Excitation mechanism of cathodoluminescence of oxisulfides

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This paper presents the first investigation on the diffusion of electron-hole pairs (generated under cathode-ray excitation) as a function of activator concentration in the oxisulfides $L_2O_2S:Tb^{3+}$ with $L =$ Gd, La, or Y. The diffusion was studied by measuring the energy efficiency of the Tb^{3+} luminescence as a function of the accelerating voltage of the primary electrons. For all three host lattices investigated the diffusion length of the electron-hole pairs is found to be essentially constant at low activator concentrations (dominated by the killer concentration); then the diffusion length decreases with increasing activator concentration (increasing transfer to activators); at still higher concentrations, where the energy efficiency starts to decrease (concentration quenching), the diffusion length increases again. As the quantum yields with 254-nm excitation show hardly any decrease, the increasing diffusion length indicates a new mechanism, leading to concentration quenching. From our experiments we determined the cross section for excitation of a Tb^{3+} ion by a thermalized electron-hole pair to be about 30×10^{-16} cm^2.

I. INTRODUCTION

Recently we used the dependence of the radiant (or energy) efficiency of phosphors under cathode-ray excitation on the accelerating voltage of the primary electrons to study degradation effects[1] and to determine the influence of surface recombination on the excitation spectrum in the x-ray ultraviolet (XUV) region.[2] In the present investigation we use this dependence to study the relation between the diffusion length of electron-hole (e-h) pairs and the activator concentration in oxisulfides ($L_2O_2S:Tb^{3+}$ with $L =$ Gd, La, or Y).

Upon cathode-ray excitation of a phosphor, a primary electron produces a number of "thermal" e-h pairs in a cascade process.[3,4] These thermalized e-h pairs can excite activators, recombine nonradiatively at bulk killers, or diffuse to the surface of the phosphor grains followed by radiationless recombination.[2,5,6] The quantum efficiency for the energy transfer from thermalized e-h pairs to the activators is called the transfer efficiency, η_t.[1,7] Once an activator is excited, it decays radiatively with efficiency η_{act}.[7] The radiant efficiency of a phosphor is proportional to $\eta_t \eta_{act}$, the product of transfer and activator efficiency. The dependence of the radiant efficiency on the activator concentration is generally explained by a transfer efficiency increasing with the activator concentration at low concentrations and activator efficiency decreasing with the activator concentration at high concentrations.[8,9]

The dependence of the radiant efficiency of oxisulfides on the activator concentration has been the subject of a number of experimental and theoretical studies.[10-13] Ozawa and Hersh[10,11] used a random-walk model for the thermalized e-h pairs, but needed some unrealistic assumptions, as was discussed by Morehead.[12] In the present investigation the diffusion length of the e-h pairs is determined for the first time as a function of activator concentration. The values obtained are in clear contra-

diction with the assumptions of Ozawa and Hersh.[10,11] From our measurements we derived a cross section for excitation of the activator by the e-h pairs. Finally, in the high-concentration region an increase of the diffusion length with activator concentration is found, which might point to a new mechanism leading to concentration quenching.

