

Article ID: 1003-7837(2005)02,03-0611-04

Study on oxide resistance of long persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}$

HUO Cheng-zhang(霍成章)¹, NI Hai-yong(倪海勇)¹,
LU Ming-yu(吕明钰)², ZHOU Shao-hui(周绍辉)¹

(1. Research Center of Rare Earth Function Materials, Guangzhou Research Institute of Non-Ferrous Metals, Guangzhou 510651, China; 2. Guangdong University of Technology, Guangzhou 510900, China)

Abstract: The heat-treated temperature and preservative time influence on oxide resistance of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ in high temperature atmosphere were studied in this paper. The result showed that oxide resistance was improved obviously by phosphor particles coated SiO_2 . The reason for the coating to craze above 900°C was also analyzed.

Key words: long persistence; phosphor; oxide resistance; rare earth; coating

CLC number: TQ482.31, O161 **Document code:** A

1 Introduction

Long persistent afterglow has been found in a number of rare earth doped luminescence materials, such as $\text{CaAl}_2\text{O}_4:\text{Nd}^{3+}, \text{Eu}^{2+}$, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. The persistent afterglow generally arises from emissions on the impurity centers. Electrons from these centers are excited to the conduction band and can fall into traps below the band. These trapped electrons can be thermally activated back to the conduction band and fall into excited state of the centers. They return to the ground state of the emission center by emitting an afterglow photon. Phosphors with long persistent phosphorescence have been studied for long time. Modern industrial production of long persistent phosphor has been switched from $\text{ZnS}:\text{Cu}$; $\text{CaSrS}:\text{Bi}^{3+}$ with a persistence time of about 1 h, to $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, which can persist for more than 10 h. It is usual now to define a long persistent afterglow as one which lasts at least 10 h before it decays to a level of 0.3 mcd/m² (the value of 0.3 mcd/m² is the accepted limit of the visual sensitivity of the normal human eyes). Only a few materials have been found with a persistence time longer than 10 h. Oxide resistance of a long persistent phosphor SrAl_2O_4 doped with $\text{Eu}^{2+}, \text{Dy}^{3+}$ by coating SiO_2 is reported in this work.

2 Experimental

The coating solution was prepared by dissolving $\text{Si}(\text{OR})_4$ into alcohol and H_2O of 99.99 % purity. Also, pH of mixed solution was chemically modified by adding 10% hydrochloric acid. The mixture was placed at room tem-

Received date: 2005-09-12

Biography: HUO Cheng-zhang (born in 1957), Male, Senior engineer.

perature for 10 h, then it turned into transparent solution colloid (Sol); long persistent phosphor was added into Sol, after being agitating and filtering, a coated phosphor was obtained by being drying at 200°C for 5 h in atmosphere.

The sample was cooled to room temperature in 101.3 kPa and irradiated by a D65 lamp for 30 min. The afterglow decay curves were recorded by using a ST-900PM spectrometer. The crystal phase and surface character of particles prepared were investigated with Regaku X diffraction and scanning electron microscope JEOL JSM-5910(SEM), respectively.

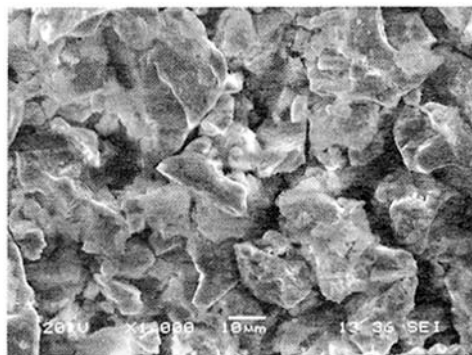


Fig.1 Coated phosphor SEM

3 Results and discussion

3.1 Surface character of coated phosphor

Surface character of coated phosphor is shown in Fig. 1. Luminescent powder surface was coated by a layer consecution SiO_2 successfully through Sol-gel.

3.2 Comparison to luminescent powder oxide resistance

Taking 50 g of coated phosphor GL-2 and uncoated phosphor GL-2 respectively and preserving them in atmosphere at 850°C for 30 min, the sample luminescent brightness is shown as in Table 1. The result shows that luminescent brightness of the uncoated phosphor and coated phosphor decreased by 96.37% and 21.7% respectively. Therefore, oxide resistance of phosphor coated SiO_2 was raised.

Table 1 Comparison to luminescent powder oxide resistance

Name	afterglow brightness /($\text{mcd} \cdot \text{m}^{-2}$)				
	1 min	2 min	3 min	4 min	5 min
Coated GL-2	2680	1472	989.32	744.07	584.27
Uncoated GL-2	124.29	56.09	33.7	23.7	17.24

3.3 Influence of temperature on oxide resistance

In order to obtain the highest temperature of oxide resistance, the coated phosphor GL-2 was preserved in atmosphere from 750°C to 950°C for 30 min. Fig. 2 shows the brightness delay curve of phosphor. When the heat-treated temperature got over 950°C, the luminescent brightness would decrease by 42.8%. It was speculated that part of oxidized divalent europium is responsible for reducing luminescent intensity of phosphor.

