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Luminescent properties of $SrAl_2O_4$: Eu, Dy material prepared by the gel method

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Abstract

$SrAl_2O_4$:Eu,Dy materials were first prepared by the gel method. Compared with samples prepared by solid state reactions, the grain size of the gel method is greatly reduced to nanometer grade. A clear blue shift occurs in the excitation and emission spectra of nano $SrAl_2O_4$:Eu,Dy, of which the peak of the excitation and emission spectra are at 323 and 500 nm respectively. The brightness of nano $SrAl_2O_4$:Eu,Dy is greatly reduced. The blue shift and the change of luminescent intensity in nano $SrAl_2O_4$:Eu,Dy materials can be attributed to the effect of surface energy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Grain size; Optical properties; Powders-solid state reaction; Sol–gel processes; $SrAl_2O_4$

1. Introduction

A growing interest in $SrAl_2O_4$:Eu,Dy, a kind of long afterglow luminescent materials, has been reported recently.[1–3] Since it has good luminescent properties such as suitable emitting color, no radiation, high initial luminescent intensity and long lasting time which may reach 16 h,[1] $SrAl_2O_4$: Eu, Dy will be widely used in the near future.

Several attempts to prepare $SrAl_2O_4$:Eu,Dy material have been conducted from the beginning of this decade. Researchers prepared this kind of materials by solid state reaction in most reports.[1,2] Kutty synthesized $Sr_nAl_2O_{3+n}$: Eu, where n is less than 1[4] by hydrothermal reaction. Katsumata used the floating-zone technique to produce $SrAl_2O_4$:Eu,Dy crystals.[5,6] Jia prepared single crystal fibers with the aid of the laser heated pedestal growth method.[7] In these reports, the sintering temperature is very high, the particle size is large and the process does not affect the final optical properties of the products.

For most luminescent materials, the luminescent properties are greatly dependent on the grain size. When the grain size reaches nanometer grade, the luminescent materials will show some attractive properties, such as the blue shift of excitation and emission spectra.[8]

The sol–gel method has been greatly applied in preparing fine ceramic powders. Douy used the polyacrylamide gel to fabricate ultrafine $YBa_2Cu_3O_{7-x}$ powders which are about 100 nm, at relatively low temperature.[9] In Douy's method, the aqueous solution, containing all the desired elements in their stoichiometric ratios, was gelled in situ with an organic polymeric network. In recent years, Douy's method has been developed as gel-casting to produce structural ceramic parts. Since then, some new water-based gel systems have been investigated intensively. This method can produce ultrafine particles, prevent introduction of impurities, and decrease the sintering temperature.

In this paper, nano $SrAl_2O_4$:Eu,Dy material was prepared by using the gel method. The phosphorescent characteristics of samples prepared by the gel method are described as a comparison with those of solid state reaction samples.

2. Experimental

Sample series A was prepared by solid state reaction. Reagent grade Al_2O_3, $SrCO_3$, Eu_2O_3 and Dy_2O_3 were mixed with the composition of $(Sr_{0.97}Eu_{0.01}Dy_{0.02})Al_2O_4$, then sintered at 1300–1500°C for 2 h in a mildly

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reducing atmosphere. This series of samples is specified as Solid-T, where T means sintering temperature.

Sample series B was prepared by the gel method. Reagent $Al(NO_3)_3{\cdot}9H_2O$, $Sr(NO_3)_2$, $Eu(NO_3)_3$ and $Dy(NO_3)_3$ were dissolved in distilled water based on the nominal composition of $(Sr_{0.97}Eu_{0.01}Dy_{0.02})Al_2O_4$. Then certain amounts of monomer, acrylamide(AM), and cross-linker, methylene bisacrylamide(MBAM), were added into the solution, and blended well. $(NH_4)_2S_2O_8$ (APS) and *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamin (TEMED) were added as free rasical initiator and catalyst respectively to form stable gel. After being dried at 60°C for 24 h, the binder was burned out at 600°C, and sintered at 1100–1400°C for 2 h. This series of samples is specified as Gel-T, T also means temperature.

Powder X-ray diffraction (RegakuD/MaxIIIB) analysis was performed to identify the crystalline phases of the samples. Their morphologies were observed by SEM(Hitachi S-450) and TEM(Hitachi H800). The excitation and emission spectra were measured by a fluorescent spectrometer (Perkin Elmer LS50B). The luminescent intensity and decay profiles were detected by a computer-based brightnessmeter (ST86-LA).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of Solid-1380 and Gel-1380, the patterns of them are similar to each other and can be assigned well to the JCPDS card of $SrAl_2O_4$.

