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Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

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To cite this Article Duan, Xiaoxia , Huang, Shihua , You, Fangtian , Xu, Zheng , Teng, Feng and Yi, Lixin(2009) 'Electrooptical characteristics of nanoscale and bulk long persistent phosphor $\text{SrAl}_2\text{O}_4 : \text{Eu}, \text{Dy}$ ', Journal of Experimental Nanoscience, 4: 2, 169 – 176

To link to this Article: DOI: 10.1080/17458080902912313

URL: <http://dx.doi.org/10.1080/17458080902912313>

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Electrooptical characteristics of nanoscale and bulk long persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}$, Dy

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(Received 5 November 2008; final version received 17 March 2009)

Nanoscale and bulk $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} were prepared, respectively, by auto-combustion of citrate gelatin (gel) and high temperature solid state method. The crystalline structure was examined by X-ray diffraction. The morphological and size aspects of nanoscale sample were carried out with transmission electron microscopy. Spectral shift of nanoscale phosphor was confirmed by measuring excitation and emission spectra. The current-voltage characteristic and optical power were measured with a Keithley source meter 2410. Ionic conductivity plays the leading role when the sample is not irradiated by light and electron conductivity should be in the charge of the current gain when the sample is irradiated by light. The result showed that light irradiation simultaneously increased the luminescence intensity and the current. The current increasing range of nanoscale phosphor is smaller than that of bulk phosphor. It was further concluded that the excited state energy levels of emission centre overlap partly with the conduction band of host crystal. Otherwise, surface effect was analysed deeply by comparing the decay curves of nanoscale and bulk $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} .

Keywords: electrooptical characteristic; nanoscale; surface effect

1. Introduction

Long persistent phosphor absorbs energy from sunlight and releases it in the darkness. As a kind of environment-friendly material, it has very high commercial value. Many researchers have focused on it [1–4]. Compared with sulphide long persistent phosphor, alkaline earth aluminate long persistent phosphor is much stabler and brighter and has a much longer decay time. It is tending to replace the outdated sulphide [5–7]. However, many aspects of the persistent luminescence mechanism still remain unclear and the presented theories are even contradictory [8,9].

In recent years, many researchers have begun to pay more and more attention to nanoscale phosphor because it has some characteristics different from bulk material [10–13]. In this work we report, for the first time, the electrooptical characteristics

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of $\text{SrAl}_2\text{O}_4:\text{Eu}$, Dy , which are helpful for probing and understanding the mechanism in depth.

2. Experiments

2.1. Synthesis of nanoscale and bulk $\text{SrAl}_2\text{O}_4:\text{Eu}$, Dy

$\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ (99.99%), $\text{Dy}(\text{CH}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ (99.99%), analytically pure $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and citric acid were used as starting materials. Deionised water was used as solvent. Ammonia was used to adjust pH value.

$\text{Eu}(\text{CH}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$, $\text{Dy}(\text{CH}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in water on the nominal composition of $\text{Sr}_{0.97}\text{Al}_2\text{O}_4:\text{Eu}_{0.01}$, $\text{Dy}_{0.02}$, two times citric acid of all metal ions was added. The pH value was adjusted to 7. The resultant transparent solution was refluxed for 4 h at 60°C and then was slowly concentrated at 80°C until semitransparent gel appeared in the system. Dried gel was obtained by heating the wet gel for 48 h at 120°C in a drying oven. The precursor was resulted after prefiring the dry gel for 2 h at 700°C . Nanoscale $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} was obtained after sintering the precursor for 3 h at 1000°C in active carbon atmosphere.

The bulk material was prepared by traditional high temperature solid state method.

2.2. Characterisations

Crystal structure of the samples was checked by Rigaku D/max-2000 X-ray diffraction (XRD), using $\text{Cu K}\alpha$ of 1.5405 \AA as the X-ray source. The particle size and morphology of nanoscale phosphor were measured by JEM-2000FX transmission electron microscope.

2.3. Electrooptical measurements

The excitation and emission spectra were measured at room temperature using a Flurolog-3 fluorescent spectrometer with a Xe lamp as light source. The nanoscale and the bulk powders were pressed into tablets, the optical power and the current–voltage characteristics were measured with an I – V – L measurement system and a Keithley source meter 2410.

