



Intrinsic and extrinsic fracto-mechanoluminescence of solids

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Abstract

Whereas nearly 50% of all inorganic salts and organic molecular solids exhibit the phenomenon of fracto ML, only a limited number of solids exhibit elastico ML and plastico ML. The fracto ML of certain crystals such as europium tetrakis (dibenzoyl methide) triethyl ammonium, ditriphenylphosphine oxide manganese bromide, Eu doped strontium aluminate, impure saccharin, etc. is so intense that it can be seen in day light with naked eye. A large number of piezoelectric and non-piezoelectric organic and inorganic crystals exhibit intrinsic and extrinsic fracto-mechanoluminescence (ML) due to the electron bombardment and electron trapping mechanisms, and only a few crystals show ML due to the chemically-induced fracto-ML and other possible mechanisms. The charged surfaces produced during fracture of solids owing to piezoelectrification, defective-phase piezoelectrification, movement of charged dislocations, baro-diffusion of defects near the crack-tip, and many other processes may cause production of very high electric field near the charged surfaces. In the case of non-photoluminescent and non-cathodoluminescent materials, the high energy electrons may be emitted from the charged surfaces and the electron bombardment (EB) mechanism may excite the molecules of surrounding gases and subsequently the gas discharge ML may be produced. In photoluminescent and cathodoluminescent solids, the electron-bombardment may cause cathodoluminescence. In certain photoluminescent crystals, the light of gas discharge may excite photoluminescence. In many solids, the free electrons produced at fracture may be captured in the traps and consequently the electron-trapping (ET) mechanism may give rise to the light emission. Few solids may exhibit chemiluminescence because of the chemical reactions at the newly created surfaces. Some solids may exhibit black body radiations because of the high temperature produced near the tip of the moving cracks. Infrared radiation may also be emitted during the fracture of certain crystals. In certain solids, the gas discharge fracto ML and the photoluminescence excited by the gas discharge disappear when the solids are fractured inside liquids; however, in certain solids the solid state fracto ML appears even inside the liquids if they are not based on the processes involving gas discharge. Overall, depending on the prevailing conditions the ML spectra consist of either the gas discharge spectra or solid state luminescence spectra or the combination of the both. The understanding of the mechanism of fracto-ML may be useful in preparing suitable fracto-mechanoluminescent materials and it may be helpful in designing the fracto-ML based devices such as fracture sensor, impact sensor, damage sensors, safety management monitoring system, fuse system for army warheads, etc.

Keywords: organic molecular solids, fracto-mechanoluminescence, sensors

INTRODUCTION

The phenomenon of mechanoluminescence (ML) has generated extensive research interest over the years because of its potential applications for fracture detection, impact detection, damage detection and visualization of stress distribution in solids. Mechanoluminescence is the emission of light from solid materials when they are deformed elastically or plastically or fractured. The light emissions induced by elastic deformation, plastic deformation and fracture of solids are called elastico ML (EML), plastico ML (PML) and fracto ML (FML), respectively [1,2]. Whereas nearly 50% of all organic and inorganic solids show ML during their fracture, only a few solids show ML during their elastic and plastic deformation [1,2]. The fracto-ML of SrAl₂O₄: Eu, europium tetrakis (dibenzoyl methide) triethyl ammonium, ditriphenylphosphine oxide manganese bromide, freshly grown impure saccharin, etc. is so intense that it can be seen in day light with naked eye.

From the point of view of the nature of electronic transitions producing light, luminescence can be divided in two major types, namely intrinsic luminescence and extrinsic luminescence. In intrinsic luminescence, there are three kinds: band-to-band luminescence, exciton luminescence and cross-luminescence. Extrinsic luminescence is divided into unlocalized type and localized

type, depending on whether excited electrons and holes of the host lattice participate in luminescence processes or whether luminescence processes are confined to localized centres. Similar to the case of photoluminescence, the intrinsic and extrinsic fracto-mechanoluminescence have also been observed. In the past, many models have been reported for the fracto-ML of solids, and therefore, difficulties arise in understanding the processes involved in fracto ML. The present paper explores in detail the models for intrinsic and extrinsic fracto ML of organic and inorganic solids and shows that only a few models such as electron bombardment (EB) model and electron-trapping (ET) model are applicable to the fracto ML of most solids and other specific models are applicable to only a few solids. The understanding of the mechanisms of intrinsic and extrinsic fracto ML may be useful in preparing suitable fracto-mechanoluminescent materials and it may be helpful in designing the fracto ML based devices such as fracture sensor, impact sensor, damage sensors, safety management monitoring system, fuse system for army warheads, etc.

