Evidence of electron multiplication in microcrystalline ZnS

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Abstract. The criterion for electron multiplication in the presence of an electric field is established for microcrystalline materials by comparing and analysing the additional light peaks on the background of photoluminescence and electroluminescence. The experimental result shows that the electron multiplication process is rather dominant in microcrystalline ZnS(Cu, Eu, Cl) when an electric field is present. In an electrical field of 2×10^4 V cm^{-1} the multiplication coefficient is estimated to be larger than 22.

1. Introduction

Because of the complication arising from contacts between crystal grains and between electrodes and crystal grains, the electron multiplication process in microcrystalline materials is difficult to identify. In this work an analysis of the luminescence kinetics under the excitation of a probe light pulse on the background of photoluminescence and electroluminescence is carried out. The electron multiplication process is shown to be a rather dominant mechanism in microcrystalline ZnS(Cu, Eu, Cl) in the presence of an electric field.

2. Experimental results

Purified ZnS powder was doped with 10^{-3} weight per weight CuCl and 10^{-4} weight per weight EuCl$_3$ and sintered in an HCl stream at 1020°C for about one hour. The sintered microcrystalline material was immersed in castor or silicone oil and sandwiched between two parallel-plate electrodes separated by 50 μm, one of which was transparent. If an alternating voltage (here in sinusoidal form) is applied to the electrodes, the cell gives electroluminescence with a broad spectral band. It peaks at 540 nm. This luminescence band can be excited by ultraviolet light too.

A triggered krypton flash-lamp with filter UG-1 was used as a pulsed-light excitation source and a high-pressure mercury lamp, GS-1000, as a constant-light excitation source.

3. Luminescence kinetics in comparison with experimental results

The relation between instantaneous luminescence intensity and the intensity of the

exciting light pulse was derived on the basis of the bimolecular recombination mechanism. For simplicity we choose the following conditions.

(i) The material has only a single type of luminescence centres with density M, and also a single type of trapping centres with density ν. The recombination cross section of the conduction electrons with the luminescence centres and the capture cross section of the conduction electrons by the trapping centres are σ_0 and σ_1.

(ii) The rise time of the photoluminescence of this material is much longer than the duration of the exciting light pulse, Δt.

(iii) The excitation level is low.

If the material was excited by pulses with frequency f_m and photon energy large enough to ionise the luminescence centre, then the density of ionised luminescence centres, or the density of the electrons in conducting band, Δn, under the excitation of one of the exciting light pulses with intensity E, can be expressed as

$$\Delta n = D\chi E \Delta t M \tag{1}$$

in which χ is the coefficient of absorption for the exciting light, and D a coefficient of proportionality. The instantaneous luminescence peak intensity J_m can be expressed as

$$J_m = \sigma_0(\Delta n + \Delta n_c)(\Delta n + N_c)/[\sigma_1\nu + \sigma_0(\Delta n + \Delta n_c)]. \tag{2}$$

Here Δn_c and N_c are considered as the residual densities of the ionised luminescence centres and the conducting electrons before the application of light pulse. They obviously depend on the light pulse frequency f_m and its intensity E, due to the finite decay time of luminescence. But if small f_m and E are used we have

$$\sigma_0(\Delta n + \Delta n_c) \ll \sigma_1\nu. \tag{3}$$

From (1) and (3) and neglecting the term $\Delta n_c N_c$ it follows that

$$J_m = \beta E^2 + CE \tag{4}$$

or

$$J_m/E = \beta E + C \tag{5}$$

in which the parameters β and C are

$$\beta = (\sigma_0/\sigma_1\nu)(D^2\chi^2\Delta t^2 M^2), \tag{6}$$

$$C = (\sigma_0/\sigma_1\nu)(D\chi\Delta t M)(\Delta n_c + N_c). \tag{7}$$

The above analysis and equation (4) can be verified by experiment. Figure 1 shows the experimental results with $\Delta t = 0.5\ \mu s$ and for f_m values of 1 and 5 per second. The photoluminescence rise time measured is larger than 3 s under the highest available excitation level. Thus if $f_m \leqslant 1$ per second, equation (4) can be used to express the relation between instantaneous intensity of the luminescence and the excitation intensity of the light pulse.