3. Results and discussion

3.1. Crystal structure and size

Figure 1 shows the XRD patterns of the prepared nanoscale and bulk crystals. The diffractive peaks in the two curves are in good accordance with the JCPDS card of 34-0379, which indicates that the nanocrystal has the same crystal type as bulk one. Both of them are well crystallised in cubic structure. Thus, they can have comparability in every aspect.

The mean crystalline size can be deduced according to the Sherrers' equation $D = K\lambda / \beta \cos \theta$. The mean calculated crystalline size of the nanoparticles is 26 nm, which is basically in accordance with which is seen in the transmission electron microscopy (TEM) (Figure 2). It is clear that the size distribution is homogeneous.

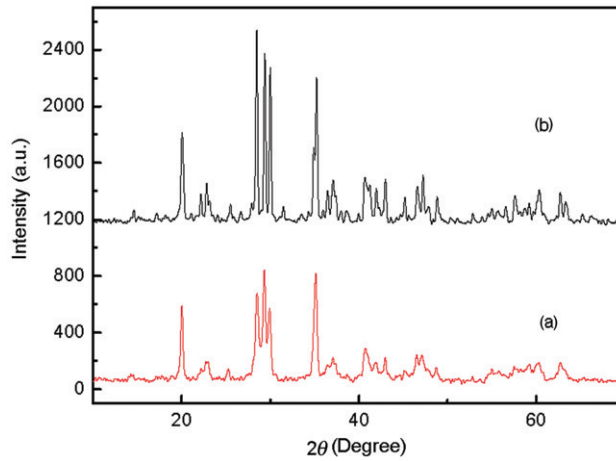


Figure 1. X-ray diffraction spectra of nanoscale (a) and bulk (b) $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{2+}$ phosphors.

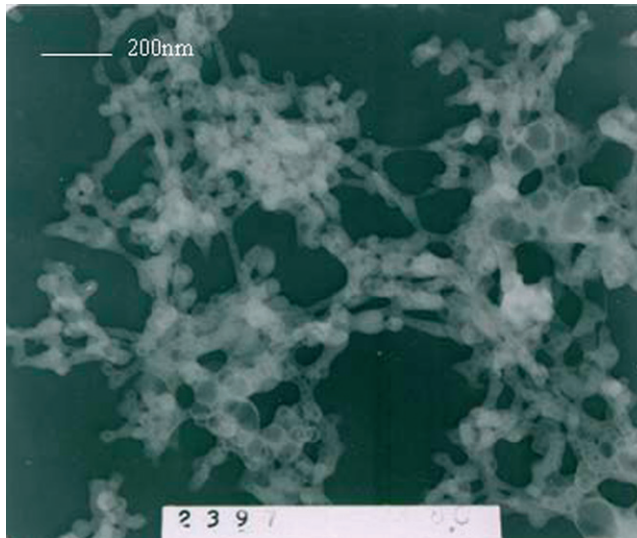


Figure 2. The TEM image of nanoscale $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

3.2. Electrooptical characteristics

Figure 3 shows the excitation and the emission spectra. The emission at 520 is attributed to the typical $4f^65d^1-4f^7$ transition of Eu^{2+} . Although the 5d electrons are exposed out of Eu^{2+} , the energy level difference between the lowest excited state $4f^65d^1$ and ground state $4f^7$ does not change clearly. So the emission spectrum of nanoscale $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ is essentially coincident with that of the bulk phosphor. However, the 5d energy level has close relation to the conduction band of host lattice. In addition, The band gap of SrAl_2O_4 will increase if the crystal size decreases to nanometre and the energy levels of doped Eu^{2+} ions will shift upward correspondingly [14]. So the energy centre of $4f^65d$ shifts upwards clearly because of

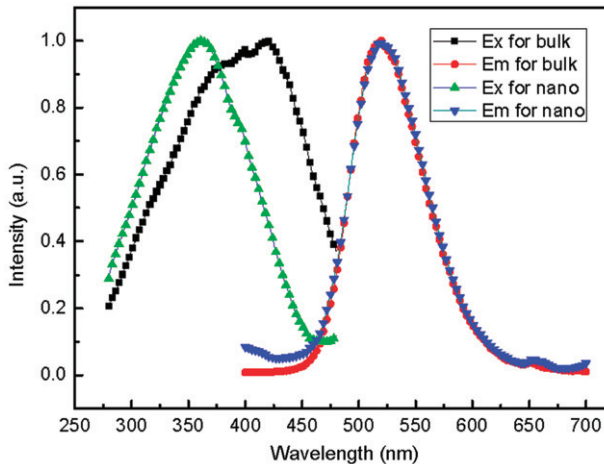


Figure 3. The normalised excitation spectra monitored at 520 nm and the emission spectra excited at 360 nm of nanoscale and bulk $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

the surrounding crystal field decreasing. As a result, the peak value of the excitation spectrum for nanometre $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ shifts to the shorter wavelength.

