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Concentration quenching of persistent luminescence

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ABSTRACT

The concentration quenching of persistent luminescence was investigated. $SrAl_2O_4:Eu^{2+},Dy^{3+}$ was taken as an instance. We proposed a model to explain the phenomenon. The concentration quenching of Eu^{2+} is attributed to competitive capturing of electrons with traps, while the concentration quenching of Dy^{3+} is interpreted by electron tunneling among traps.

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1. Introduction

Luminescence is the light emission subsequently occurring after absorption of energy from an excitation source. Luminescence usually involves a process where energy absorption occurs but the emission process is delayed. In general, it is divided into fluorescence, phosphorescence and persistent luminescence, depending on the characteristic time of decay [1]. Fluorescence is based on spin-allowed transitions and thus exhibits short radiative relaxation decay time (10^{-9}–10^{-3} s). Radiative relaxation processes with decay time in the range of (10^{-3}–1 s) are called phosphorescence, commonly due to the spin-forbidden nature of transitions [1,2]. Persistent luminescence refers to the type of luminescence which remains for a long time (from seconds to hours) after the removal of excitation sources [1,3,4].

Luminescent materials (i.e., phosphors) are usually composed of a transparent solid inorganic host and a small amount of intentionally doped activator(s) [5,6]. If the concentration of an activator is higher than an appropriate value (typically several mol%), the emission intensity of the phosphor mostly will be decreased. This is called concentration quenching. The origin of this phenomenon is due to energy transfer between activator ions [7]. Energy transfer can bring the excitation energy far from the site where the absorption occurred and the energy finally sinks at quenching sites. Energy transfer is not effective at low concentrations, because the average distance between activator ions is too large and the energy transfer probability is low. Energy transfer accounts for the concentration quenching of fluorescence and phosphorescence. However, when it comes to persistent luminescence, this model should be revised in view of the difference between persistent luminescence and fluorescence/phosphorescence. Indeed, the optimal concentration of fluorescence (OCF) is usually different from the optimal concentration of persistent luminescence (OCPL). Some reference data are tabulated in Table 1. These facts indicate that OCPL is always lower than OCF. The existing theory cannot explain this discrepancy as well as the concentration quenching of auxiliary ions (e.g., Dy^{3+} and Tm^{3+} in Table 1). In this study, we proposed a model to depict the mechanism of concentration quenching of persistent luminescence. We took $SrAl_2O_4:Eu^{2+},Dy^{3+}$ as an instance, but the whole discussion is valid for all Eu^{2+}-doped persistent phosphors.

2. Experimental

Powder samples of $Sr_{1-x-y}Al_2O_4:xEu^{2+},yDy^{3+}$ were synthesized by the high-temperature solid-state reaction method. The starting materials were $SrCO_3$ (A.R.), Al_2O_3 (A.R.), Eu_2O_3 (4N) and Dy_2O_3 (4N). The raw materials were stoichiometrically weighed and thoroughly mixed in an agate mortar with 8 mol% of H_3BO_3 (A.R.) as flux. The mixed powders were then calcined in corundum crucibles at 1300 °C for 3 h in a H_2(15%)+N_2(85%) atmosphere. Finally the samples were cooled down to room temperature and ground again.

The crystalline phase of the synthesized phosphors were checked by a powder X-ray diffractometer (XRD, Beijing PGENERAL XD-2, 36 kV, 20 mA, Cu Kα, 10–70°, 6°/min). The photoluminescence spectra were recorded by a Hitachi F-7000

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Table 1
Optimal concentrations of four selected persistent phosphors.

Phosphors	OCF of Eu (x)	OCPL of Eu (x)	OCPL of Dy/Tm (y)
$SrAl_2O_4$:xEu^{2+}, yDy^{3+}	0.06[a]	0.01[b]	0.02[b]
$(Sr,Ca)_2MgSi_2O_7$:xEu^{2+},yDy^{3+}	0.03[c]	0.01[d]	0.03[d]
$Ca_2Si_5N_5$:xEu^{2+}, yTm^{3+}	0.02[e]	0.01[f]	0.01[f]
$Sr_3Al_2O_5Cl_2$:xEu^{2+}, Tm^{3+}	0.15[g]	0.015[h]	0.03[h]

[a] Ref. [8].
[b] Ref. [9].
[c] Ref. [10].
[d] Ref. [11].
[e] Ref. [12].
[f] Ref. [13].
[g] Ref. [14].
[h] Ref. [15].

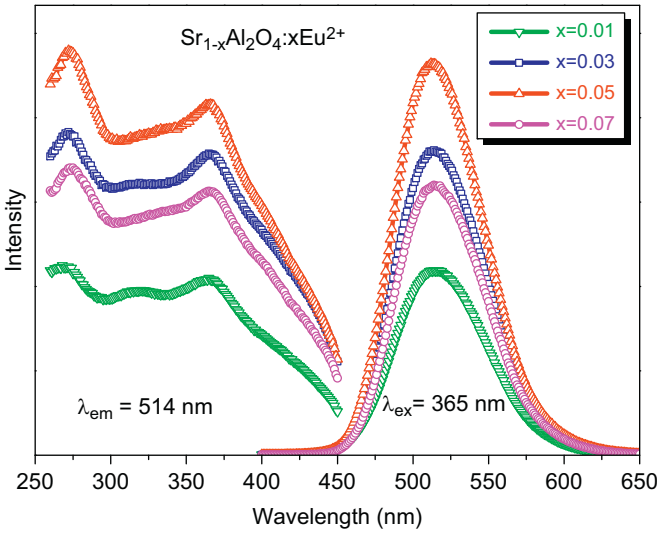

Fig. 1. Emission and excitation spectra of $Sr_{1-x}Al_2O_4$:xEu^{2+} phosphors.

