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Electron Trapping Model for the Elastico-Mechanoluminescence OF CRYSTALS

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Abstract

The mechanism of the intrinsic and extrinsic elastico-mechanoluminescence (EML) of several crystals are studied. It is found that, although the EML of crystals can be either intrinsic or extrinsic, the EML emission is generally caused by the electon trapping mechanism. According to this mechanism, the electrons from filled traps are detrapped either by mechanical interaction between bending segments of dislocations and filled electron traps, electrostatic interaction between bending segments of dislocations and filled electron traps, and piezoelectrically-induced detrapping of electrons from filled electron traps. Subsequently, the capture of detrapped electrons moving in the conduction band in hole centres gives rise to the light emission or the light energy produced during the electron-hole recombination excites the activator centres. The mechanism of elastico ML discussed in this paper may be helpful in preparing new elastico mechanoluminescent materials useful in mechano-optical devices.

Keywords : Mechanoluminescence, Triboluminescence, $SrAl_2O_4$:Eu, Elastic sensors.

1.INTRODUCTION

Elastico-mechanoluminescence (EML) is the phenomenon of cold light emission induced by elastic deformation of solids [1, 2]. Whereas nearly 50% of all inorganic salts and organic molecular solids show mechanoluminescence (ML) during their fracture, only a few solids exhibit ML during their elastic and plastic deformation. The examples of elastico mechanoluminescent materials are: X or γ-irradiated 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 and certain variety of rubbers have also been reported to be elastico mechanoluminescent. The EML intensity of $SrAl_2O_4$:Eu, ZrO_2:Ti, $Ca_2Al_2SiO_7$:Ce, etc. is so intense that it can be seen in day light with naked eye. As EML is the non-destructive phenomenon and the diminished EML intensity caused by deformation can be recovered by irradiation, the EML has attracted the attention of a large number of researchers The present paper reports the elecrron trapping model for the elastico-mechanoluminescence of crystals.

2.ELECTRON TRAPPING, ELECTRON BOMBARDMENT AND OTHER MECHANISMS OF MECHANOLUMINESCENCE

Although several mechanisms of ML excitation have been proposed [1,3], the two basic mechanisms that are applicable to a large number of materials are: (i) electron capture or electron trapping (ET) mechanism, and (ii) electron bombardment (EB) mechanism. In addition to these two mechanisms, the chemiluminescence (CL) mechanism and some other mechanisms are also applicable to a limited number of solids. Whereas, ET mechanism becomes possible by the motion of dislocations and vacancies, the EB mechanism becomes possible by the electric field generated by piezoelectricity, charged dislocations and other processes of polarization. In CL mechanism, the recombination of free radicals produced during deformation with the defects gives rise to the light emission. Furthermore, in the case of fracture, the chemical reaction between the freshly created surfaces and surrounding gases causes the light emission.

In the following paragraphs, the electron trapping mechanism for the elastico ML of crystals is discussed.

3. ELECTRON TRAPPING MECHANISMS OF THE ELASTICO-ML OF CRYSTALS

Fig. 1(I, ii, iii, iv) shows the schematic diagrams for the mechanism of the EML of: (i) γ-irradiated alkali halide crystals, (ii) ZnS:Mn crystals, (iii) $SrAl_2O_4$:Eu crystals and (iv) CdS crystals at liquid nitrogen temperature.

(i) Elastico ML of X or γ-irradiated alkali halide crystals

In the expansion region of the dislocations or dislocation segment the energy gap between the bottom of the energy level of the F-centres and dislocation band is reduced, and it becomes comparable with the thermal energy kT of the electrons [1]. Therefore, the F-centre electrons near the dislocation segments or dislocation lines jump from F-centre level to the dislocation band, and thus the F-centre electrons are captured by the dislocation segments bending near the F-centres. With this concept the elastico ML in X- or γ -irradiated alkali halide crystals can be understood with respect to the following steps [2]:

(i) The elastic deformation causes bending of the dislocation segments.

(ii) The bending dislocation segments capture electrons from the interacting F-centres lying in the expansion region of the dislocation segments.

(iii) The captured electrons from F-centres move with the dislocation segments and they also drift along the axes of dislocations.

(iv) The recombination of dislocation-captured electrons with the holes lying in the dislocation donor band gives rise to the light emission characteristic of the halide ions in V_2 centres or other hole centres.

Thus, The elastico ML of X or -irradiated alkali halides is caused by ET mechanism.

(ii) Elastico ML of ZnS:Mn crystals

The elastico ML in ZnS:Mn crystals can be understood with respect to the following steps [2]:

(i) The deformation of ZnS:Mn crystals produces piezoelectric field because the crystal – structure of ZnS is non-centrosymmetric [2]. In ZnS:Mn the piezoelectric field near Mn^{2+} ions may be high due to the change in local structure.

(ii) Because of the decrease in the trap-depth due to the piezoelectric field or due to the band bending the detrapping of electrons from filled-electron traps takes place, and therefore, electrons reach the conduction band.

(iii) The electrons reaching the conduction band may recombine with the holes trapped in the defect centres or they may jump to the valence band and subsequently energy may be released non-radiatively.

(iv) The energy released non-radiatively during electron-hole recombination may be transferred to the Mn^{2+} ions whereby Mn^{2+} ions may get excited.

(v) The de-excitation of excited Mn^{2+} ions gives rise to the light emission characteristic of the Mn^{2+} ions.

Thus, the elastico ML in ZnS:Mn crystals is caused by the ET mechanism. In case of EB mechanism, the ML intensity should increase rapidly with the increasing stress or the piezoelectric field F, because the mean free path of free electrons increases linearly with increasing F and consequently the probability p of impact ionization increases as, $p = p_0 \exp(-b/F)$, where p_0 and b are constants. Practically, at a given strain rate, the elastico ML intensity increases linearly with the increasing stress or the piezoelectric field F. This result supports the ET mechanism in the elastico ML of ZnS:Mn crystals.