A TEM photograph of Gel-1380 and SEM photograph of Solid-1380 are shown in Figs. 2 and 3 respectively. From the TEM photograph, some whiskers could be found, indicating that $SrAl_2O_4$:Eu, Dy whisker can be made by the gel method. Based on previous reports, no one has observed such phenomena, but only ball-like particles. A detailed description of this phenomena will be given in another paper. In this paper, we calculated the average grain sizes only on the ball-like particles. The average grain sizes are shown in Table 1. With the sintering temperature increasing, the grain size of gel samples increases. But, even when the sintering temperature reaches 1380°C, the grain size is less than 100 nm, suggesting that the luminescent powder is nanometer grade while the average grain size of Solid-1380 is about 3000 nm. Compared with the solid state reaction samples with the same sintering process, the mean grain size can be greatly reduced by using the gel method.

Figs. 4 and 5 show the excitation and emission spectra of Solid-1380 respectively. The phosphor sample reaches a maximum at 320 and 360 nm in excitation

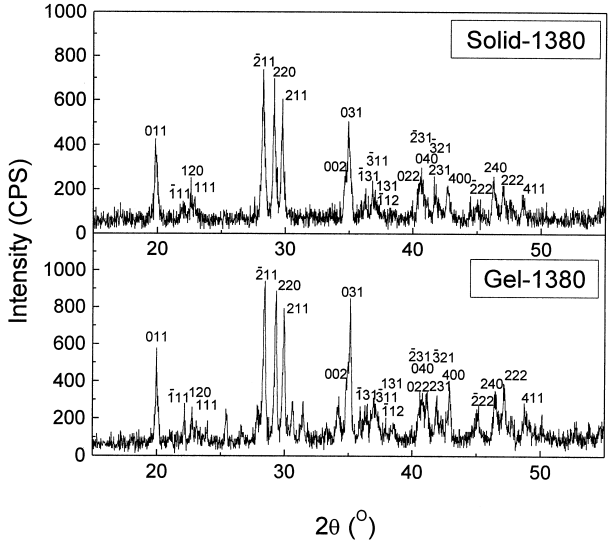

Fig. 1. X-ray diffraction patterns of different samples.

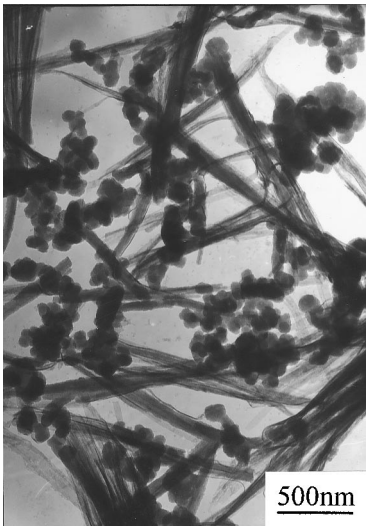

Fig. 2. TEM micrograph of Gel-1380.

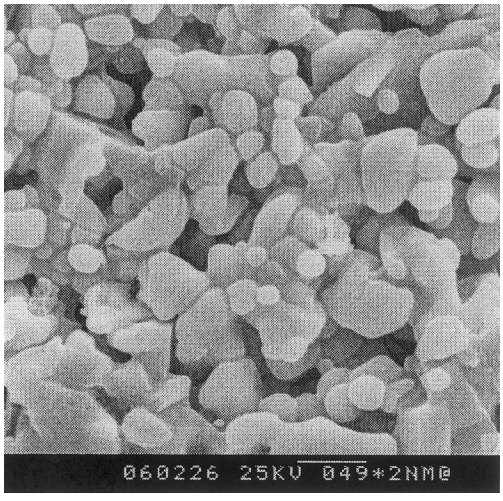

Fig. 3. SEM micrograph of Solid-1380.