II. EXPERIMENTAL

Gadolinium, lanthanum, and yttrium oxisulfide powders activated with terbium were prepared by the usual ceramic techniques.[14] The mean diameter of the grains was measured to be about 10 μm. The actual Tb^{3+} concentration was determined from chemical analysis [inductive coupled plasma–optical emission spectroscopy (ICP-OES)]. The external radiant efficiencies under cathode-ray excitation were measured at room temperature in a demountable tube as a function of accelerating voltage. Low excitation densities were used to avoid luminescence saturation effects. The diffusion length of the e-h pairs, l, the reduced surface recombination velocity, S, and the thickness of a possible dead layer at the surface of the grains, d, were obtained following the method described in Ref. 2. The asymptotic value at high accelerating voltages was scaled relative to a standard phosphor[15] and used as the "bulk" radiant efficiency. It should be noted that a one-dimensional model for the diffusion of the e-h pairs is used (see Ref. 2 and references cited therein). The range of the primary electrons (see Fig. 1) is much smaller than the grain diameter. The diffusion lengths determined in our experiments (see Sec. V and Fig. 3) are more than 2 orders of magnitude smaller than the grain diameter. Therefore a one-dimensional description of the diffusion fully suffices. Quantum yields under 254-nm excitation were determined at room temperature using the experimental setup described in Ref. 16.
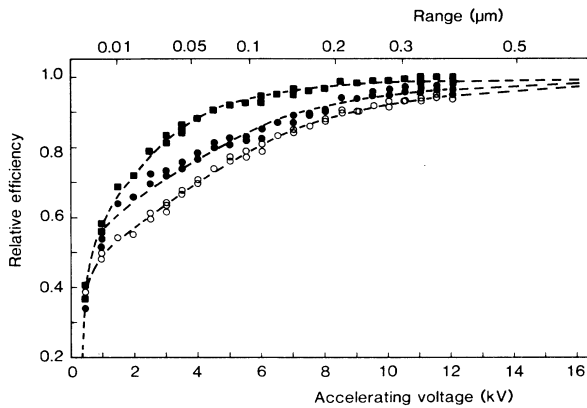
FIG. 1. Relative radiant efficiency (normalized to the bulk radiant efficiency) of Gd_2O_2S with various Tb^{3+} concentrations as a function of accelerating voltage (bottom) and range (top) of the primary electrons. Solid circles indicate a Tb^{3+} concentration of 0.01 mol %; solid squares indicate a Tb^{3+} concentration of 0.3 mol %; and open circles indicate a Tb^{3+} concentration of 10 mol %. The dashed curves result from the fits (see text).

III. RESULTS

Figure 1 shows the relative radiant efficiency as a function of the accelerating voltage for three Gd_2O_2S samples with various Tb^{3+} concentrations. As the range of the primary electrons increases with the accelerating voltage, the number of generated e-h pairs that diffuse to the grain surface and recombine there nonradiatively decreases. Consequently, the steeper the increase of the radiant efficiency with the accelerating voltage, the smaller is the energy loss due to diffusion of e-h pairs. From Fig. 1 it can be seen that at a Tb^{3+} concentration of 0.3 mol % at the diffusion of e-h pairs to the surface followed by radiationless recombination is less important than at a Tb^{3+} concentration of 0.01 mol %, whereas at a concentration of 10 mol % diffusion plays again a more important role. The dashed curves are the results from the fits,[2] which are in good agreement with the experimental data. For
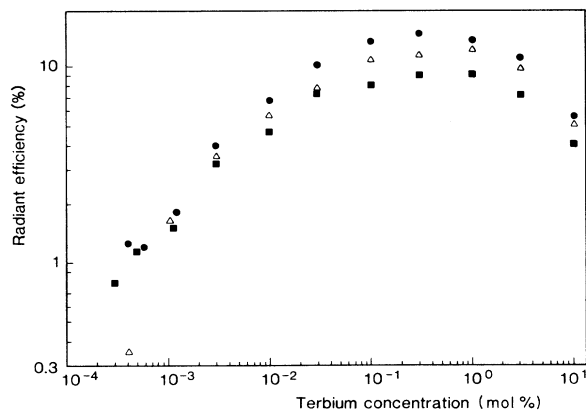

FIG. 2. Radiant "bulk" efficiency of Gd_2O_2S (solid circles), La_2O_2S (solid squares), and Y_2O_2S (triangles) as a function of the Tb^{3+} concentration.
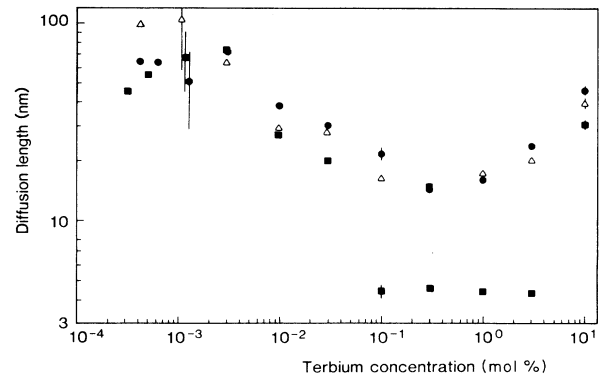