3.4 Influence of preservative time on oxide resistance

Fig. 3 shows that luminescent brightness was greatly affected by preservative time. Luminescent brightness was in inverse ratio to preservative time. Luminescent brightness would critically decrease by 86.6% in comparison with phosphor which was not heat-treated when coated phosphor was prepared at 950°C for 60 min in atmosphere. The reason to decrease brightness is as the same as temperature influence on oxide resistance (part 3.3).

3.5 Reason to decrease luminescent brightness

The oxide resistance of phosphor was improved radically by coating SiO_2 as shown in Fig. 1 and Table 1. But as shown in Fig. 2 and Fig. 3, as temperature and preservative time in atmosphere increased, the luminescent brightness decreased. The crystal phase and surface character of particles prepared was investigated with X diffraction and SEM, respectively.

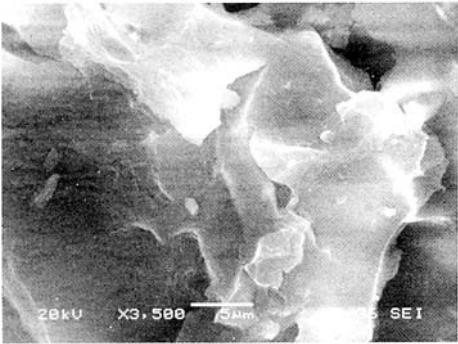


Fig. 2 Brightness delay curve

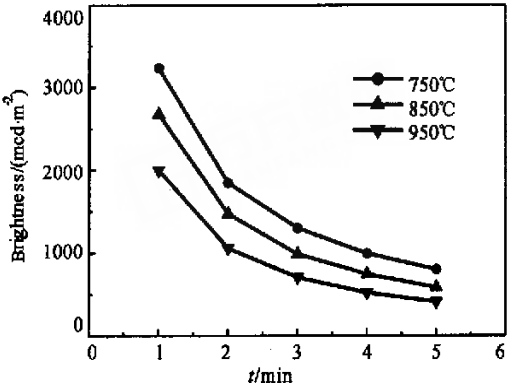


Fig. 3 Brightness delay curve

Figs. 4, 5 show that heat-treated phosphor crystal structure was still monocline and the chap of long persistent phosphor surface was observed. The reason is that film layer SiO_2 crystal phase will transform from α -quartz into β -quartz above 900°C , the volume of this process will be enlarged by 16%, which cause film layer to craze. When divalent europium in the structure of SrAl_2O_4 was oxidized trivalent europium, phosphor brightness decreased with increasing temperature and preservative time.

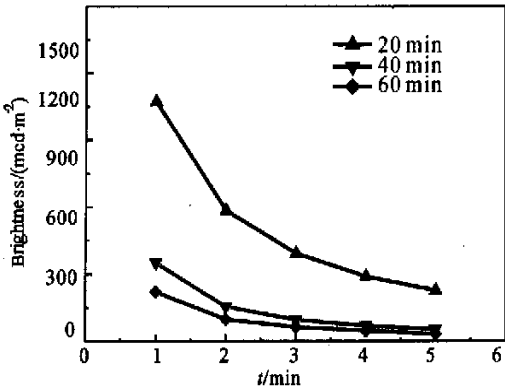


Fig. 4 Heat-treated phosphor X diffraction

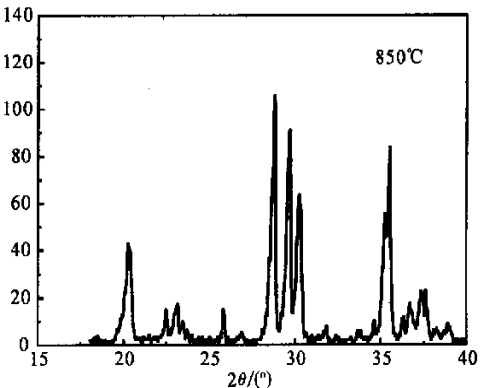


Fig. 5 Heat-treated phosphor SEM

4 Conclusion

- (1) The oxide resistance of phosphor was improved obviously by coating SiO_2
- (2) Coated phosphor crystal phase was still monocline after being prepared at 950°C for 60 minutes in atmosphere.
- (3) Film layer SiO_2 crystal phase will transform from α -quartz into β -quartz above 900°C , the volume of this process will be enlarged by 16%, which cause film layer to craze.

References

- [1] Yamamoto H, T suzawa. Mechanism of long phosphorescence of $\text{SrAl}_2\text{O}_4 : \text{Eu}, \text{Dy}$ and $\text{CaAl}_2\text{O}_4 : \text{Eu}, \text{Nd}$ [J]. J Lumin, 1997, 72 : 287—289.
- [2] Katsumata T, Nabaie Tsasajima K, *et al.* Effects of composition on the long phosphorescent $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor crystals[J]. J Electrochem Society, 1997, 144: 243—245.
- [3] Chen C R, Chen T M. Sol-gel synthesis and the effect of boron addition of the phorescent properties of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors[J]. J Mater Res, 2001, 16: 644—651.
- [4] Jia W, Yuan H, Lu L, *et al.* Phosphorescent dynamics in $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ single crystal fibers[J]. J Lumin, 1998, 76: 424—428.
- [5] Matsuzawa T, Aoki Y, Takeuchi N, *et al.* A new phosphorescent phosphor with high brightness, $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ [J]. J Electrochem Soc, 1996, 143: 2670—2673.