



Mechanoluminescence Properties of Ba Doped LiF Crystal Induced by Applying Varying Pressure

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Abstract: LiF crystals having different concentration of Ba were synthesized by Bridgman technique and its mechanoluminescence (ML) properties were studied by applying gradually increasing/decreasing pressure. 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 study the surface morphology of the sample. When LiF:Ba crystal was deformed by applying continuously increasing pressure, number of peaks observed in time versus ML intensity curve, however less number of peaks observed, when continuously decreasing pressure applied on to the sample. The optimum ML intensity was observed for the sample having concentration of 60 ppm of Ba and 1.395 kGy gamma dose.. The ML intensity of LiF:Ba crystal increases with increasing γ doses in the dose range 0.15-1.395 kGy and seems to saturate for higher γ -doses. It is suggested that de-trapping of trapped charge carriers followed by recombination is responsible for ML in this system.

1.1 Introduction

The various aspects of luminescence and complex process involved in the origin of light emission offer challenging problems to the research workers in this field [1]. Last two decades have witnessed a tremendous growth in research and application of Mechanoluminescence (ML). This has been chiefly due to two reasons. First, that the phenomenon of ML provides an ultrasensitive microprobe for the investigation of cracks in solid and second, it has been proved that the highly efficient materials may be used for various applications such as mechano-optico transducers and other sophisticated devices.

Mechanoluminescence (ML) is the phenomenon of light emission induced by a mechanical stress such as compression, torsion or friction of solids [2]. It is classified in to two categories, namely fracto-luminescence (fracto-L) and deformation luminescence (DL), depending on whether luminescence is induced by fracture or mechanical deformation, respectively. The latter category (DL) is further divided in to plastic-luminescence (plastico-L) and elastic-luminescence (elastico-L) according to the type of the deformation involved. Of these,astico-L has been reported in a variety of materials, including polymers and alkaline halides, while little was known about elastico-L materials. Recently, elastico-L materials have been attracting considerable attention due to their potential for application in smart sensors, which can detect damage, fractures or deformation in various structures [3].

It is known that host material and intentionally added impurity play an important role in the luminescence process; usually fluorides are attractive host materials as the efficiency of up-conversion is quite high due to their low phonon energies [4].

LiF is often preferred among alkali halides, because it is not damaged by moisture and color centers are optically stable. The hardness of the sample, allow us to apply more pressure using pressure device. LiF is widely used thermoluminescent phosphors in dosimetric application. The effective atomic number is sufficiently near to that of human tissue [$Z_{\text{eff}}(\text{LiF}) = 8.14$ and $Z_{\text{eff}}(\text{Tissue}) = 7.4$]. Kher et al, 2002 have studied and reported the ML of Ba, Ca and Sr doped LiF crystal, excited by impulsive technique [5]. The survey of literature shows that no systematic investigations have been made on the ML of γ -ray irradiated LiF:Ba crystal, excited by applying gradually varying pressure. Hence, in the present investigation we have studied and reported the ML of γ -ray irradiated Ba doped LiF crystal excited by applying continuously varying pressure.

1.2 Material and Methods

LiF crystals doped with different concentration of Ba grown by Bridgman technique under 10^{-6} torr vacuum is used [6]. The grown crystals were cleaved and annealed at 400°C for one hour in muffle furnace before irradiation with γ -ray. The crystalline phase and surface morphology of the resulting sample was examined by X-ray diffraction analysis (XRD model D8 Advance Bruker AXS) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data have been collected by step scanning 2θ from 30° to 70° and 9.6s swept time at each step at room temperature.

In order to study the surface morphology of the crystal scanning electron microscopy (SEM) (model LEO-0435 VP) has been carried out. Above characterization (XRD and SEM) were performed at Institute Instrumentation Centre, Indian Institute of Technology Roorkee, Uttranchal, India. Gamma irradiation was carried out by using a ^{60}Co source having exposure rate of 0.930kGy/hr , at Nuclear Chemistry Research Lab, Department of Chemistry, R.T.M. University Nagpur, India. ML was excited by applying continuously varying pressure on to the sample using pressure device [7] (Fig. 1).

1.3 Results and Discussion

Figure (2) shows the XRD pattern of LiF:Ba sample. The XRD pattern of LiF:Ba sample matched well with standard JCPDS [8] data (File No. 00-001-1270).

Figure (3) shows the XRD reference pattern of the standard LiF compound.

