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Models for intrinsic and extrinsic fracto-mechanoluminescence of solids

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ABSTRACT

A large number of noncentric and centric 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 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. 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 sensor, safety management monitoring system, fuse system for army warheads, etc.

1. Introduction

Mechanoluminescence (ML) is a type of luminescence induced by any mechanical action on solids. ML can be excited by compressing, stretching, bending, loading, shaking, cutting, cleaving, grinding, scratching, crushing or impulsive deformation of solids. It can also be excited by thermal shocks caused by drastic cooling or heating of materials or by the shock-waves produced during the exposure of samples to laser pulses or ultrasonic waves. ML also appears during the deformation caused by the phase-transition or growth of certain crystals as well as during the separation of two solids in contacts [1,2]. The physical processes involved in inducing ML in solids indicate that basically there should be two types of ML, namely, deformation ML (DML) and tribo ML (TML). The former is produced owing to the physical processes induced during deformation of solids, whereas the later is produced due to the contact phenomena such as triboelectricity, tribochemical reaction and tribothermal generation induced during the contact or separation of two dissimilar materials in contact. DML depends only on the material under deformation and is independent of the material used to produce the deformation and the contact phenomenon. TML, on the other hand, depends on the nature of the material under deformation as well as on the material used to produce it, and arises solely owing to the contact phenomena. DML may further be subdivided into

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three types, namely, elastico ML (EML), plastico ML (PML) and fracto-ML (FML), in which the ML is induced by elastic deformation, plastic deformation and fracture of solids, respectively. TML may further be subdivided as electrically induced TML, chemically induced TML and thermally induced TML, in which the TML is induced by triboelectrification, tribochemical reaction and tribothermal generation, respectively. For example, the light produced during elastic deformation, plastic deformation and fracture of ZnS:Mn crystal is DML as it is independent of the material of which the rod used for deformation is made; however, the light produced during separation of an adhesive tape from the substrate is TML as it depends on the materials of both the tape and the substrate and occurs owing to triboelectrification.

Materials play very important role in any type of luminescence. 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. ML has been observed in insulators and semiconductor as well as in certain conductors. ML appears in crystalline, amorphous, polymeric, ceramic and composite materials. The examples of elastico mechanoluminescent materials are: coloured alkali halide crystals, ZnS:Mn, $SrAl_2O_4$:Eu, $SrAl_2O_4$:Ce, $SrAl_2O_4$:Ce,Ho, $SrAl_2O_4$:Er, $SrAl_2O_4$:Eu,Er, $SrMgAl_6O_{11}$:Eu, $SrCaMgSi_2O_7$:Eu, $SrBaMgSi_2O_7$:Eu, $Sr_2MgSi_2O_7$:Eu, $Ca_2MgSi_2O_7$:Eu,Dy, $CaYAl_3O_7$:Eu, (Ba,Ca)TiO_3:Pr^{3+}, $ZnGa_2O_4$:Mn, $MgGa_2O_4$:Mn, $BaAl_2Si_2O_8$:rare earth element, $BaSi_2O_2N_2$:Eu^{2+}, $Ca_2Al_2SiO_7$:Ce (Gehlenite, one of the brightest elastico mechanoluminescent materials), ZrO_2:Ti, and ZnMnTe. The rare earth dopant can be Eu. A few polymers have also been reported to be elastico mechanoluminescent. In addition to all the elastico mechanoluminescent materials mentioned above, alkaline earth oxides, certain non-coloured alkali halide crystals, certain varieties of rubber and certain metals also exhibit plastico ML. The examples of intense fracto-mechanoluminescent materials are: $SrAl_2O_4$:Eu, $SrMgAl_6O_{11}$:Eu, $Ca_2Al_2SiO_7$:Ce, ZrO_2:Ti, ditriphenyl phosphine oxide manganese bromide, europium tetrakis (dibenzoyl methide) triethyl ammonium, impure saccharin, cholesterol salicylate, N-acetylanthranilic acid, phenanthrene, uranyl nitrate hexahydrate, sucrose, tartaric acid, etc. The fracto-ML of certain crystals such as europium tetrakis (dibenzoyl methide) triethyl ammonium, ditriphenylphosphine oxide manganese bromide, Eu doped strontium aluminate, freshly grown impure saccharin, etc. is so intense that it can be seen in day light with naked eye. Generally, non-centrosymmetric crystals, i.e. piezoelectric crystals, exhibit ML and with a few exceptions those crystals that do not show ML are non-piezoelectric [1]. Certain centrosymmetric crystals also exhibit ML, in which the ML is caused either by the defective piezoelectric phase or it has a non-piezoelectric origin. Chandra and his co-workers have reported the spectroscopy, intensity and crystal structure-ML correlation of some 1000 organic and inorganic crystals [1,2].