Mechanisms of fracto ML

The piezoelectric origin of fracto ML is revealed by the following important observations:

- (i) With few exceptions, all piezoelectric crystals show fracto ML and all the crystals not exhibiting fracto ML are non-piezoelectric.
- (ii) The fracto ML has been measured in many polymorphic crystals, e.g. anthranilic acid, hexaphenylcarbodiphosphorane, acetamide, etc..It has been found that only the piezoelectric form exhibits fracto-ML and the others forms do not.
- (iii) Certain crystals e.g. sucrose, tartaric acid, ethylene diatartrate, etc. do not show fracto ML when they are cleaved in a plane parallel to their pyroelectric axis, although fracto ML is produced from all other cleavage planes.

Langevin model for the creation of charged surfaces during the movement of a crack in a piezoelectric crystal has been found suitable to explain the fracto ML of the piezoelectric crystals [1]. The piezoelectric constant and the stress needed to separate the surfaces of crystals are generally of the order of 10^{-12} - 10^{-11} Coulomb per Newton (CN^{-1}) and 10^8 Nm^{-2} , respectively. Thus, the charge density ρ of the newly created surfaces is of the order of 10^{-4} - 10^{-3} Coulomb m^{-2} . The electric field F between the oppositely charged surfaces will be, $F = \rho / \epsilon_0$, where ϵ_0 is the permittivity of free space, equal to 8.85×10^{-12} $C^2N^{-1}m^{-2}$. Thus, an electric field of the order of 10^7 - 10^8 Vm^{-1} may be produced between the newly created oppositely charged surfaces. This field may cause the dielectric breakdown of the surrounding gases and in turn may give rise to the gaseous discharge ML. The field may also cause the dielectric breakdown of the crystals, and the recombination of free carriers may give rise to recombination luminescence. The capture of electrons in deep traps may also give rise to the light emission. Furthermore, the accelerated electrons moving from negatively charged surfaces towards the positively charged surface may excite cathodoluminescence (CL). Thus, it seems that the piezoelectricity that results from a noncentric crystal structure is the fundamental structural cause of ML. What is the fundamental is the charging of the new surface and its electric field that is the source of energy for most of the phenomena.

It has been found that, in addition to the piezoelectric crystals, a large number of non-piezoelectric crystals also exhibit ML. Thus, it seems that the charging of newly created surfaces also takes place due to the movement of charged dislocations, baro-diffusion of defects in crystals, local piezoelectric field caused by impurities and defects, creation of noncentric structure by the stress required for fracture, local piezoelectric field caused by the large strain at fracture, fracturing of centric ionic crystals in a direction which actually generates charged surfaces, the presence other phases in solvated materials, presence of noncentric phase due to disorder in materials, charging of the sites (like oxygen, halogen, etc) of different electro-negativity in neutral polar molecules, etc.

If there is total transfer of energy from the excited gas molecules to the luminescence centres or the light produced due to gas discharge is absorbed completely by the crystals, then only the solid state ML will be produced. Moreover, if the electric field will not be sufficient to cause the gas discharge, then also the gas discharge ML will not be observed. On the other hand, if there is partial transfer of energy from the excited gas molecules to the luminescence centres or partial absorption of the light produced due to the gas discharge by the crystals, then the combination of both the solid state ML and gas discharge ML will be observed. Furthermore, if the

crystals do not possess luminescence centres, then there will be no transfer of energy from the excited gas molecules to the luminescence centres or absorption of gas discharge by the luminescence centres, and only the gas discharge ML will be observed. Thus, depending on the prevailing conditions either gas discharge or ML resembling other types of luminescence or combination of these two may be observed.

When solids are subjected to deformation, then during the fracture and for some time after, electrons, ions and neutral species are emitted from the surface of solids. In fact, some are formed by the violence of the fracture itself, some by dislocation pop out and some by electron bombardment. In fact, both in the crack and above the new surface, there is a gas and plasma of fragments. In vacuum, that is, in the absence of gases, these fragments cause increase in the local pressure and thus increase the discharge current and its luminescence.

It is to be noted that the number and variety of materials for which the energy transferred to surface electrons is sufficient for their expulsion is amazing and there seem to be multiple pathways for the energy transfer. Frequently, the dislocations can pop out the surface of piezoelectric to release electrons with energies of several hundred electron volts or even 1MeV. On the other hand, most electrons have much lower energies. Another way by which the surface can relax is by the neutralization of charges. This fact becomes easy if the material is conducting, but even metals eject electrons from their surface on plastic deformation and fracture. All the solids that have been examined on fracture release electrons (exoelectrons) and most release atoms and molecular fragments that are charged. A considerable fraction of materials also emit light and such light emission may provide energy to assist in additional electron expulsion. In fact, the process of release of charged fragments and the coronal discharge help to dissipate the energy somewhat, as does tunneling along the surface.

