EFFECTS OF HYDROSTATIC PRESSURE ON TRIBOLUMINESCENT MATERIALS

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Hydrostatic pressures have been applied to ZnS: Cu and ZnS: Mn crystals in such a way to produce an electric polarization higher than that arising from the electric fields needed to excite Electroluminescence. It has been shown that these pressures do not excite Triboluminescence and do not perturb the fluorescent emission or the afterglow curve of the u.v. excited phosphors. These results seem to give a further experimental evidence that the mechanism responsible for Triboluminescence is related to the presence of dislocations.

TRIBOLUMINESCENCE (TL) is a form of conversion of mechanical energy into light, that can be realized in certain organic and inorganic substances. Since its discovery, different methods have been used to excite TL. The authors of reference (1) developed a technique that allows one to observe the stress-strain curves both in hard and fragile materials, with an effective sensitivity in the strain measurements of about 1000 Å. Cyclic deformations were also carried out on phosphors in order to observe the details of TL yield. It has shown that TL is an irreversible process for any value of the applied stress and two mechanisms are advanced for TL production: impact of dislocations with luminescent centres, and unpinning of dislocations from luminescent centres.

A different interpretation of TL has been given recently by Meyer, Obrikat and Rossberg. In particular they emphasize that ZnS doped crystals excited with mechanical and electric waves of the same frequency give emission spectra with very similar features, as already pointed out by Alzetta, Chella and Santucci. Since ZnS is piezoelectric, the above authors conceive the TL of zinc sulphide crystals as triboinduced Electroluminescence (EL).

However, a recent report on the electrical and optical properties of hexagonal ZnS crystals has allowed a preliminary theoretical analysis of this hypothesis. In the paper it is shown that a hydrostatic pressure of about $10^2$ kg/cm$^2$ is needed to produce the same electrical polarization as that of an electric field of the order of $10^5$ V/cm. Since electric fields of $10^5$ V/cm are already large enough to produce EL, we have tested if TL emission occurs when pure hydrostatic pressures up to $10^4$ kg/cm$^2$ are applied on ZnS crystals. The aim of this communication is to report these results.

We have obtained rapid compressions and dilatations of different intensity and rate by dropping appropriate weights along a guide. We have employed different fluid pressure media such as silicone oil, n-pentane-isoamyl alcohol, and distilled water. Seal problems have been resolved by means of suitable teflon and soft rings. Background luminescence from the transparent glass window has been carefully avoided. Quartz pick-ups of the model 401 (SLM PZ-14) and 6211 of the Kistler line has been used to measure the pressure intensity. The rate in the pressure change has been followed in a dual trace plug-in oscilloscope.
In the first trace, we have observed the light emission through the glass window and a Job-Yvon monochromator using a RCA 6810A phototube with a conventional low-noise circuit. Measurements have been performed on ZnS: Cu single crystals grown by sublimation from an improved flow method and on ZnS: Mn crystalline powder. The observation of birefringence in a polarizing microscope, the position of the absorption edge and X-ray examinations showed that both monocrystal and powder phosphor had hexagonal structure.

Let us first examine the effect of hydrostatic pressure on monocrystals. When ZnS: Cu monocrystals are introduced in the pressure cell, we do not observe any TL emission for pressure steps (1 ms rise time) up to $10^4$ kg/cm$^2$. The magnitude of the external field $E_0$ which leads to the same polarization as a pressure $p$ in wurtzite type crystals, is

$$E_0 = \frac{2(d_{31} + d_{33}) \varepsilon_r \varepsilon_0}{\varepsilon_0 (\varepsilon_r - 1)} p$$

where $\varepsilon$ is the vacuum permittivity, $\varepsilon_r$ is the static dielectric constant, and $d_{ij}$ are the non-vanishing piezoelectric coefficients. Using for $\varepsilon_r$ the experimental value $9$ of 9.6, for $d_{31}$ and $d_{33}$ the values of $10^{-11}$ Coul./Kg and $3.3 \times 10^{-11}$ coul./kg measured in reference (4), for $p$ the value of $10^4$ kg/cm$^2$ we obtain

$$E = 6.7 \times 10^6 \left[\frac{V}{cm}\right]$$

Since the value (1) is at least two orders of magnitude higher than the electric fields needed to produce EL$^6$, we conclude from the previous analysis that it is unlikely to consider TL as triboinduced EL.

