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Trapping mechanism in the afterglow process of the rare-earth activated Y_2O_2S phosphors

Eiichiro Nakazawa[a,*], Hajime Yamamoto[b]

[a]Department of Electronic Engineering, Kogakuin UniversityNakano-machi, Hachioji-shi, Tokyo 192-0015, Japan
[b]School of Bionics, Tokyo University of Technology Katakura, Hachioji-shi, Tokyo 192-0982, Japan

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Abstract

Phosphorescence properties are investigated in Y_2O_2S phosphors doped with rare-earth (lanthanoid, Ln) ions. Luminescence afterglow with a decay time of several ten milliseconds is observed at room temperature in the phosphors activated by Nd, Sm, Eu, Dy, Ho, Tm, Er, and Yb. The depths (thermal activation energies) of the traps causing the afterglow are measured with the transient luminescence method.

It is concluded that the excited electron and the hole in the conduction and valence bands are trapped separately in the states (impurity levels) located in the vicinity of the Ln^{3+} ion. The trapping depths of the level range from 0.3 to 1.1 eV and are dependent on the electron affinity of the Ln^{3+} ion estimated from the energy difference between the $4f^{n+1}$ and the $4f^n$ configurations in the 4f shell of the ion.
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1. Introduction

Rare-earth oxysulfides doped with rare-earth ions, for example, $Y_2O_2S:Eu^{3+}$, $La_2O_2S:Eu^{3+}$, $Gd_2O_2S:Pr^{3+}$, and $Gd_2O_2S:Tb^{3+}$, are phosphors used in various fields [1]. Trapping of the excited electrons and holes prolongs the luminescence afterglow of phosphors and often causes faults in the image quality of display devices. On the other hand, Yamamoto and Kano [2] found that the Y_2O_2S phosphors activated by rare-earth (lanthanide, Ln) ions show thermoluminescence and that the traps formed by the codopant Pr^{3+} or Tb^{3+} ions play an important role also in the luminescence process under continuous excitation.

This report investigates the trapping mechanism of the excited electrons and holes in the conduction band and the valence band in the rare-earth (lanthanide, Ln) activated Y_2O_2S phosphors. The thermal activation energies of the trapped carrier, i.e., trapping depths, are measured by the transient thermo-luminescence method [3] and analyzed by the recently proposed theoretical method for obtaining the activation energy of traps related to rare-earth ions [4]. In case of the persistent phosphorescence of the Eu^{2+}-activated strontium aluminate phosphors codoped with another Ln^{3+} ion, the excited electron is trapped "within the 4f shell" of the codopant Ln^{3+} ion. [4] In the present cases however, it concluded that the excited electrons and holes are trapped "in the vicinity" of the activator Ln^{3+} ion.

2. Experimental

The samples of Y_2O_2S microcrystalline powder doped with 1 mol% of the rare-earth element, Ln (= Ce, Pr, Nd, Sm (2 mol%), Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb), were prepared by firing the mixed material of rare-earth oxides, S, Na_2CO_3 and a small amount of K_2PO_4 at 1150 °C in a quartz crucible [2]

The thermal activation energy of the trapped carrier, i.e., trap depth, is measured by the method of transient thermo-luminescence (TTL) [3] as follows.

The sample is excited periodically by a UV (254 nm) square wave of 0.4 Hz under slowly varying temperature ranging from 80 to 430 K, and the relative intensities of the luminescence afterglow, $I(T, t_s)/I(T, 0)$, are measured at

*Corresponding author. Tel.: +81 42 75 3908.
E-mail address: enakazaw@rd6.so-net.ne.jp (E. Nakazawa).

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five sampling points of time t_s (= 10, 33, 100, 325, and 1000 ms), after the cessation of excitation in each cycle. Then the TTL curve, i.e., the temperature dependence of the afterglow intensity at a sampling time ($I(T, t_s)$/ $I(T, 0)$ vs. T), makes a peak at temperature T_m for each trap. At the peak, the sampling time t_s and the thermal activation probability of a trapped carrier per unit time, a (= $s\exp[-E_t/kT]$), are related to each other as $cat_s = 1$, where k is the Boltzmann constant and cs is a modified frequency factor. Then the depth of the trap (activation energy), E_t, is given by the following relation [3]:

$$Et = kT_m \ln(cst_s). \quad (1)$$

Therefore, both E_t and cs can be obtained from the slope and the intercept of the line on the plots of the observed $1/T_m$ vs. $\ln(t_s)$. The emission intensity is monitored through the glass filters and a monochromator set at the spectral peak of the characteristic emission of each Ln^{3+} ion.