Models for Intrinsic and Extrinsic Fracto-Mechanoluminescence

Chandra and Rathore [3] have proposed 21 possible models for the ML emission in solids. It has been found that, out of these 21 models, the electron bombardment (EB) model and electron trapping (ET) model are able to explain the ML of most solids. Fig.1 shows the schematic diagram for the ML emission produced during fracture of solids. Now, the electron bombardment induced fracto ML of non-photoluminescent and non-cathodoluminescent materials, electron bombardment induced fracto ML of photoluminescent and cathodoluminescent materials, electron-trapping induced fracto ML and chemically –induced fracto ML produced during fracture of solids will be discussed.

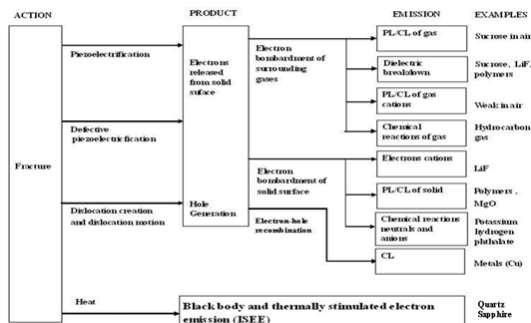


Fig 1. Schematic diagram for the mechanisms of fracto-ML.

Electron bombardment induced fracto ML Non-photoluminescent and non-cathodoluminescent materials

When the materials in air at atmospheric pressure or down to about 0.01 Atm are fractured, the electrons released by the newly created charged surface possess enough energy to ionize molecules on the surface and in the surrounding gas to produce even more electrons. Subsequently, this electron multiplication can cause dielectric breakdown, either between patches on the new surface or between pairs of surfaces when they separate. The similarity of ML spectra obtained during fracture of the non-photoluminescent materials like sugar and lithium sulphate with the emission spectra of dinitrogen is concrete proof for the occurrence of the that dielectric breakdown of the solids. The process of dielectric breakdown gives rise to a huge increase in the bombardment and excitation of molecules and ions both of the gas and the surface. Furthermore, the intense pulse of current during breakdown produces broadband radio signals.

Many solids have no photoluminescence and cathodoluminescence of their own. In such solids, the only source of luminescence is from a gas discharge in which the gas molecules are bombarded by electrons. In such discharge, the impact of energetic electrons may transfer energy to molecules or atoms to excite or ionize them. It is to be noted that, ionization can create a conducting path or a coronal discharge in low electric fields. On the other hand, if the electric field is great enough, then the acceleration of the electrons is sufficient to create a conducting path to another surface and they can lead to full dielectric breakdown. For the material in air, the dominant emission occurs due to a triplet-to-triplet excited-state transition manifold of dinitrogen, the ${}^3\Pi_u \rightarrow {}^3\Pi_g$ or second positive group. The appearance of more lines from and from N^+ and N^{++} in macroscopic lightning, indicates that the overall energy of the discharge is greater. In fact, the huge overall intensity of macroscopic lightning may permit detection of even the weaker lines. However, the differences observed between the spectra of different non-photoluminescent solids and between the spectra of one sample at different times are not large enough to draw conclusions about discharge energy. Similar discharges have been observed in other gases, excluding sulfur hexafluoride and dioxygen.

Photoluminescent and cathodoluminescent materials

In ML, the solids whose molecules are photoluminescent is interesting. Longchambon [4,5] proposed that the fracture of such solids produces sufficient electric field for a discharge through the surrounding atmosphere, in which emission in air is in the spectral region optimal for absorption by typical photoluminescent materials, and thus for the excitation of their photoluminescence. In this way, the molecules of the material can absorb the light emitted by the discharge and subsequently, their normal photoluminescence can be emitted. The fact that certain photoluminescent materials exhibit dinitrogen lines with their intensity reduced in the range, supports the process of the light absorption causing photoluminescence and such result provides evidence for the ML excitation by the gas discharge produced during fracture. Despite the clear evidence of the absorption of the lightning lines, it has not been satisfactorily known that this absorption is responsible for the excitation of the observed photoluminescence. It is to be noted that the appearance of lightning lines in the ML of materials with photoluminescence that can be excited by them is not very common. It has been found that most of

such uncommon materials exhibit very weak photoluminescence or their photoluminescence is caused by impurities. In this regard, the ML spectra of saccharin can be taken as an example. The photoluminescence of uranyl disalicylate crystals excited by 440 nm light is very weak as compared to the photoluminescence excited by 300 nm light. If such increase in photoluminescence intensity is caused by the absorption by the uranyl ion, then the suggested process may explain the faint lightning lines in uranyl nitrate. As such, if absorption of the lightning lines occurs, it is usually very efficient and can hide the fact that lightning had occurred.