Figure (4) shows the SEM morphologies of the sample. SEM pattern shows that the crystallites have sharp surface morphology like single crystalline grains.

Figure (5) shows the time dependence of ML of γ -ray irradiated LiF:Ba (60 ppm, γ -irradiation 1.86 kGy) crystal. ML intensity was measured by applying continuously varying pressure on to the sample using pressure device. For ML measurement of Ba doped LiF crystals of size $1 \times 1 \times 1 \text{ mm}^3$ is used. When ML is excited by applying continuously increasing pressure ($1.114 \times 10^7 \text{ N/m}^2\text{-sec}^{-1}$) on to the sample, number of peaks of different intensity is observed at different times. The maximum pressure applied on the sample was $11.7 \times 10^7 \text{ N/m}^2$. In the present investigation we have observed that ML also appears, when the pressure was decreased after attaining maximum value. When the pressure on to the sample was decreased with same rate ($1.114 \times 10^7 \text{ N/m}^2\text{-sec}^{-1}$) the number of ML peaks observed in the ML intensity versus time curve, however number of peaks and their intensities are relatively less as compared with those observed during application of increasing pressure.

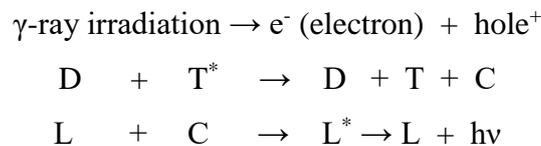
Figure (6) shows the dependence of total ML intensity of LiF:Ba crystal on concentration of Ba. The ML intensity increases with increasing doping concentration, approaches an optimum value and then decreases with further increase in doping concentration. The optimum ML intensity was observed for the sample having concentration of 60 ppm of Ba and γ -dose of 1.86 kGy.

Figure (7) shows the dependence of total ML intensity of LiF:Ba (60 ppm) crystal on gamma doses given to the sample. The ML intensity increases with increasing gamma doses in the dose range 0.15 to 1.395kGy and seems to be saturate for higher gamma doses (1.86kGy) given to the

sample. Total ML intensity (i.e. area below time versus ML intensity curve) is calculated using MATLAB software.

It is well known that the doping of the cation impurity increases the number of charged dislocations in alkali halide crystals [9]. When a foreign atom is introduced at an interstitial site; this will be accompanied by the distortion in the host lattice. The distortion arises from a size mismatch between the doped and substituted ions in the matrix [10]. The ionic radii of Li^{1+} and Ba^{2+} are 0.66\AA and 1.35\AA respectively. When a large ion of Ba^{2+} is introduced in LiF crystal the divalent Ba^{2+} replaces mono-valent positive Li^{1+} ion having different ionic radii, then lattice of the crystal will therefore contract. Alkali halide crystals irradiated with X or γ - rays shows ML during the elastic, plastic deformation as well as during their fracture [11]. When the stress is loaded the movement of dislocation set in the motion by applied pressure. The mobile dislocation in the LiF crystals may excite ML.

Investigation made in the past [12-19] indicate that, ML in alkali halide is associated with the release of trapped carriers from electronic point defects in the crystal, by the movement of dislocation. It seems that the movement of dislocation D excites the charge carriers C from the filled traps T^* and the subsequent recombination of the electrons and holes in the luminescence center L give rise to luminescence [20-24]. This process can be represented as follow:



Two important facts observed in the present investigation are; first the number of ML peaks observed during the application of continuously increasing pressure applied on to the sample and second, the ML is also produced, when the pressure was released from the sample after applying maximum pressure. However, less number of peaks was observed during the decreasing pressure as compared to that observed during the application of increasing pressure.