SrAl_2O_4 has a wide band gap (6.52 eV) [14], the light ranging from 280 to 480 nm cannot excite the electrons from the valence band to the conduction band. According to the above analysis, it is the electrons of emission centre (Eu^{2+}) that is excited but not that of host crystal. If these electrons do not relate the emission centres with the electron traps, the exciting light would not intensify the afterglow. In fact, it was found in the experiment that all the exciting light could give intensification of afterglow. In view of this, some of the electrons must have been to the trap level. In order to confirm how the excited electrons get to the trap level, we design the following experiment.

The synthesised bulk and nanoscale powders were pressed into pallets with the same diameter and thickness. The two electrodes of Keithley source meter 2410 cramped either of the two pallets. Figures 4 and 5 show the current-voltage characteristics in dark and in light. In general, SrAl_2O_4 has a very wide bandgap and the theoretical current should be very weak. Here the experimental value reaches 10^{-7} order of magnitude. In fact, only electron conductivity cannot give such a high conductivity. It is considered that ionic conductivity plays the leading role when the sample is not irradiated by light. It can also be seen in Figures 4 and 5 that the current of the pallet radiated by light is higher than that in dark under the same voltage, which is fit for both nanoscale and bulk materials. This phenomenon indicates that light irradiation can increase current, that is to say, the electrons are excited to the conduction band of host lattice. This conductivity is electron conductivity. The increased range of nanoscale phosphor is smaller than that of bulk phosphor because the energy level difference between the excited state and the ground state increases with size decreasing. In addition, the built in voltage comes into being and increases as external voltage. The current gain decreases at first and then reaches a stable value, so the slopes of the $I-V$ curves decrease at first and then get stable.

The optical power characteristic was measured by maintaining the voltage at 0 V and the inspected wavelength at 520 nm which is the characteristic emission of the afterglow.

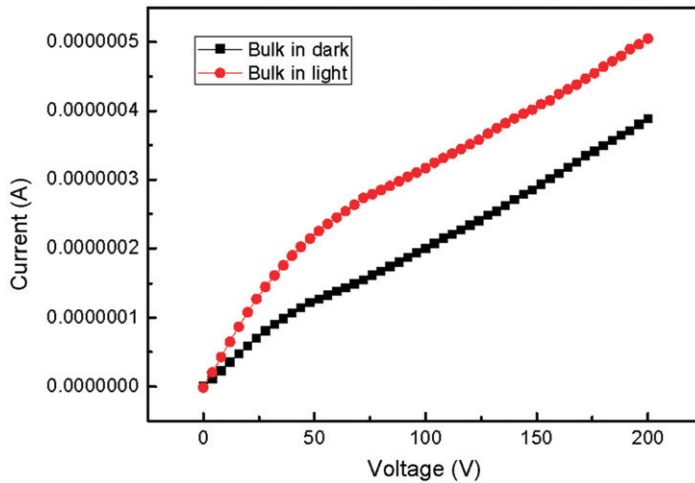


Figure 4. I - V curve of bulk $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ in dark or in light, V : 0–200 V.

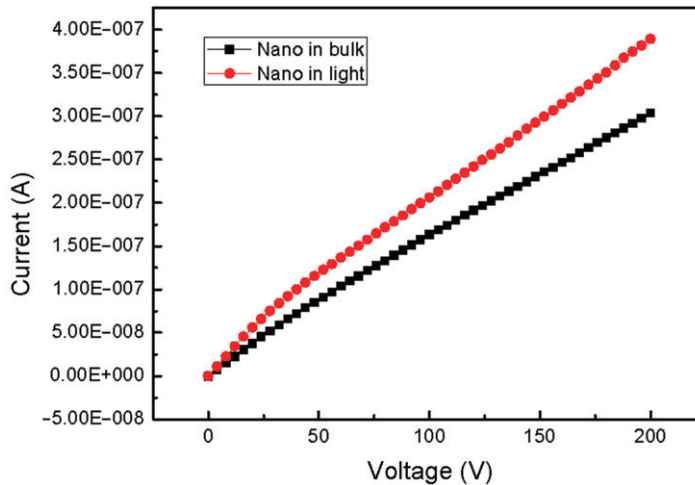


Figure 5. I - V curve of nanoscale $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$ in dark or in light, V : 0–200 V.