FIG. 3. Diffusion length of e-h pairs as a function of the Tb^{3+} concentration for Gd_2O_2S (solid circles), La_2O_2S (solid squares), and Y_2O_2S (triangles). The error bars at the Tb^{3+} concentrations of 0.001, 0.1, and 10 mol % are typical for the low-, medium-, and high-concentration region.

each sample typically 50–100 experimental data points were used in the fit.

The values for the radiant "bulk" efficiencies obtained from the fits are plotted in Fig. 2 as a function of the Tb^{3+} concentration for Gd_2O_2S, La_2O_2S, and Y_2O_2S. It should be noted that, whereas the emission spectra of Gd_2O_2S and La_2O_2S do not change with Tb^{3+} concentration, the emission spectra of Y_2O_2S show a slight change as a function of the Tb^{3+} concentration (see Ref. 17 and references cited therein). Therefore we corrected the radiant efficiency of these samples by multiplying by the ratio of integrated photon- and energy-corrected emission spectra, taking this ratio equal to 1 at high Tb^{3+} concentrations. At a Tb^{3+} concentration of 10 mol %, the radiant efficiency under cathode-ray excitation has decreased to 0.38 (Gd_2O_2S), 0.44 (La_2O_2S), and 0.42 (Y_2O_2S), respectively, of its maximum value. For Gd_2O_2S no decrease of the quantum yield under 254-nm excitation was observed, whereas for La_2O_2S and Y_2O_2S a decrease to 0.85 and 0.90 of the maximum value was found at a Tb^{3+} concentration of 10 mol %.

In Fig. 3 the diffusion lengths are given as a function of the Tb^{3+} concentration. The large errors at low Tb^{3+} concentration are due to the fact that at these activator concentrations the luminescence at low accelerating voltage is very weak. The general features observed are a constant diffusion length at low activator concentrations, followed by a decrease with increasing concentration and an increase with the concentration at still higher activator concentrations. The values found for the reduced surface recombination velocity S varied between 0.5 and 1.4, quite independently of host lattice and activator concentration. The values obtained for the thickness d of the dead layer at the surface of the grains varied between 0.2 and 1 nm.

IV. THEORETICAL INTERPRETATION

In this section we will derive a relation between the radiant efficiency and the diffusion length. Then we will

give an expression for the cross section for excitation of an activator ion by an e-h pair.

In a simple energy flow model[1,7] the bulk lifetime of the e-h pairs, τ, is given by

$$\tau = \frac{1}{\alpha N + \beta} , \tag{1}$$

where N is the activator concentration, α is the rate constant of energy transfer of e-h pairs to activator ions, and β is the rate of energy transfer of e-h pairs to bulk killers. The efficiency for energy transfer from e-h pairs to activators, η_t, is then given by

$$\eta_t = \frac{\alpha N}{\alpha N + \beta} . \tag{2}$$

Indicating the maximum attainable radiant efficiency with η_{max}, one can write for the radiant efficiency η_{cr},

$$\eta_{cr} = \eta_{max} \eta_t \eta_{act} . \tag{3}$$

Using the relation between lifetime of the e-h pairs, τ, and diffusion length l,[5,6]

$$l = \sqrt{D\tau} , \tag{4}$$

manipulation of Eqs. (1)–(3) yields

$$1 - \frac{\eta_{cr}}{\eta_{max}\eta_{act}} = \frac{\beta}{D} l^2 , \tag{5}$$

where D is the diffusion constant of the e-h pairs. In the region of low activator concentrations η_{act} is constant and is taken equal to unity. So by plotting $1 - \eta_{cr}/\eta_{max}$ on a double-logarithmic scale versus the diffusion length l, we can determine β/D.