(iii) Elastico ML of Rare Earth Doped Srontium Aluminates and other Persistent Luminescent crystals

The steps involved in the EML emission of $SrAl_2O_4$:Eu crystals are as given below[2] :

(i) The application of pressure produces local piezoelectric field in the crystals whereby the piezoelectric field near activator ions may be high due to the change in local structure.

(ii) The local piezoelectric field may reduce the trap-depth of the carriers or it may cause the band bending.

(iii) In the case of decrease in trap-depth of the carriers, thermal detrapping of the carriers may be produced. In the case of band bending the trapped charge carriers may tunnel to the respective band, that is, the trapped electrons may tunnel to the conduction band.

(iv) Subsequently, the electrons moving in the conduction band may be captured in the excited state of the activator ions located adjacent to the bottom of the conduction band whereby excited ions, for example, excited Eu^{+2} ions are produced.

(vi) The de-excitation of excited activator ions may give rise to the light emission characteristic of the excited ions.

The mechanism of EML described for $SrAl_2O_4$:Eu crystals is also applicable to other rare earth doped persistent luminescent crystals as the mechanism of the photoluminescence of these crystals is similar to that of the $SrAl_2O_4$:Eu crystals. In this way, the elastico ML of rare earth doped strontium aluminate and other rare earth doped persistent luminescent crystals occurs due to the ET mechanism.

(iv) Elastico ML of CdS crystals at low temperatures

When a CdS crystal cooled at liquid nitrogen temperature and exposed to ultraviolet radiation is gently tapped, then a green flash of light is emitted from the body of crystal [4]. It is shown that impulses involving energies of 750 ergs. or smaller are sufficient to excite the effect. The squeezing of the crystal by slowly applying a unilateral compression does not excite emission for the pressure up to the breaking point of the crystal.Also, the setting the crystal into ultrasonic vibration does not cause emission. One reliable method of excitation is to drop spheres of known weight from a calibrated height to the surface of the crystal. It is found that the impact is most effective when applied parallel to the c-axis. When examined in detail, the flash appears to consist of streamers of light emanating from the point of impact and radiating predominantly in a direction parallel to the c-axis. The photographic evidence indicates that the flashes are composed of most, if not all, of the spectral lines which comprise edge emission. In addition, it is found that the emission is polarized with the F-vector perpendicular to the c-axis, in accord with the direction of polarization observed for normal edge emission, indicating that a Γ_7 to Γ_9 transition appears to be operative. Repeated tapping produces a flash for each tap. Of the order of a thousand flashes may be obtained from a well-stimulated crystal by tapping more or less uniformly over the whole surface. After the stimulation is exhausted, the crystal can be re-activated by a brief illumination, and the process of obtaining multiple flashes by tapping can be repeated. The green luminescence in the elastico ML of ultraviolet-irradiated CdS crystals at low temperatures is intrinsic luminescence [5] and the red luminescence is related to some impurity and it is extrinsic luminescence. The exposure of ultraviolet light causes filling of shallow traps in the CdS crystal kept at liquid nitrogen temperature and subsequently, the tapping produces piezoelectric field in a direction suitable for the EML excitation. Later on, the transition of electron from the conduction band to the valence band gives rise to the intrinsic edge emission.

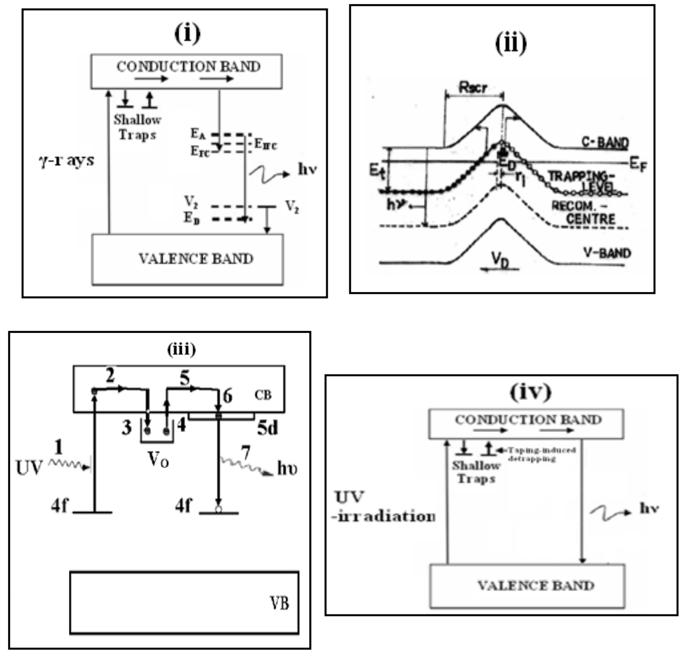

Fig.1 Schematic diagrams for the mechanism of the EML of: (i) γ-irradiated alkali halide crystals, (ii) ZnS:Mn crystals, (iii) $SrAl_2O_4$:Eu crystals (1-excitation of Eu^{2+}, 2- electron movement in CB, 3-electron trapping, 4-electron release, 5-electron movement in CB, 6-electron-capture at 5d of Eu^{2+}, 7- light-emission, and V_o is the oxygen vacancy), and (iv) CdS crystals at liquid

4.CONCLUSION

The mechanism of the intrinsic and extrinsic elastico-mechanoluminescence of several crystals are studied. It is found that, although EML can be either intrinsic or extrinsic, their EML is caused by the electon trapping mechanism. The mechanism of elastico ML discussed in this paper may be helpful in preparing new elastico mechanoluminescent materials useful in mechano-optical devices.

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