Three kinds of devices are needed for the ML measurements: (i) devices for deforming the samples, (ii) devices for monitoring ML and (iii) devices for spectral measurements. Different deformation techniques used for the systematic measurements of ML are compression technique, bending technique, stretching technique, loading technique, piston impact technique or impulsive technique, needle impact technique, cleaving and cutting technique, laser technique, ultrasonic technique, shaking technique, air blast technique, scratching technique, grinding and milling technique and tribo or rubbing technique. The compression technique and piston impact or impulsive techniques have been used by many workers. The simple method of measuring the mechanoluminescent output intensity is via a high-gain detector such as a photomultiplier tube or a semiconductor diode. Some workers have also utilized a CCD camera to capture the ML emission. The ML spectra can be recorded using a spectrograph and a photographic film or an image intensifier or a dual-beam spectrometer or non-intensified optical multichannel analyzers. The later devices are now widespread within the spectroscopy community since they are significantly less expensive than the systems incorporating an image-intensifier tube. This apparatus offers advantages of speed of collection, cost, portability, ease of use and fiber-optic delivery of the ML emission to the spectrometer. Spectral measurements have played a very important role in understanding the phenomenon of ML. 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 [1,2].

In fact, the intensity of ML accompanying fracture is almost always greater than that accompanying elastic and plastic deformation. The fracture cannot be accomplished without a great deal of deformation. What makes fracture most different from deformation is the formation of large energetic new surfaces where light emission usually overwhelms the residual deformation luminescence. The new surfaces sputter off electrons, ions, neutral molecules and fragments of molecules, many of which are involved in the production of ML. Fracto-mechanoluminescence has a great deal of potential to understand the following facts and devices [3]: (i) Earthquake and mine failure,(ii) earthquake lights and moonquake lights, (iii) dynamics and mechanics of fracture, (iv) design of fracture sensor, (v) design of impact sensor, (vi) design of damage sensor and (vii) design of safety management monitoring system and (vii) design of fuse-system for army warheads. Such potentials of fracto-ML require deep understanding of the correlation between fracto-ML and fracture. It is expected that the models of deformation and fracture to explain ML may help to understand and predict earthquakes. In this connection laboratory studies on minerals and theories that focus on piezoelectric voltage, dislocation motion, electric field oscillation, coronal discharge or dielectric breakdown have already improved our understanding [3].

From the point of view of the nature of electronic transitions producing light, luminescence can be divided in two major types [4], 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. Luminescence owing to band-to band transition, that is, to the recombination of an electron in the conduction band with a hole in the valance band can be observed in very pure crystals at relatively high temperature. The band-to-band luminescence has been observed in Si, Ge and some IIIb–Vb compounds such as GaAs. It is to be noted that the light emission from very bright type light emitting diodes (not popular type) and semiconductor laser is caused by the band-to-band luminescence. In fact, at low temperature, band-to-band luminescence is transformed into exciton luminescence.

Electron–hole bound pair is known as exciton and there are two kinds of excitons: the Wannier (or Wannier–Mott) exciton and the Frenkel exciton. The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in the valence band bound together by the Coulomb interaction. In other words, a Wannier exciton is analogous to a hydrogen atom. This model works well for inorganic semiconductors such as IIIb–Vb and IIb–VIb compounds. The Wannier exciton moves in a crystal but does not contribute to electrical conduction as its total charge is zero. It emits luminescence by the recombination of the electron and hole composing it. The expanse of the wavefunctions of electron and hole in a Wannier exciton is usually much larger than the lattice constant. Wannier excitons are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy. Luminescence of