leads to increased recombinations and hence affect the TL and ultimately increase in TL is obtained as compared to single crystal. However, these defects may not support ML. Again the less ML intensity in microcrystalline powder may be due to the destroying of the defects responsible for ML or annihilation of defects during crushing.

4 Conclusions

The ML and TL of NaCl doped with dysprosium have been investigated and it is found that two peaks in ML glow curve. The ML peak intensity is dependent on dopant concentration of dysprosium and gamma ray irradiation dose. The enhanced intensity in ML spectra of doped crystals with broad peak at 482 nm signifies the participation of impurity ions in the ML phenomenon. The TL results show variation in the peak temperature and total TL intensity with dopant concentration, particle size and gamma ray irradiation. The glow peak shifts, change in the shape of glow curves and variation in TL output are observed in the present study. The ML intensity is obtained more in the single crystal than microcrystalline powder, whereas the TL intensity is obtained more for microcrystalline powders than for single crystals. Although variation in ML and TL intensity is almost similar with concentration of dopant and irradiation doses, different types of defects are involved in the ML and TL process.

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