In the beginning of 1930's, Longchambon expected that the lightning lines would be present in the mechanoluminescent spectra of all the solids. Therefore, he proposed that a discharge through the atmosphere was an intermediate step for all the mechanoluminescence of photoluminescent solids, whereby the ML was excited by absorbing the lightning. For certain materials the absorption of lightning lines in photoluminescence is consistent with the Longchambon's proposal. In contrast, the recording of ML spectra using modern sensitive detectors has indicated that lightning lines are not found in the ML spectra of most photoluminescent materials. Furthermore, when they are found, they are often independent of the photoluminescence. The absence of lightning lines could mean that most photoluminescent materials completely absorb such lightning lights or another possible explanation is that the mechanism proposed by Longchambon is not correct for all the solids. Thus, although Longchambon considered the possibility of photoluminescence excitation by the light of gas discharge at fracture, he did not consider the possibility that the molecules of photoluminescent materials could be also excited by electron bombardment, in a similar way the dinitrogen is excited. Whereas, the excitation of the photoluminescence of dinitrogen needs an energy of the order of 11eV, most of the molecules of the photoluminescent materials can be excited by less than 5 eV, which is equivalent to an excitation wavelength of nearly 250 nm. In the measurement of the electron emission produced during fracture, the electrons with energies greater than 5 eV have been observed. Thus, it seems that at least some part of the ML resembling solid state luminescence may be excited by the electron bombardment (EB) mechanism. There is only limited spectroscopic evidence in support or in opposition of this possibility, because the few available cathodoluminescence spectra are similar to the photoluminescence spectra of the solids. There are many photoluminescent molecules, whose excitation optimum lies below 300 nm, and therefore, it does not seem possible that the excitation is caused by a discharge through air, because the dinitrogen lines of the gas discharge are extremely weak in that region. Thus, it seems that the photoluminescence from these molecules are most likely excited by the electron bombardment mechanism. However, it has been found that the ML spectra of certain solids do not correspond well to the photoluminescence spectra. For examples, in 3,6-dibromocarbazole, the peak of the ML spectra lies at 480 nm, which is primarily its 77K phosphorescence lying at 475 nm, and it does not correspond to its room temperature fluorescence (peak at 384 nm). The similarity between the low-temperature phosphorescence and room temperature ML peak has also been found for the ML of coumarin, acenaphthene and phthalic anhydride. SiC is non-photoluminescent, but it shows cathodoluminescence, therefore, its fracto ML may be due to the cathodoluminescence caused by electron bombardment. Also large differences between the relative intensities of ML emission lines and those of photoluminescence have been observed in

hexacelsians. Thus, it seems that the excitation by electrons populates the states differently, and therefore, the population difference appears between the ML and photoluminescence spectra. In fact, the electron bombardment can populate the states that are not coupled to the ground state by an allowed transition. For example, the conversion of singlet into triplet can take place by the electron bombardment, which knocks out an electron and replaces it with a different spin in a process called resonant transfer. Other explanations may also be possible for such difference in the spectra.

In high vacuum, many mechanoluminescent materials do not show the light emission during their fracture. Only a few materials emit light under high vacuum, whereby less study has been done to examine the spectra of the light and thereby to determine its origin. In fact, some solids showed a weak photoluminescence or defect-recombination emission when the discharges were suppressed. It seems that, in certain materials, air discharge facilitates the neutralization of the charged patches on the surface by the electrons and cations. In contrast, there is no possibility of a discharge under vacuum, and consequently, the lifetime of these patches and the resulting electron emission is much longer. Since there are charged patches, electrons may leave the surface and return to bombard another part of the surface with more energy to stimulate desorption of more ions, electrons and molecular fragments. In this way, such self-bombardment or self-flagellation may cause the neutralization of the patches. It has been suggested that the molecular fragments produced near the crack tip can generate sufficient pressure for micro discharges. Despite the fact that, a discharge can occur through the vapor and plasma continuously created by dislocation pop out and electron bombardment, to date the spectral evidence has been obtained only for a limited cases. The spectra of the light produced during peeling adhesive tape from copper give a strong evidence in support of the discharge through molecular fragments where lightning could be observed in air, and a series of bands, which could be assigned to molecular fragments, were found in high vacuum. In fact, these emissions were found to reduce below 1% in SF₆, in which reduction in any discharge could be possible.