Now we consider a more general case in which the crystal has had a background luminescence excited by a constant light, or by an electric field, with ionised luminescence centre density n and conducting electron density N. Using an analysis analogous to that
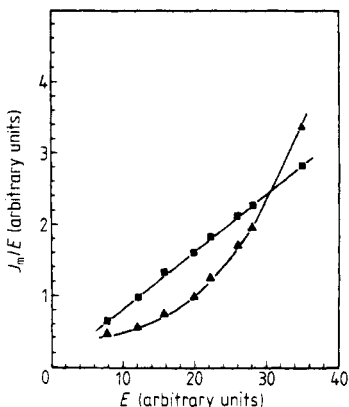
Figure 1. Measured J_m and E expressed as J_m/E against E, for $f_M = 5\,s^{-1}$ (triangles) and $1\,s^{-1}$ (squares).
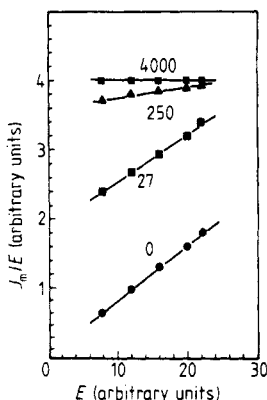

Figure 2. J_m and E measured at different background photoluminescence values J, in relative units (given on curves).
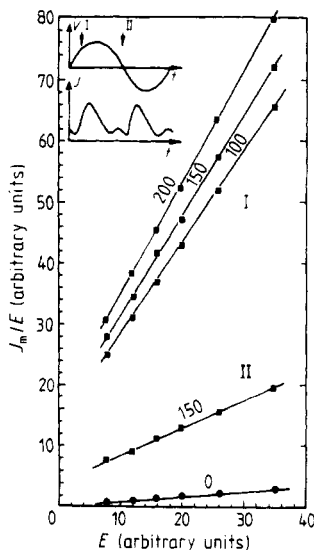

Figure 3. J_m and E measured at different background electroluminescence levels (the applied voltages (in V(RMS)) on the cell are given on the curves) and without background luminescence. The light pulses are fixed at two phase positions I and II, as indicated in the inset. The upper inset shows the applied voltage wave and the lower gives the brightness wave form of the electroluminescence.

given before, the extra instantaneous luminescence peak induced by a light pulse can be expressed as

$$J_m = \sigma_0(n + \Delta n + \Delta n_c)(N + \Delta n + N_c)/[\sigma_1\nu + \sigma_0(n + \Delta n + \Delta n_c)]$$
$$- nN/(\sigma_1\nu + \sigma_0 n). \tag{8}$$

Neglecting the terms including n_c and N_c equation (8) can be simplified as follows:

$$J_m = \sigma_0[\Delta n^2 + \Delta n(n + N)]/(\sigma_1\nu + \sigma_0 n) \tag{9}$$

or

$$J_m = \beta^* E^2 + C^* E \tag{10}$$

or

$$J_m/E = \beta^* E + C^* \tag{11}$$

in which

$$\beta^* = \sigma_0 D^2\chi^2\Delta t^2 M^2/(\sigma_1\nu + \sigma_0 n) \tag{12}$$

and

$$C^* = \sigma_0 D\chi\Delta t M(n + M)/(\sigma_1\nu + \sigma_0 n). \tag{13}$$

Equations (12) and (13) show that when the background luminescence increases (this means that n and N increase) the parameter β^* decreases and C^* increases. If the background luminescence is sufficiently intense we have $n \gg \Delta n$. Then the first term of the right-hand side of equation (10) will be much smaller than the second term. Equation (10) obeys the following relation:

$$J_m = C^*E. \tag{14}$$

Equations (11) and (14) can be examined experimentally.