The time delay designed was 0.2 s. We defined the horizontal coordinate as time by 0.2 multiplied by a positive integer. It can be seen that the initial intensity of bulk material is stronger than that of nanoscale one and the former decays more slowly than the latter (Figure 6). The numbers of surface bonds, surface defects and surface absorptions of hydrated or carbohydrate species increase suddenly when the particle size decreases, which leads to non-radiative relaxation [15–17]. As a result, the initial emission intensity decreases greatly when the size decreases to nanometre. At the same time, the energy transmission between luminescence centre and surface quenching centre increases the phosphorescence decay. In short, surface effect decreases the initial luminance power and increases the rate of decay [18,19].

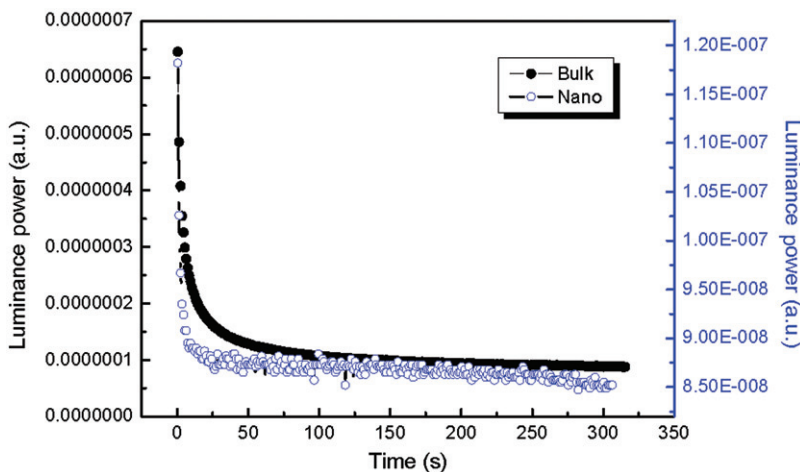


Figure 6. Luminescence power vs. time (s).

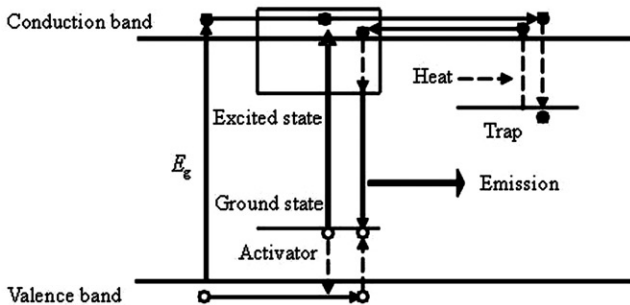


Figure 7. Mechanism of long persistent phosphorescence.

3.3. Theoretical model

The electrons in the valence band of host lattice or the ground state of activator ions are excited to the conduction band, then they migrate in the conduction band and some of them relax to traps and are stored there. Afterwards, these electrons may be released slowly by heat back to the conduction band, migrate and relax to the excited state of the activators. The irradiative transition from the excited state to the ground state is the long persistent luminescence. The key point is that the excited state energy levels of the emission centre overlap with the conduction band of host crystal (Figure 7).

4. Conclusion

Nanoscale $\text{SrAl}_2\text{O}_4:\text{Eu, Dy}$ long persistent phosphor was prepared by auto-combustion of Citrate Gels. It has the same emission peak at 520 nm as bulk material, but the excitation spectrum shifts to the shorter wavelength because of energy level shifting. Surface effect decreases the initial optical power and increases the rate of decay. The electrons always arrive at conduction band at first after they are excited by light irradiation.

The excited state energy levels of the emission centre overlap partly with the conduction band of host crystal.

Acknowledgements

The authors express their thanks to the support extended by the National Natural Science Foundation of China (10774012) and Beijing Jiaotong University Program (2007XM048, 2006XM038).

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