To date, only a limited mechanoluminescent materials have been studied for the effect of gas identity or pressure on their ML emissions. The pyroelectric luminescence of N-isopropylcarbazole showed a maximum when the pressure of argon was reduced. The ML intensity of N-isopropylcarbazole decreased in order under He, Ne, Ar, N₂, O₂ and SF₆, which is in favour of the fact that discharge is the source of ML excitation. The ML intensity of certain mechanoluminescent materials have been found to be unaffected under the atmosphere of helium or carbon dioxide. This fact suggests that the ML excitation might not be caused by the light emissions of the gas, but it should be caused by the electrons themselves.

Some solids exhibit fracto ML when they are fractured under liquids, and clearly this observation seems to be inconsistent with an electron bombardment mechanism. In these materials, the ML emission by electron trapping mechanism is also not possible, because the ML spectrum is not the chemiluminescence of a reduction but it is the photoluminescence of the host material. If it is considered that the material has been prepared in such a way as to exclude air pockets, then there are several possibilities. The most likely process is that electron bombardment may occur so quickly after separation of the faces that the liquid could not reach that part of the surface. There is a possibility that the electron bombardment may also occur across internal micro cracks or excitation is

accomplished by the electrons carried by dislocations during plastic deformation even without micro cracks. The investigation of the ML of such materials in the deformation and fracture regions under different atmospheres may provide important informations, especially if it is compared with photoluminescent materials which lose their ML activity under liquids.

Zinc sulphide, aluminosilicates and polymers are three major classes of materials whose ML has been studied with dopants. Generally, the doped materials are made by mixing powder or solution of the luminescent component with the solids, compressing and heating (sulfides and ceramics) or by dispersing the solid in a mixture of monomer and catalyst or a solution of polymer. Only a limited films have been prepared by methods that ensures a molecular level distribution, such as vapor deposition or magnetron sputtering followed by annealing. In this way, most of the doped solids bear a strong resemblance to filled polymers in having islands of other material. In fact, the islands in doped solids in turn resemble macroscopic interfaces like polymers on metals, in which charge transfer is inevitable, and this fact causes increase in the new surface area formed. The large increase in the ML intensity and related emissions from filled polymers compared to unfilled polymers indicates that interfacial failure is a major factor for the ML emission. The coarsely doped ceramic materials may exhibit both contact charging and interfacial failure. Since the ML spectrum of doped zinc oxide is inconsistent with photoluminescence excitation of emission of the ceramic, it has been shown that the electron bombardment between the grains is responsible for both ML and electroluminescence.

Zinc sulphide doped with ions such as Mn²⁺ exhibits ML whose spectra are similar to its photoluminescence and electroluminescence spectra. In this case, the energetic electrons to excite the dopants could come from defects carried by charged dislocation motion in the ZnS or they may also be generated by the field produced by ZnS piezoelectricity. Since the newly created surfaces of ZnS:Mn crystals get charged due to the movement of charged dislocations or piezoelectrification, similar to the other piezoelectric photoluminescent crystals, the accelerated electrons between the walls of cracks can cause the light emission from the Mn²⁺ ions near the newly created surfaces by the electron bombardment mechanism. As the ML intensity of ZnS:Mn crystals does not increase rapidly with the piezoelectric field which increases linearly with the impact pressure or impact velocity of the ball used to deform the crystals, it seems that the Mn²⁺ ions inside the solids are not excited by the electron bombardment, but they are excited by the energy released during the electron-hole recombinations. Thus, the fracto ML of ZnS:Mn crystals is caused by both the electron bombardment mechanism and the electron trapping mechanism. For ZnS:Mn, the reports of ML activity under liquid are conflicting. In addition to solid state ML, lighting has also been reported as part of the ML and it seems to be consistent with its piezoelectricity; however, lighting in this case has been attributed to contact charging.

Some materials have been prepared that incorporate mechanoluminescent lanthanide complexes into various polymers such as polycarbonate and epoxy. Most of the initial energy for excitation of the lanthanides may come from the host material by any of the mechanisms described previously, but most probably it may occur by electron bombardment. This idea is supported by following four observations: (i) the polymers used as host produce electric fields on their deformation and fracture and subsequently emit electrons, photons and molecular fragments, (ii) complexes

that are not mechanoluminescent in pure powders form are just as effective in producing their characteristic luminescence when the polycarbonate is fractured as the related mechanoluminescent complexes, (iii) the emissions show two lifetimes in air in which the first is consistent with a discharge emission from polymer (UV, lifetime less than 2 μ s) and the second is consistent with the phosphorescence lifetimes of the europium complex and the ML of pure powder (wavelength 520 nm, lifetime 600 μ s), and (iv) the europium complex-doped polycarbonate exhibits more strongly mechanoluminescence in high vacuum as compared to that in air. The gas discharge ML in polymer has been shown to continue in high vacuum through molecular fragments, but air may react with some of the high-energy surface states of the polymer.