Table 1
Average grain size of different samples

Sample name	Average grain size (nm)
Gel-800	26
Gel-1000	50
Gel-1380	90
Solid 1380	3170

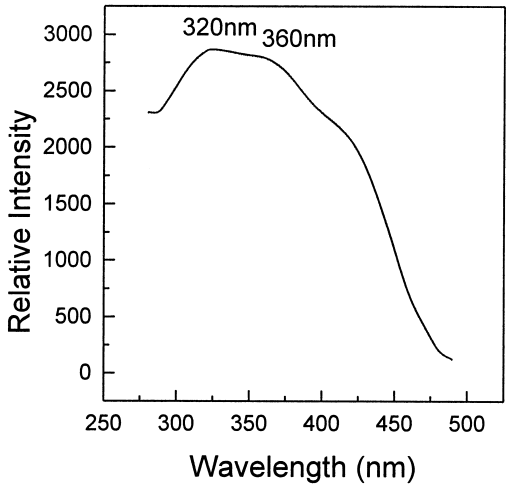

Fig. 4. Excitation spectra of Solid-1380.

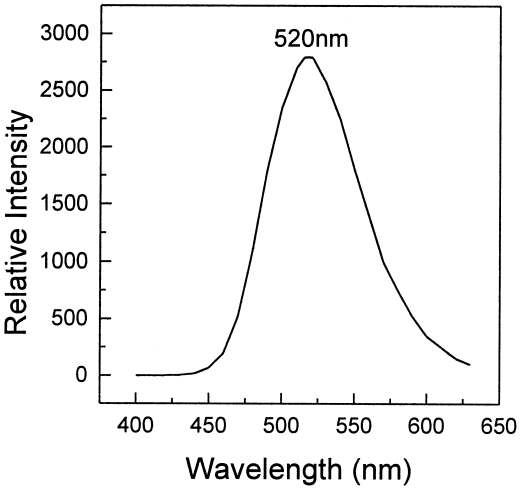

Fig. 5. Emission spectra of Solid-1380.

spectra and exhibits a broad band peak at 520 nm in emission spectra. However, in Gel-1380, although the excitation and emission spectra, as shown in Figs. 6 and 7 have a similar shape to Solid-1380, both of them shift to the blue side of the spectra. The excitation is at 304 and 321 nm, the emission spectra are at 500 nm. We can calculate the energy based on Eq. (1), where E is Energy, h is Planck constant, v is the frequency, c is the

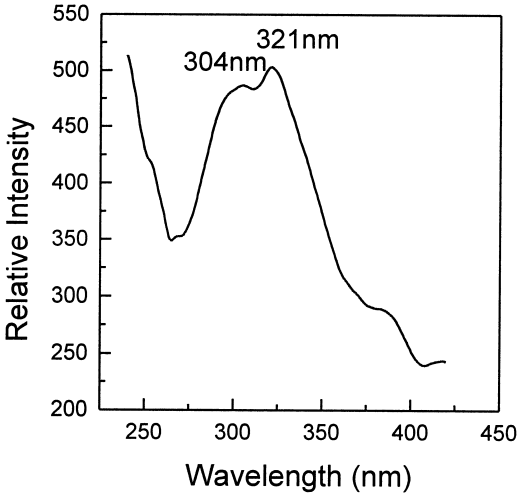

Fig. 6. Excitation spectra of Gel-1380.

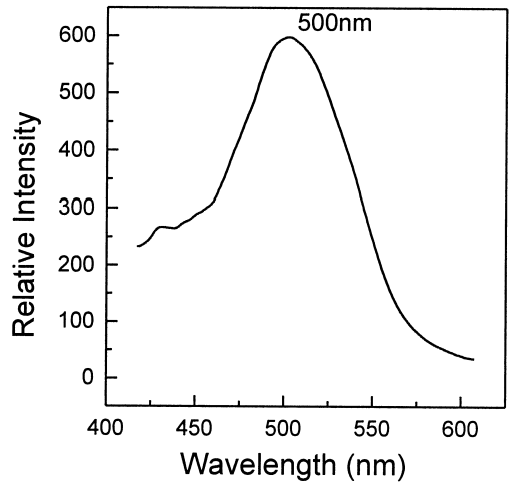

Fig. 7. Emission spectra of Gel-1380.

velocity of light, and λ is the wavelength of light. the excitation and emission energy of nano $SrAl_2O_4$:Eu,Dy are 3.835 and 2.480 eV respectively, which of micron $SrAl_2O_4$:Eu,Dy are 3.444 and 2.384 eV.

$$E = hv = h\frac{c}{\lambda} \tag{1}$$

Explanations of the luminescent mechanism of micron $SrAl_2O_4$:Eu,Dy can be found in other documents.[1–3] Here, we would like to provide a brief description of the luminescent mechanism of nano $SrAl_2O_4$:Eu,Dy. As we know, because of the nanosize of the grain, the surface energy should be increased dramatically, which results in the distortion of atom structure and the change of the crystal field around Eu^{2+}. Although the 4f electron of Eu^{2+} is not sensitive to

lattice environment because of the shielding function of the electrons in the inner shell, the 5d electron may be coupled strongly to the lattice. Consequently, the mixed states of 4f5d will be split by the crystal field, as a result, some jumps which are not allowed in micron $SrAl_2O_4$:Eu,Dy, can take effects in nano $SrAl_2O_4$:Eu,Dy and thus lead to the blue shift occurrence in the excitation and emission spectra.