When continuously increasing pressure applied on the crystals the dislocation source become operative and dislocation starts moving within a certain distance between the dislocation and traps containing hole, the energy difference between the dislocation band and defect centre level may be comparable with KT and due to which some of the holes in defect center may be transferred to the interacting dislocations and captures holes from the later defects. If the moving dislocation containing holes interacts with defect centers containing electrons, the dislocation holes may be captured by these centers and ML emission arise due to the radiative electron-hole recombination. It may be assumed that shallow traps present in the crystals are ionized during the application of initial lower pressure and other deeper traps may be responsible for the ML emission during further increasing pressure applied on the crystal. Therefore electrons released first from the shallow traps at lower applied pressure and electrons released from deep traps at higher pressure. The released electrons from traps during the deformation of the crystal may either recombine with the holes or get re-trapped. When crystal is compressed, the number of defects in the crystal will increase with increasing pressure [25]. The increasing number of defects with the increasing value of applied pressure may increase the probability of re-trapping. Further, it may be possible that the dislocation loops may not sweep through a virgin area of the crystal at lower pressure. When the pressure continuously increasing, the movement of the dislocation continues and electrons from deep traps are released at higher pressure corresponding to the trap depth and required pressure to release the electrons. Since the applied pressure increases the number of electrons simultaneously released from different trap depth at different pressure, the process of re-trapping and release of electrons continue and recombination of released free electrons at different pressure, with holes may give rise to ML emission. Therefore recombination of electrons released from different trap and holes is responsible for number of ML peaks.

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 [26]. Many of the color 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 [27].

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 color 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.

It has been shown that the release of holes/electrons from defect centers at characteristic traps initiates the luminescence process in the material. It has been found that ML intensity is optimum for a particular concentration of the activator in the phosphor.

It has been found that the ML intensity of γ -ray irradiated LiF:Ba crystal increase with increasing level of dopant. This may be due to the increase in the number of charged dislocation in the crystals. Furthermore, the increase in ML intensity by adding divalent impurities (Ba^{2+}) may either be due to the creation of emission centers or due to trapping centres in the crystal lattice. For the longer duration of the γ -ray irradiation more color centers are formed in the crystals. Therefore moving dislocation may interact with more number of color centers and consequently there may be more ML emission from the crystal having larger density of the color centers. It is anticipated that the ML intensity should depend linearly on the density of color centers in the crystals.

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 optimum 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 observed that the ML intensity of LiF:Ba crystal initially, increases with gamma doses, attains an optimum value and seems to saturate for higher gamma doses given to the sample. Initially the color centers increases with increasing gamma doses given to the sample. Therefore the moving dislocation may interact with more color centers and consequently there may be more ML emission from the crystals having larger density of the color 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.



1.4 Conclusions

ML of γ -ray irradiated LiF:Ba crystal has been investigated by applying gradually increasing/decreasing pressure on to the sample. Number ML peaks is observed, when continuously increasing varying pressure is applied on to the sample. When continuously decreasing pressure is applied with the same rate, less number of peaks were observed as compared to that of observed during the application of increasing pressure. The optimum ML intensity is observed for the sample having doping concentration of 60 ppm, gamma dose 1.86kGy of Ba. The ML intensity of LiF:Ba increases with γ - dose in the dose range 0.15-1.395kGy and seems to saturate for dose level 1.86 kGy.

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Figures and Figure Captions

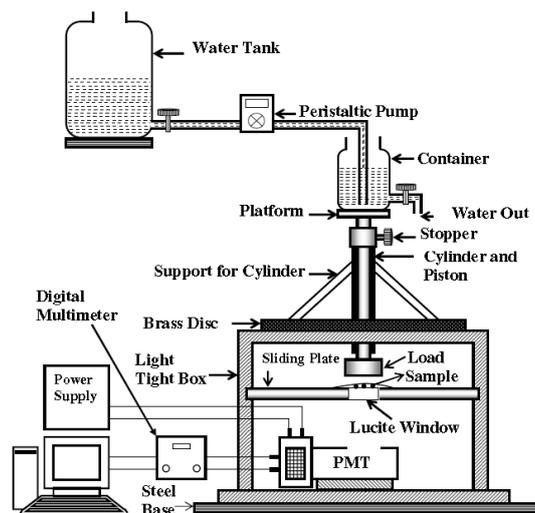


Fig.1 Schematic diagram of experimental set-up used for deforming the sample and measuring the ML.