We now examine the effect of hydrostatic pressure on crystalline powders. When ZnS: Mn powder is freely suspended in the fluid medium, we indeed observe a strong TL emission during loading, as first found by Alzetta, Minnaja and Santucci$^{10}$. We emphasize, however, that light emission does not occur at all when the ZnS: Mn powder is pasted with silicon grease on the glass surface, or arranged in a pressure-transmitting cap. The light observed by us and by the authors of reference (10) when ZnS: Mn powder is freely suspended in the fluid medium is not due, therefore, to pure hydrostatic pressure, but to impact stress with the piston, crushing etc.

In order to investigate further the effects of a piezoelectric field, we have applied pressure pulses both during the fluorescence and during the afterglow of doped ZnS excited by means of a Wood lamp, in order to test if the Gudden-Pohl$^{11}$ or the Déchène$^{12}$ effects occur. A typical experimental result is reported in Fig. 1, where no transient flashes of light are observed when pressure pulses (lower trace) are imposed or removed.

While the experiments with hydrostatic pressure above described do not produce TL, it is known that small shearing stresses are able to produce a TL emission$^1$ and a strong flash of light if they are applied during the fluorescence or the phosphorescence of u.v. excited phosphors.$^{13}$ We wish now to discuss the basic difference between hydrostatic and shearing stresses effects.

If we consider TL as triboinduced EL, we cannot, evidently, explain this different behaviour. If, on the contrary, the mechanisms of TL production advanced in (1) are accepted, we can explain the above effects. We notice that a uniform pressure $p$ changes the band edges with respect to one another$^{14}$. The shift with pressure in the absorption edge in ZnS can be estimated from the results reported in references (15) and (16) to be

$$\frac{d\Delta E_g}{dp} = 9 \times 10^{-6} \text{ [ev/kg cm}^{-2}\text{]}$$

This effect is so small that it has no importance for ionization energy. On the other hand no effect on dislocations can be ascribed to a pure hydrostatic pressure. In fact, according to (17), an external stress produces per unit length of a dislocation whose tangent vector is $t$, the force

$$F_j = t \cdot \Delta \hat{G}$$

where the $i$th component of the vector $\hat{G}$ is given by
We recall that $b_j$ are the components of the Burgers vector and $\sigma'_{ij}$ is defined as

$$\sigma'_{ij} = \sigma_{ij} + p \delta_{ij}$$

Since the hydrostatic pressure $p$ is equal to

$$p = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

it turns out that $\sigma', \text{ and therefore } F'$, vanishes if the Burgers vector is a lattice translation vector. As a matter of fact, a real crystal has always grow-in dislocations connected to stacking faults. The Burgers vector of a partial dislocation has an 'anomalous' edge-component since the spacing of the atomic plane on either side of a stacking fault is different from the spacing in the unfaulted part of the crystal. The effect of such a component in the Burgers vector is ordinarily ignored in the description of a partial dislocation. Indeed there is, up to now, no experimental evidence of motion of dislocation due to hydrostatic pressure. For example, in reference (18) it is shown that the application on aluminium crystals of high and sufficiently fast hydrostatic pressure at elevated temperature does not cause dislocation to climb.

Since hydrostatic pressure has a negligible effect both on ionization energy of doping

**FIG. 1.** Oscillogram showing no momentary flash of light when pressure pulses (1 msec rise time; $8 \times 10^3 \text{ kg/cm}^2$ height) are imposed during the fluorescence and the afterglow (upper trace) of u.v. excited ZnS phosphors. The oscillogram refers both to ZnS:Cu single crystals and to ZnS:Mn crystalline powder.

impurities and on dislocations, we can conclude that the experimental results obtained can be interpreted on the basis of the model explained in reference (1). Furthermore strong experimental evidence that TL cannot be attributed to electric polarization fields is obtained.

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On a soumis différents monocristaux de ZnS : Cu et de ZnS : Mn à des pressions uniformes jusqu'à $10^4$ Kg/cm$^2$. On n'a observé ni emission de Triboluminescence, ni effets de perturbation sur la fluorescence ou la phosphorescence u.v. des mêmes phosphores. A la lumière de nos précédents études, ces résultats nous amènent à conclure que la piezoelectricité des matériaux ne joue pas un rôle fondamental dans leur Triboluminescence.