Figure 2 shows the experimental results for background luminescence, J, of 0, 27 and 250 in arbitrary units. The factor β^* decreases and C^* clearly increases. For high background luminescence, $J = 4000$, the relationship between J_m and E approximates to equation (14).

4. The criteria for electron multiplication processes in crystals

Applying an alternating sinusoidal voltage of 100 V (RMS) and 40 Hz to the electrodes of a cell, causes it to emit electroluminescence. The brightness wave form is shown in figure 3. Because the intensity of electroluminescence varies with the voltage applied to the electrodes, the probe light pulse ought to be used at a constant phase position of the voltage, for example at I shown in figure 3, and the electroluminescence at this point can be considered as a mean background luminescence as before. Equation (11) is still valid but with modified factors which reveal the influence of the electric field. We have

$$J_m/E = K_1\beta^*E + K_2C^* \tag{15}$$

in which β^* and C^* can be considered as the factors of a mean background luminescence at a constant phase of the voltage. The factor K_1 is the influence of the electric field on conduction electrons excited from luminescence centres by the light pulse. The factor K_2 involves the influence of the field on C^*.

Now we consider the influence of the inhomogeneity of the electric field on the factor β^*. Because a high field arises only in a small region in crystal, according to the result we obtained in (1) and (2), β^* must be smaller in this region. This means that, in spite of the inhomogeneity of the luminescence, the factor β^* of all regions of the cell under the action of electric field must be smaller than β for the cell without an applied field.

Only if the light-pulse-induced conduction electrons in the electrical field are multiplied will the factor K_1 be larger than 1, and if $K_1 \gg 1$, even if $\beta^* < \beta$, the factor $K_1\beta^*$ can still be larger than β. The criterion for the electron multiplication process is $K_1 > 1$. $K_1\beta^* > 1$ can be used as a criterion of the electron multiplication process too, because it is convenient to compare the factors $K_1\beta^*$ and β by experiment.

5. Experimental proof for the electron multiplication process in crystal

Figure 3 gives the experimental results. The probe light pulse is fixed at phase position I as shown in the inset of figure 3. The relationship between J_m and E is measured at 100, 150 and 200 V (RMS). This relationship can be expressed well by equation (15). Comparing the experimental values it is found that

$$K_1\beta^*_{V=100} = 22\beta_{V=0} \qquad \text{or} \qquad K_1 > 22. \tag{16}$$

This means that, in this situation, the electron multiplication process is acting as a dominant mechanism in the crystal.

6. Conclusion

Because the electric field alternates at different phase positions of voltage in the crystal, it is found that if the light pulse is fixed at the position I before the primary peak of the brightness wave, then $\beta^* = \beta^*_{max}$ can be obtained. Figure 3 shows $\beta^*_{V=150}$ at the phase position II; at this position the applied voltage is nearly zero. The conduction electrons are influenced by the internal polarisation field, which gives in general the second peak of the brightness wave forms. Of course, at this instant the electron multiplication is weaker than that at position I. So the factor $K_1\beta^*_{V=150}$ at position II is much smaller than that at position I. By means of this analysis we can examine the multiplication process at different phases of a time-dependent electric field.

The results for different voltages are also given in figure 3. As expected the factor $K_1\beta^*$ increases with voltage. In figure a quantitative estimation of β^* as a function of voltage and the distribution of electric field in crystals should be investigated. At any rate, the lowest evaluation of the multiplication coefficient of electrons in our case is larger than 22 at a mean electric field intensity of $2 \times 10^4\,\mathrm{V\,cm^{-1}}$.

References

Xurong Xu 1955 *Rep. Acad. Sci. Sov. Union* **103** 585
Xurong Xu and Rensong Dai 1963 *Dig. Rep. Ann. Conf. Phys. Soc. China* p 109