

An outlook of rare-earth activated persistent luminescence mechanisms

HAN Shaochun (韩少春), WANG Yuhua (王育华)*, ZENG Wei (曾巍), CHEN Wenbo (陈文波)

(Key Laboratory for Special Function Materials and Structure Design of the Ministry of Education, School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China)

Received 8 December 2014; revised 28 December 2015

Abstract: By studying energy transfer and persistent energy transfer properties in Eu, Mn co-doped calcium aluminate CaAl_2O_4 , it was found that traditional persistent luminescence mechanisms had difficulty in explaining persistent energy transfer property between Eu^{2+} and Mn^{2+} ions. Based on this question, a mechanism was suggested in which vibrational energy levels were considered as a Morse potential, and trap centers were distinguished into barriers and wells. Then, this phenomenon was explained by allowing energy transfer and persistent energy transfer could have different preference to different vibrational energy levels. Properties of trap centers were also discussed by using the concept of Madelung energy.

Keywords: persistent luminescence; rare earths; phosphor; aluminate

Long persistence phosphor (LPP), also known as long lasting phosphor (LLP), can emit photons damply for several minutes or hundreds of days after excitation was stopped^[1]. It is worth noticing that its glow duration is orders of magnitudes larger than fluorescence lifetime^[2]. For its passive emission features, it can be used for display devices, emergency beacon, optical storage, radiation detection and so on^[3–12].

Most important LPP host matrix materials such as ZnS, CaAl_2O_4 , SrAl_2O_4 , are ionic crystals, which are known as being formed by static electricity forces between cations and anions. This implies that it is natural to consider static electricity interactions between host ions and dopant atoms' electrons, which are playing crucial role in LPP. At this point, distances are natural parameters of these interactions. For example, Clabau et al. employed this kind of point of view and suggested that distribution by distance of co-dopant cations around luminescence centres can strongly influence luminescent properties^[13]. Their work shows for LPP traps there are more parameters than just a depth, and suggests that distance should also be counted in. This implies that thermoluminescence (TL) curves would not be sufficient in describing LPP traps because these curves are actually non-injective—mapping two parameters depth and distance to only one parameter which is temperature here. So there is some necessity to find other means to supplement TL. In our work, by analyzing energy transfer (ET) phenomenon of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Mn}^{2+}$, it is found that emitting spectra can be expected for this purpose.

As we all know, both ET and persistent luminescence

are interesting phenomena which widely exist among various luminescent materials. While the former is deemed to lie on electric and magnetic multipole interactions and already had a semi-quantitative expression^[14], the latter is considered as a consequence of charge carrier trapping-detrapping process and only has "human imagination" by now^[15].

For ET can convert donor activator atoms' high energy photons into acceptor atoms' low energy photons to produce some new peaks at relative long-wave side in Photoluminescence (PL) spectrum, it can alter emitting colors of phosphors. If this process was imported to LPPs, it presumably could change their AG (afterglow, the more exact terminology "persistent luminescence"^[15] is not used here for avoiding being confused with another terminology "photoluminescence") spectra. Our group also did several work based on this idea, and found that it did work for $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}$ by co-doping Mn^{2+} ion as acceptor^[16], but it hardly worked for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ with Mn^{2+} playing the role of acceptor also^[17].

No further explanation is given for these contrasts at the first time until inspired by concept "persistent energy transfer" (PET), which was emphasized by Brito et al.^[15]. The possibility PET which might be a dissimilar phenomenon when comparing to ET was not considered at that time.

When analyzing PL and AG spectra of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Mn}^{2+}$ in this work, Nd^{3+} ion was absent to reduce complicity. It is found that some modifications of traditional persistent luminescence mechanisms are needed to explain this distinction of PL and AG spectra. If this

Foundation item: Project supported by the National Natural Science Foundation of China (51372105)

* **Corresponding author:** WANG Yuhua (E-mail: wyh@lzu.edu.cn; Tel.: +86-931-8912772)

DOI: 10.1016/S1002-0721(16)60021-2

analysis made some sense in some level, also one additional result would be gained which suggests that PL emitting spectra can be used to explore AG property as long as that LPP's PL and AG spectra are made a comparison.

1 Experimental

$\text{CaAl}_2\text{O}_4:0.1 \text{ mol.}\% \text{Eu}^{2+}, 1.5 \text{ mol.}\% \text{Mn}^{2+}$ phosphor was synthesized by a solid-phase reaction between CaCO_3 , Al_2O_3 , Eu_2O_3 and MnCO_3 . No flux was added for reducing complicacy. All raw materials were analytical reagent, and wet ground in an agate mortar for 30 min with absolute ethyl alcohol added. Then they were loaded to an alumina crucible and pulled into a tube furnace. Under atmosphere of $1\text{H}_2:10\text{N}_2$, they were calcined at 1400°C for 4 h. The reaction product was dry ground up to powder in a porcelain mortar for later testing. All spectra were measured by an FLS-920T spectrometer (Edinburgh Instruments Ltd.) at room temperature.

2 Discussion

Based on our group's previous result, the peaks near 539 nm were caused by Mn^{2+} ion which acted as an acceptor while Eu^{2+} acted as a donor^[17]. In Fig. 1 curve marked "10 s" was PL emitting spectrum of $\text{CaAl}_2\text{O}_4:0.1 \text{ mol.}\% \text{Eu}^{2+}, 1.5 \text{ mol.}\% \text{Mn}^{2+}$ phosphor obtained after the sample was excited for 10 s at 360 nm, and correspondingly, 2 min for the "2 min" one. Comparing these curves, it can be seen that heights of this peaks near 539 nm seldom changed (1.03 times) while the one near 444 nm grew almost twice as much as 1.87 times from the 10 s to the 2 min.