For the diffusion constant one can write

$$D = \frac{1}{3} l_{coll} v_{th} , \tag{6}$$

where v_{th} is the thermal velocity of the e-h pairs and l_{coll} is the mean free path of the e-h pairs between the collisions during the diffusion process. Using Eq. (6) we can write for the cross section σ for excitation of an activator ion by and e-h pair

$$\sigma = \frac{\alpha}{v_{th}} = \frac{1}{3} \frac{\alpha}{D} l_{coll} = \frac{1}{3} \frac{\alpha}{\beta} \frac{\beta}{D} l_{coll} . \tag{7}$$

The ratio of α and β can be obtained directly from the present experiments. Manipulation of Eqs. (2) and (3) yields

$$\frac{\eta_{max}\eta_{act}}{\eta_{cr}} - 1 = \frac{\beta}{\alpha} \frac{1}{N} . \tag{8}$$

So by plotting the radiant efficiency as $\eta_{max}/\eta_{cr} - 1$ on a double-logarithmic scale versus the activator concentration N, we can determine β/α from the low-concentration region.

It should be noted that for the determination of the cross section σ, the first two variables on the right-hand side of Eq. (7) are determined experimentally in the present investigation; in the next section an estimate is made for the collision length l_{coll}.

V. DISCUSSION

At low activator concentrations the diffusion length of the e-h pairs is determined by the bulk killers (see Fig. 3). At higher concentrations the activators form a competing recombination channel: The radiant efficiency starts to increase (see Fig. 2) and the diffusion length decreases (see Fig. 3). For activator concentrations between 0.1 and 1 mol % the radiant efficiency and the diffusion length are almost constant, the latter being about 14 nm. For La_2O_2S the diffusion length levels off at an extremely low value of about 4 nm. At activator concentrations above 1 mol % the radiant efficiency starts to decrease and the diffusion length starts to increase again.

The diffusion lengths found are much smaller than the average grain diameter, which was measured to be about 10 μm. This is in clear contradiction with the hypothesis of Ozawa and Hersh,[10,11] who assumed the diffusion length to be larger than the grain diameter. This assumption was also adopted by Morehead.[12] A diffusion length larger than the grain size is essential in theories as presented by Ozawa and Hersh[10] and by Morehead[12] to explain the dependence of the efficiency on the grain size as observed by Ozawa and Hersh. They found for Y_2O_2S activated with 0.01 mol % Eu^{3+}, that the efficiency of grains with an average diameter of 20 μm was a factor of about 3.4 larger than the efficiency or grains with an average diameter of 3 μm.[10,11] We note that by careful preparation without grinding or sieving the phosphor powder, we obtained Y_2O_2S powders activated with 0.01 mol % Tb^{3+} with average grain diameters ranging from 4 to 20 μm and efficiencies that were equal within the experimental accuracy.

In Fig. 4 we have plotted the reduced radiant efficiency as a function of the diffusion length as suggested by Eq. (5). The numerical values obtained in the interpretation hardly depend on the values used for the maximum attainable radiant efficiency η_{max}; they were chosen 10% higher than the maxima actually obtained. It is remarkable that the radiant efficiency as a function of the
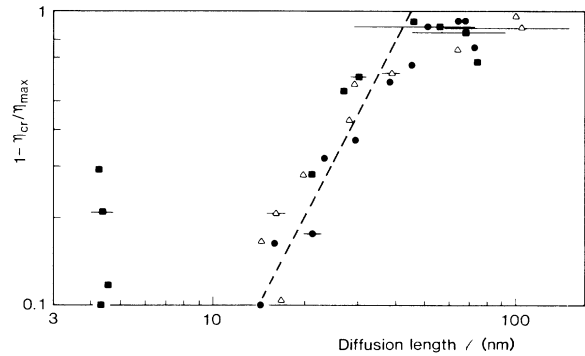

FIG. 4. Reduced radiant efficiency (see text) as a function of the diffusion length of e-h pairs for Gd_2O_2S (solid circles), La_2O_2S (solid squares), Y_2O_2S (triangles). The error bars are indicated for the same points as in Fig. 3. The dashed line has a slope of 2 (see text).