Fig. 8 shows the decay curve of nano and micron $SrAl_2O_4$:Eu,Dy. The luminescent intensity of nano grade is much less than that of the micron grade. This also can be attributed to the surface energy. As to the mechanism of the long afterglow, it is the hole trapped-transported-detrapped process that results in the properties of long afterglow of $SrAl_2O_4$:Eu,Dy phosphor, in which Dy ions play a role of a trapped energy level that can attract vacancies during the excitation and thus decrease the initial luminescence and prolong the luminescent duration. From the point of view of energy level, it may be suggested that the surface energy level is much deeper than the trap level of Dy and then can attract more vacancies than Dy, so that the initial luminescent intensity decreases greatly.

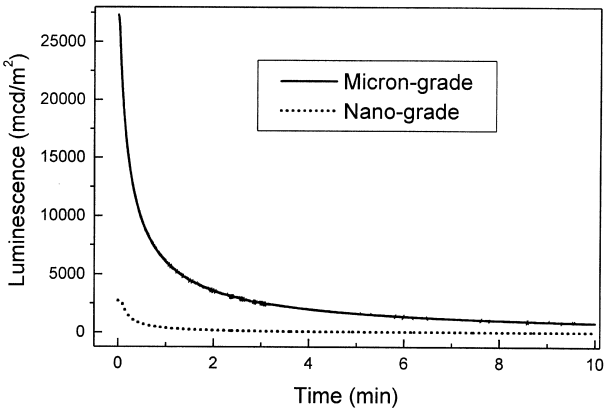

Fig. 8. Decay curves of nano and micron $SrAl_2O_4$:Eu,Dy.

Acknowledgements

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References

1. Matsuzawa, T., Aoki, Y., Takeuchi, N. and Murayama, Y., A new long phosphorescent phosphor with high brightness $SrAl_2O_4:Eu^{2+}$, Dy^{3+}. *J. Electrochem. Soc.*, 1996, **143**(8), 2670–2673.
2. Takasaki, H., Tananbe, S. and Hanada, T., Long-lasting afterglow characteristics of Eu, Dy codoped $SrO–Al_2O_3$ phosphor. *J. Ceram. Soc. Jap*, 1996, **104**(4), 322–326.
3. Yamamoto, H. and Matsuzawa, T., Mechanism of long phosphorescence of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and $CaAl_2O_4:Eu^{2+},Nd^{3+}$. *J. Lumin.*, 1997, **72-74**, 287–289.
4. Kutty, T. R. N., Jagannathan, R. and Rao, R. P., Luminescence of Eu^{2+} in strontium aluminates prepared by the hydrothermal method. *Mat. Res. Bull*, 1990, **25**, 1355–1362.
5. Katsumata, T., Nabae, T., Sasajima, K. and Matsuzawa, T., Growth and characteristics of long persistent $SrAl_2O_4$- and $CaAl_2O_4$-based phosphor crystals by a loating zone technique. *J. Crystal Growth*, 1998, **183**, 361–365.
6. Katsumata, T., Sasajima, K., Nabae, T., Komuro, S. and Morikawa, T., Characteristics of strontium aluminate crystals used for long-duration phosphors. *J. Am. Ceram. Soc.*, 1998, **81**(2), 413–416.
7. Jia, W., Yuan, H., Lu, L., Liu, H. and Yen, W. M., Phosphorescent dynamics in $SrAl_2O_4:Eu^{2+},Dy^{3+}$ single crystal fibers. *J. Lumin.*, 1998, **76-77**, 424–428.
8. Blasse, G. and Grabmaier, B. C. *Luminescent Materials*, Springer Verlag, 1994.
9. Douy, A. and Odier, P., Polyacrylamide gel: a novel route to ceramic and glassy oxide powders. *Mat. Res. Bull*, 1989, **24**(9), 1119–1126.