3. Experimental Results

Fig. 1 shows the observed TTL curves, i.e. $I(T, t_s)/I(T, 0)$ vs. T, of the $Y_2O_2S:Ln^{3+}$. The intensities of the main peaks of the TTL curves are more than 20% of the initial value, i,e., $I(T, 0)$, for $t_s = 10$ ms for Ln = Sm, Eu, Dy, Ho, Er,

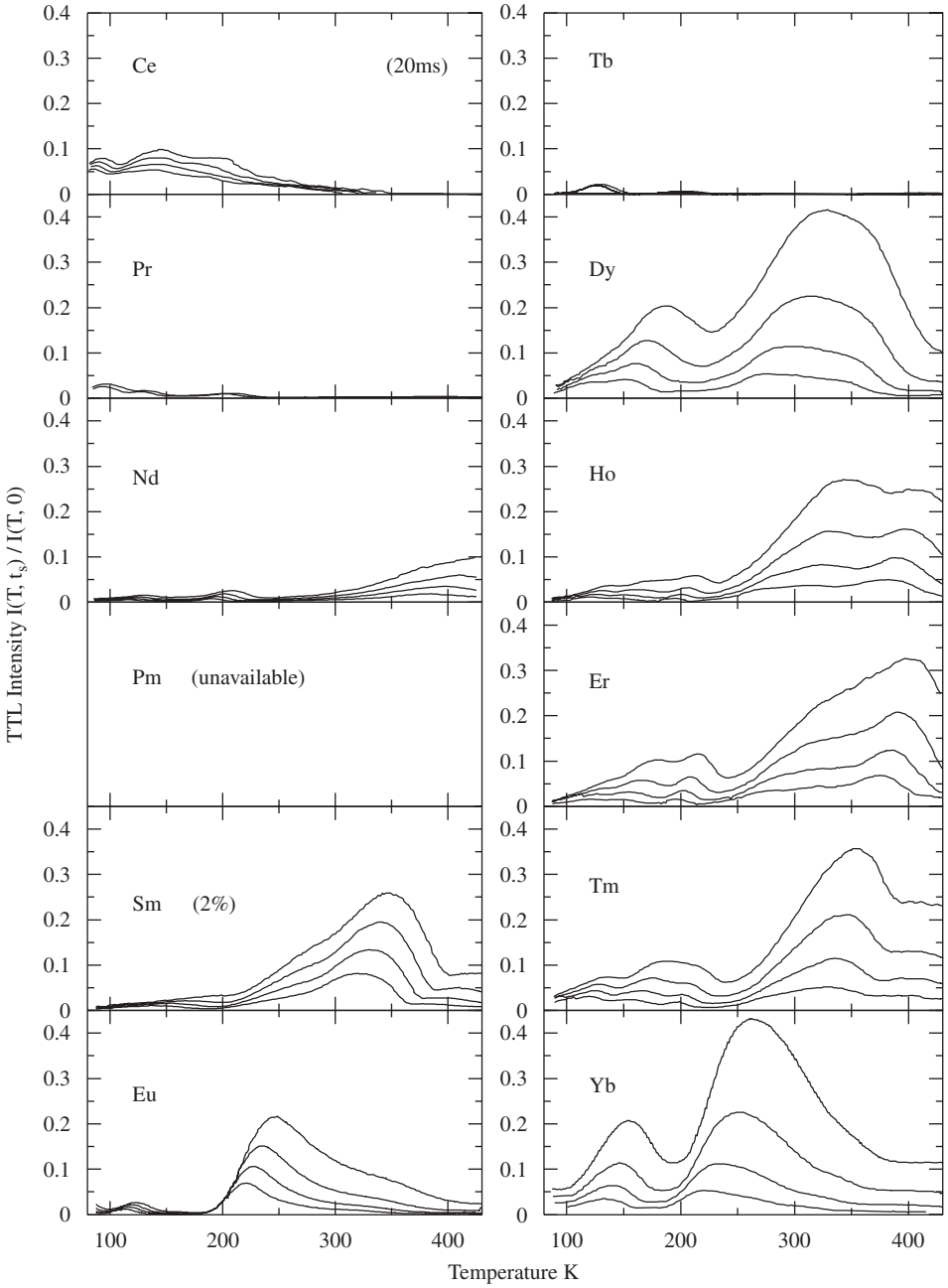

Fig. 1. Transient thermo-luminescence (TTL) curves of $Y_2O_2S:Ln$ at sampling time $t_s = 10$, 33, 100 and 325 ms from top to bottom. The glow intensity $I(T, t_s)$ at a temperature T for a sampling time t_s is normalized to the intensity under the excitation, i.e., at $t_s = 0$, at the same temperature.

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