Fluorescence Spectrophotometer. The decay curves were measured by a GFZF-2A single-photon counter system. Prior to the decay measurement, all samples were excited by a 15 W mercury lamp (254 nm) for 1 min.

3. Results and discussion

Fig. 1 shows the emission and excitation spectra of $Sr_{1-x}Al_2O_4$:xEu^{2+} phosphors. The emission and excitation are attributed to the $4f \leftrightarrow 5d$ transitions of Eu^{2+}. The optimal concentration of Eu^{2+} was determined to be ca. 0.05, which agrees with Ref. [8].

Fig. 2 shows the persistent luminescence intensity as a function of time after 1 min excitation with a mercury lamp. Clearly, it is best to keep the concentrations of Eu^{2+} and Dy^{3+} below 0.01 and 0.03, respectively. These are also in line with Ref. [9].

The persistent luminescence for these compositions has been analyzed by curve fitting. The decay curves can be fitted successfully based on the following double exponential equation [16,17]:

$$I(t) = I_0 + A\exp\left(\frac{-t}{\tau_1}\right) + B\left(\frac{-t}{\tau_2}\right) \quad (1)$$

where $I(t)$ and I_0 are the persistent luminescence intensities at time t and 0; A and B are constants, and τ_1 and τ_2 are the decay time for the short and long decay component, respectively. The fitting results of

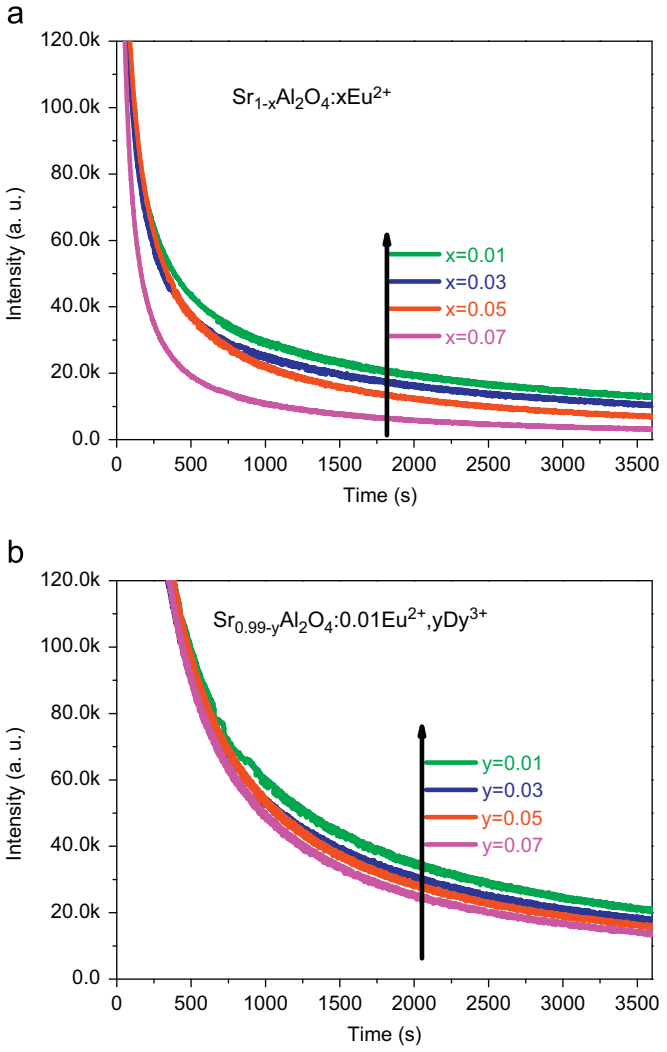

Fig. 2. Persistent luminescence at room temperature of (a) $Sr_{1-x}Al_2O_4$:xEu^{2+} and (b) $Sr_{0.99-y}Al_2O_4$:$0.01Eu^{2+}$,yDy^{3+}.

Table 2
Fitting results of the decay curves of $Sr_{1-x}Al_2O_4$:xEu^{2+}.

x	τ_1 (s)	τ_2 (s)	Adj. R^2
0.01	31.0	506.8	0.99054
0.03	31.8	482.1	0.98966
0.05	37.2	457.6	0.99243
0.07	24.7	275.9	0.99242

$Sr_{1-x}Al_2O_4$:xEu^{2+} and $Sr_{0.99-y}Al_2O_4$:$0.01Eu^{2+}$,yDy^{3+} are tabulated in Tables 2 and 3, respectively. The values of τ_2 in the tables imply that

- higher concentrations of Eu^{2+}or Dy^{3+} result in shorter decay time;
- although Dy^{3+} can enhance the persistent luminescence intensity of $SrAl_2O_4$:Eu^{2+}, it cannot increase the decay time.

The photoluminescence and the persistent luminescence (not shown) spectra of $SrAl_2O_4$:Eu^{2+},Dy^{3+} have practically identical band shape and width. Although there are two Sr^{2+}/Eu^{2+} sites in the host [18], these do not result in the discordance of OCF and OCPL of Eu^{2+}.

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