diffusion length can be described by Eq. (5) with $\eta_{act}=1$ for all activator concentrations, except, of course, for the minimum values of the diffusion length found for La_2O_2S. The decrease in radiant efficiency at high activator concentrations is therefore due to a decrease in transfer efficiency rather than in activator efficiency. The fact that there is hardly any decrease in the quantum yields under 254-nm excitation also points towards a constant activator efficiency. A second conclusion that can be drawn from Fig. 4 is that, even at high Tb^{3+} concentrations, the diffusion constant is quite independent of this concentration. Consequently, the increase in diffusion length and decrease in radiant efficiency should be ascribed to a decrease in cross section for excitation of activators by e-h pairs. It is, however, rather puzzling that this occurs under cathode-ray excitation only and not under 254-nm excitation, for at this wavelength excitation takes place via the host lattice only. This was verified by measuring the excitation spectra for various Tb^{3+} concentrations. The lowest $5d$ band of the Tb^{3+} ions has its maximum at about 300 nm and its intensity increases with the Tb^{3+} concentration. In the oxisulfides investigated this band is clearly separated from the host lattice excitation at 254 nm. Moreover, the absorption coefficient at the maximum of this $5d$ band increased with the Tb^{3+} concentration, whereas the absorption at 254 nm was independent of the Tb^{3+} concentration.

From the dashed line in Fig. 4 we obtained a value of 5×10^{10} cm^{-2} for β/D, leading to a diffusion length of 45 nm for the unactivated material (killers only). In Fig. 5 the inverse radiant efficiency is plotted as a function of the activator concentration as suggested by Eq. (8). From the dashed line in Fig. 5 we obtained a value of 2.3×10^{18} cm^{-3} for β/α.

A lower limit of the diffusion length is the mean free path of the e-h pairs between the collisions during the diffusion process. The optical-phonon mean free path in silicon is about 5 nm,[18] whereas published values for amorphous SiO_2 range between 1.3 and 3.5 nm.[19] As these materials are quite different, the optical-phonon mean free path for oxisulfides is likely to be also in this range. Moreover, the diffusion length found for La_2O_2S levels off at about 4 nm for Tb^{3+} concentrations between
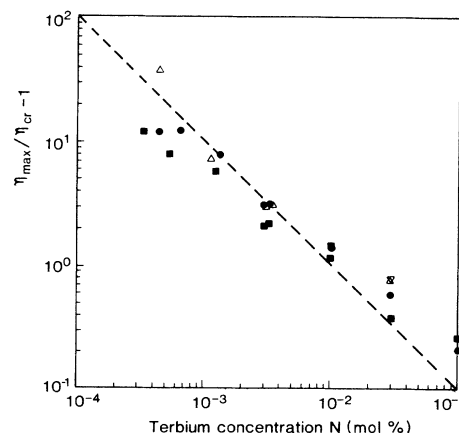

FIG. 5. "Inverse" radiant efficiency (see text) as a function of the Tb^{3+} concentration for Gd_2O_2S (solid circles), La_2O_2S (solid squares), and Y_2O_2S (triangles). The dashed line represents a linear dependence.

0.1 and 3 mol %. Therefore a value of 4 nm for the mean free path of the e-h pairs in oxisulfides seems a reasonable estimate. Using Eq. (7) we find for the cross section for excitation of a Tb^{3+} ion by an e-h pair a value of 30×10^{16} cm^2.

VI. CONCLUSIONS

In the present investigation the diffusion length of e-h pairs has been determined for the first time as a function of the activator concentration in phosphors. Moreover, from the experimental data the cross section for excitation of an activator by an e-h pair was determined to be about 30×10^{-16} cm^2.

In the materials investigated the onset of concentration quenching of the efficiency under cathode-ray excitation seems to be caused by a decrease in transfer efficiency rather than by a decrease in activator efficiency. The underlying mechanisms are not yet clear and will be the subject of future investigations.

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