Let's mark these time-dependent photon number intensity with $n(t)$ s and write some relationship equations:

$$n_{\text{Em}}(t, T) = n_{\text{PL}}(t) + \eta_{\text{ET}} \cdot n_{\text{ET}}(t) + n_{\text{AG}}(t, T) \quad (1)$$

$$n_{\text{Ex}} \cdot n_{\text{Ex}}(t) = n_{\text{PL}}(t) + n_{\text{ET}}(t) + n_{\text{Trapping}}(t) \quad (2)$$

$$\frac{\partial N_{\text{Occupied traps}}(t)}{\partial t} = n_{\text{Trapping}}(t) - n_{\text{AG}}(t, T) \quad (3)$$

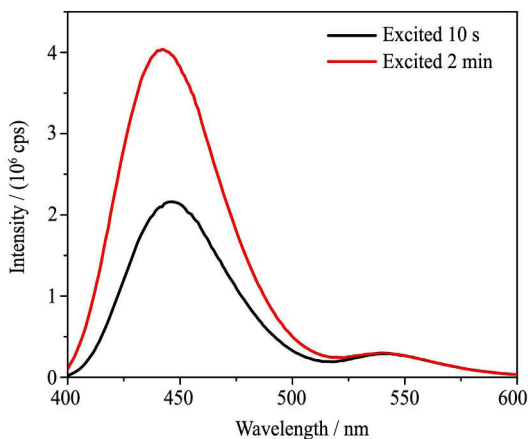


Fig. 1 PL emitting spectra of $\text{CaAl}_2\text{O}_4:0.1 \text{ mol.}\% \text{Eu}^{2+}, 1.5 \text{ mol.}\% \text{Mn}^{2+}$ phosphor, being excited at 360 nm for 10 s and 2 min respectively

$$n_{\text{AG}}(t, T) = \alpha(T) \cdot N_{\text{Occupied traps}}(t) + \eta_{\text{ET}} \cdot n_{\text{PET}}(t) \quad (4)$$

In Eq. (1), $n_{\text{Em}}(t, T)$ means spectrometer recorded emitting intensity which is a function of variables t for time and T for temperature. Then $n_{\text{PL}}(t)$ means intensity of direct photoluminescence which is Eu^{2+} emission near 444 nm in our case, and $n_{\text{ET}}(t)$ is ET rate from Eu^{2+} to Mn^{2+} , and η_{ET} is quantum efficiency bringing ET excited Mn^{2+} to emitting, and $n_{\text{AG}}(t)$ is intensity of afterglow. In addition, the independent variables of the left side of the equal sign are time and temperature. When the right side was regarded as one function, its independent variables are also time and temperature. Eq. (1) expresses components of emitting intensity which are made up by PL, ET and AG, while Eq. (2) enumerates distributary of excitation photon stream. In Eqs. (3) and (4), $N_{\text{Occupied traps}}$ denotes number of already occupied traps.

Eq. (1) gives a decomposition of emitting photons detected by the PL spectrometer by separating them into constituents with different physical properties, which are photoluminescence, energy transfer and afterglow respectively. And efficiency issue of the energy transfer process is expressed by the coefficient η_{ET} . Eq. (2) gives a decomposition of the phosphor received excitation photons which are emitted by the PL spectrometer's xenon lamp. These photons act on photoluminescence, energy transfer and afterglow processes, respectively. Efficiency issue of excitation is expressed by the coefficient η_{Ex} . Eq. (3) gives a relation between the trap release rate and the current net trap number intensity. It is a linear relation. Eq. (4) decomposes the afterglow photons into the temperature and time dependent thermoluminescence part and the time dependent energy transfer part. Efficiency issue of the energy transfer process is expressed by the coefficient η_{ET} .

When applying partial derivative of time to both sides of Eqs. (1), (2), and (4), the results are Eqs. (5), (6), and (7) as follows:

$$\frac{\partial n_{\text{Em}}(t, T)}{\partial t} = \frac{\partial n_{\text{PL}}(t)}{\partial t} + 0 + \frac{\partial n_{\text{AG}}(t, T)}{\partial t} \quad (5)$$

$$0 = \frac{\partial n_{\text{PL}}(t)}{\partial t} + 0 + \frac{\partial n_{\text{Trapping}}(t)}{\partial t} \quad (6)$$

$$\frac{\partial n_{\text{AG}}(t, T)}{\partial t} = \alpha(T) \cdot \frac{\partial N_{\text{Occupied traps}}(t)}{\partial t} + \eta_{\text{ET}} \cdot \frac{\partial n_{\text{PET}}(t)}{\partial t} \quad (7)$$

Through inserting Eqs. (3) to (7), finally Eq. (8) is obtained as follows:

$$\frac{\partial n_{\text{AG}}(t, T)}{\partial t} = \alpha(T) \cdot (n_{\text{Trapping}}(t) - n_{\text{AG}}(t, T)) + \eta_{\text{ET}} \cdot \frac{\partial n_{\text{PET}}(t)}{\partial t} \quad (8)$$

Zero in Eq. (5) comes from the fact in Fig. 1 that ET peaks near 539 nm of two curves do not change while time goes on, so as the zero of the right hand side of Eq. (6). Zero in left hand of Eq. (6) comes from the fixed excitation beam of the spectrometer. These zeros are criti-

Download English Version:

<https://daneshyari.com/en/article/1258323>

Download Persian Version:

<https://daneshyari.com/article/1258323>

[Daneshyari.com](https://daneshyari.com)