So far as the ML of lanthanide-doped and natural fluorites on sawing is concerned, it is more complex, probably because different excitation mechanisms excited different sites. It seems likely that the ML in these materials is caused by both electron capture and electron bombardment, as the relative intensities of the spectral bands are sensitive to heating and γ -irradiation.

Some of the organic compounds are only mechanoluminescent when they are impure and give spectrum of the impurity or dopant. For example, impure saccharin gives the ML spectrum of p-toluenesulfonamide at 480 nm and nearly equal intensity from lightning lines. In this case, the photoluminescence also has a band at 320 nm from p-toluenesulfonamide contamination. The fact that it does not contribute to the ML spectrum indicates that the excitation is actually by Longchambon's mechanism, that is, the excitation by the gas discharge dinitrogen emission spectrum. The other materials such as Wintergreen candy and triphenylmethane also provide clear evidence of partial absorption of the lightning lines. It is possible that both, the electron bombardment mechanism and the photoluminescence excitation by the gas discharge light are often present, but that a larger fraction will be seen from indirect excitation, i.e., by lightning photons, when the mechanoluminescence comes from a low concentration of photoluminescent impurities. It is to be noted that, photons travel through the material and they are unimpeded until they strike an absorbing material like the photoluminescent impurity. On the other hand, the electrons are decelerated whether they excite any luminescence or not. As such, the ML from the direct electron bombardment mechanism will be suppressed by the low concentration of the emitting species more as compared to the ML from the indirect mechanism using photons from the discharge emissions. Such possibility needs testing under other atmospheres.

In recent years, the fracto ML of organic and inorganic crystals have been reported by many workers, in which the electron bombardment is able to explain the photoluminescence emission and gas discharge emission.

Electron-trapping induced fracto ML

Fracto-ML of X or γ -irradiated alkali halide crystals

When X or γ -irradiated alkali halide crystals are fractured in atmosphere, then the crystals such as KCl, KBr, KI, etc. having low density of charges in charged dislocations, emit only the solid state luminescence involving trapping of dislocation captured electrons from F-centres in hole centres. Thus, the ML in these crystals involves ET mechanoluminescence. On the other hand, the X or γ -irradiated crystals such as NaCl, LiF, NaF, etc. having comparatively higher density of charges in charged dislocations exhibit the solid

state ML superimposed by the gas discharge ML. Thus, the fracto ML of such crystals involves the ET mechanism for solid state ML and EB mechanism for gas discharge ML.

Fracto-ML of rare earth oxide crystals

MgO and other rare earth oxides show only the solid state ML during their fracture, in which the gas discharge ML does not occur. In this case, the motion of dislocations brings defects of opposite sign into proximity for recombination or ET, such as O-defect (a VI defect) to reduce them to O²⁻. This recombination of high-energy electrons and holes can result in an excited product, whose light emission, a form of electro generated chemiluminescence of ECL, is characteristic of that defect in that crystal environment.

Fracto-ML of II-VI semiconductors

When impurity doped II-VI semiconductors are fractured, then the solid state ML resembling their PL and EL in spectra is observed. As discussed previously in the case of ZnS:Mn, the fracto ML involves both the EB mechanism as well as the ET mechanism caused by the high electric field produced due to the charging of newly created surfaces by the movement of charged dislocations and piezoelectrification. In some cases, a weak gas discharge ML has also been reported which arises as a result of the contact electrification between the metallic rod used for grinding. Probably, the intensity of the ML induced by EB mechanism is less as compared to the intensity of the ML induced by ET mechanism because most of the dtrapped electrons are captured by the holes and trapped hole centres.