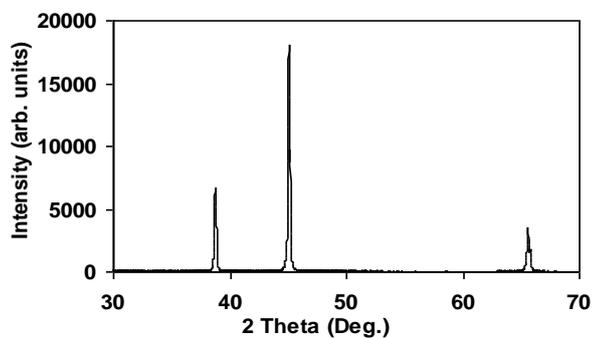


Fig. 2 X-ray diffraction (XRD) pattern of LiF:Ba (60ppm) crystal

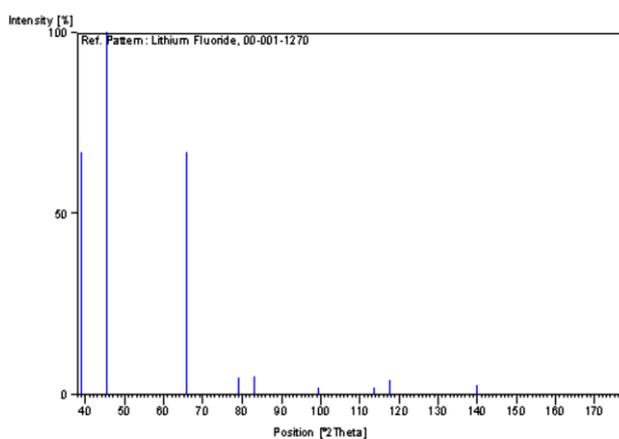


Fig. 3 X-ray diffraction (XRD) pattern of standard LiF phosphor (JCPDS file no 00-001-1270)

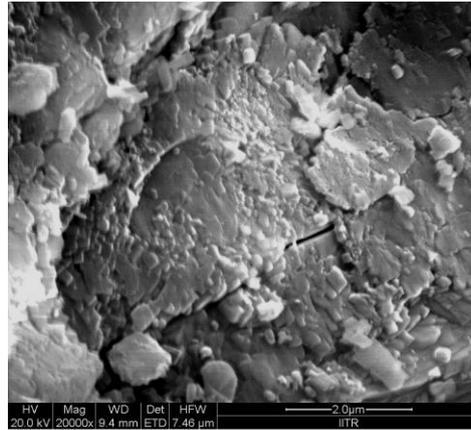


Fig. 4. SEM photograph of LiF:Ba (60 ppm) crystal

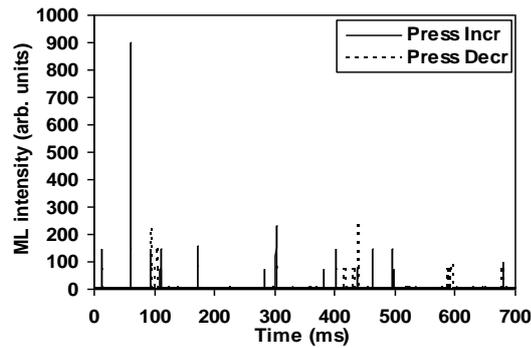


Fig. 5 Time dependence of ML of LiF:Ba (60 ppm) crystal (Gamma dose 1.86 kGy)

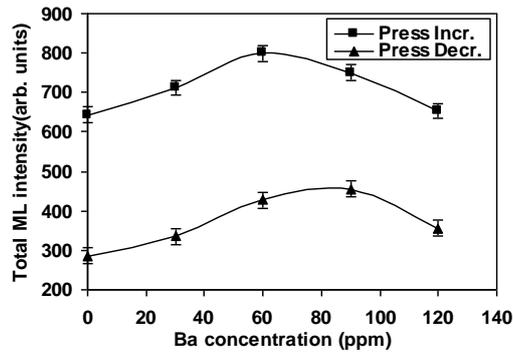


Fig. 6 Dependence of total ML intensity of LiF:Ba crystal on concentration of Ba (Gamma dose 1.86 kGy)

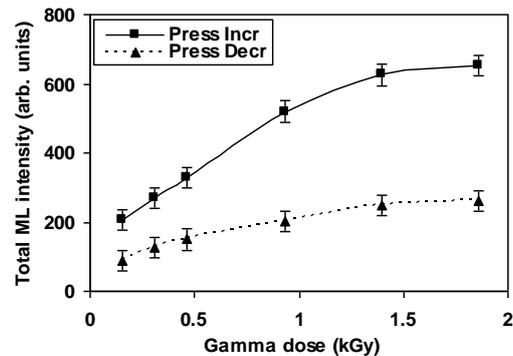


Fig. 7 Dependence of total ML intensity of LiF:Ba (60 ppm) on gamma doses given to the sample (Increase in pressure $1.14 \times 10^7 \text{ N/m}^2 \text{ sec}^{-1}$)