Fracto ML of rare earth doped aluminate and silicate crystals

The ML has been studied in doped silicates and aluminosilicates such as ceramics like strontium aluminates, yttrium silicates, hexacelsian (a barium aluminosilicates), zirconia, zinc aluminate and gallates (spinel). These materials are extremely hard materials like quartz. It has been found that the undoped hexacelsian produces gas discharge on fracture, but the activity of other pure materials is not known . The preparation of the materials usually involves grinding of reagent oxides, followed by sintering. Among the doped aluminates and silicates the ML of strontium aluminate doped with Eu has been studied in detail and it has been shown that the fracto ML of rare earth doped strontium aluminate and silicate phosphors can also be understood using electron-trapping model. As the piezoelectric field produced during fracture is high, a part of the fracto ML in these phosphors may also arise due to the electron bombardment. In noncentric piezoelectric materials and in defective phase piezoelectric materials the local piezoelectric field causes the detrapping of trapped electrons. Subsequently, the detrapped electrons move in the conduction band and they are captured in the excited state of activator centres lying adjacent to the conduction band, whereby the activator ions get excited and the de-excitation gives rise to the light emission characteristics of the activator like Eu. Thus, the electron trapping (ET) mechanism is responsible for the major part of the fracto-ML of the aluminate and silicate phosphors. In such materials a fraction of fracto ML may also be due to the electron bombardment mechanism.

Fracto-ML of calcium fluorite crystals

In fact, pure calcium fluorite has not been reported to be mechanoluminescent. Natural fluorites (CaF_2) are very complex because they are doped with metal ions and irradiated in Situ. Early observations showed that the ML, photoluminescence and thermoluminescence emissions were the same, but spectroscopic observations indicated significant differences [96]. Natural fluorite possesses a variety of luminescent sites. The studies on the effect of heat and irradiation on the spectrum allowed some to be assigned to impurities (e.g. Tb^{3+} at 550 nm) and some to radiation damage (480 and 580 nm). The thermoluminescence spectra are clearly different. Doping pure fluorite with lanthanides produces a very complex ML spectra with the relative intensities of the lanthanide transitions (from Tb^{3+} , Dy^{3+} , or Eu^{3+}) are quite different from those in its photoluminescence.

Fracto-ML of silica

Various forms of silica emit infrared upon fracture. In the light emission induced by fracture of silica, in addition to the blackbody radiation, two air-sensitive bands with different lifetimes in the visible ML spectrum are extended into the IR. The high energy band at 460 nm, assigned to SiO^- , developed later and lasted longer than the low energy band at 660 nm, assigned to trapped oxygen. Thus, the fracto ML of silica occurs due to electron-trapping mechanism.

Fracto-ML of elemental and III-V semiconductors

Interesting studies have been made on the cleavage-induced ML of elemental and III-V semiconductors. It has been shown silicon emit IR from 3300 nm to 4800 nm upon fracture but not upon abrasion. Since abrasion does not stimulate the emission, the ML of silicon has been assigned to surface states rather than blackbody radiation. From the ML bands obtained using filters, measurement of ML lifetimes and the effect of air, it has been concluded that the long-lived near-IR band was from bulk band-gap transitions, the long-lived mid-IR band was from surface-state transitions and the short-lived near-IR band was from surface defects. Gallium arsenide and indium phosphide also produce IR emissions during their cleavage. On the basis of the experiments performed similar to those for silicon, it has been reported that indium phosphide's ML band at 1000 nm, found only in vacuum, was from bulk band-gap transitions, and the ML band at 660 nm occurring in both vacuum and air was from surface defects. The germanium film crystallizes and lifts off the surface by being pricked with a sharp point and subsequently, mechanoluminesce sufficiently which can be photographed using infrared film. The experiment with filters indicated two bands of different lifetimes and different air sensitivities. The silicon-germanium mixtures exhibit similar emissions- a high-energy, short-lived air-insensitive band from surface defects and a lower energy long-lived (indirect) bulk band-gap emission seen only in the experiment made in vacuum. The formation of crack-induced localized states is responsible for the ML excitation produced during the cleavage of elemental and III-V semiconductors. According to this mechanism, as the atoms are drawn away from each other in advancing crack tip, the decreasing wave-function overlap across the crack may result in localized states which are associated with increasing electron energy. If the energy of these localized states approaches that of the conduction band, the transition via tunneling would be possible. These transitions may be further facilitated by shifts in the conduction band energy due to high stress fields near

the crack tip. The recombination of the electrons excited by cleavage into conduction band with the holes in the valence band may give rise to the edge emission. Furthermore, the transition at shallow traps, upper surface states and defect centres may produce the light having different wavelengths.

It is worth to mention here that, in addition to elemental and III-V semiconductors, sodium chloride, metals, quartz, pentaerythritol tetranitrates (PETNs) and silica have been reported to emit infrared during their fracture.

FractoML of doped CaSO_4 crystals

In γ -irradiated rare earth doped CaSO_4 crystals, detrapping of holes takes place because of the band bending caused by the electric field produced due to newly created charged surfaces. In this the case, capture of electrons in detrapped holes gives rise to the light emission. Thus, ET mechanism operates in the fracto ML of γ -irradiated rare earth doped CaSO_4 crystals.

Fracto-ML of metals

During the fracture of metal like Cu, the emergence of dislocations onto surface produces holes and subsequently the electron-hole recombination gives rise to the light emission. Thus, the fracto ML of metals can be assigned to ET mechanism.

Chemically –induced fracto ML

Chemical reaction may take place between the atoms or ions liberated during the fracture of crystals, and subsequently release of energy may give rise to luminescence. Furthermore, the molecules of the surrounding gases may get absorbed or adsorbed on the newly created surfaces at fractures and the release of energy in this process may cause luminescence. Kasemo and Walden have The spontaneous emission of photons and electrons during chemisorption of chlorine on sodium has been reported. The luminescence produced during chemisorptions of oxygen on aluminium and magnesium surfaces has been observed. When aluminium is fractured, then the chemical reaction between the newly created surfaces and atmospheric oxygen takes place, giving rise to Al_2O_3 . During this chemical reaction light emission occurs due to the chemiluminescence.

The light emission, which occurs on hydration (or other salvation) and dehydration of clays, certainly involves fracture and it could be classified as ML. The preliminary evidence has shown that the emissions are primarily ultraviolet, since the visible intensity increases upon adding a fluorescent amine. Such emission is in accord with the gas discharge emission. The fact that clay hydration provides both light and catalyst surface for photochemistry makes it potentially important to understanding the origins of life on earth.

Sometimes the chemical reactions are accompanied by ML. When solid dispiro (adamantine_{1,2} dioxetane) is struck, it decomposes to adamantanone, but the reaction is accompanied by the light emission only if the solid contains an europium complex ($\text{Eu}(\text{fod})_3$) as a catalyst (cocrystallized or mechanically mixed). In this case, the electronically excited product is not itself visibly photoluminescent, but transfers its energy to the phosphorescent complex. The solid-solid phase transition of methanol shatters the material and produces CO , H_2 and CH_4 and light. Titanium and aluminium form the oxide when cut in dioxygen and they form the

nitride when they are cut in dinitrogen, in which the number of pulses of light is proportional to the heat of formation of the product.

CONCLUSIONS

The important conclusions drawn from the present investigation are as given below:

- (i) A large number of noncentric and centric organic and inorganic crystals exhibit intrinsic and extrinsic fracto-ML due to the electron bombardment and electron trapping mechanisms, and only a few crystals show ML due to the chemically-induced fracto-ML and other possible mechanisms.
- (ii) The charged surfaces produced during fracture of solids owing to piezoelectrification, defective-phase piezoelectrification, movement of charged dislocations, baro-diffusion of defects near the crack-tip, and many other processes may cause production of very high electric field near the charged surfaces.
- (iii) In the case of non-photoluminescent and non-cathodoluminescent materials, the high energy electrons may be emitted from the charged surfaces and the electron bombardment mechanism may excite the molecules of surrounding gases and subsequently the gas discharge ML may be produced.
- (iv) In photoluminescent and cathodoluminescent solids, the electron- bombardment may cause cathodoluminescence. In certain photoluminescent crystals, the light of gas discharge may excite photoluminescence.
- (v) In many solids, the free electrons produced at fracture may be captured in the traps and consequently the electron-trapping (ET) mechanism may give rise to the light emission.
- (vi) Few solids may exhibit chemiluminescence because of the chemical reactions at the newly created surfaces.
- (vii) Some solids may exhibit black body radiations because of the high temperature produced near the tip of the moving cracks.

- (viii) Infrared radiation may also be emitted during the fracture of certain crystals.
- (ix) In some solids, the gas discharge fracto ML and the photoluminescence excited by the gas discharge disappear when the solids are fractured inside liquids; however, in certain solids the solid state fracto ML appears even inside the liquids if they are not based on the processes involving gas discharge.
- (x) Overall, depending on the prevailing conditions the ML spectra consist of either the gas discharge spectra or solid state luminescence spectra or the combination of the both.
- (xi) The fracto-ML of SrAl_2O_4 : Eu, europium tetrakis (dibenzoyl methide) triethyl ammonium, ditriphenylphosphine oxide manganese bromide, freshly grown impure saccharin, etc. is so intense that it can be seen in day light with naked eye.
- (xii) The understanding of the mechanism of fracto-ML may be useful in preparing suitable fractomechanoluminescent materials and it may be helpful in designing the fracto-ML based devices such as fracture sensor, impact sensor, damage sensors, safety management monitoring system, fuse system for army warheads, etc.

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