Journal of Alloys and Compounds 753 (2018) 35–40

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

A surface corrosion and expansion mechanism on thermal degradation of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}

Weikang Peng [a], Haofu Xia [a], Zhanhui Zhang [a, b, *], Tonggang Qi [a], Shijin Kong [a], Wubin Dai [a, b], Zhiliang Huang [a, b]

[a] School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, PR China
[b] Key Laboratory of Plasma Chemistry and Advanced Materials of Hubei Province, Wuhan Institute of Technology, Wuhan 430205, PR China

ARTICLE INFO

Article history:
Received 12 February 2018
Received in revised form
16 April 2018
Accepted 18 April 2018
Available online 20 April 2018

Keywords:
$SrAl_2O_4:Eu^{2+}$
Dy^{3+} phosphor
Heat-treatment
Thermal degradation
Surface corrosion and expansion mechanism

ABSTRACT

The thermal degradation of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor limits its application in high temperature products. To clarify its thermal degradation mechanism, a heat-treatment process was carried out, and the interrelation of luminescent degradation, surface chemical composition and heat-treatment temperature was investigated. The results revealed that the afterglow properties degraded obviously with the increasing heat-treatment temperature, while the instantaneous emission intensity appeared two maximum values. According to the luminescent mechanism of long afterglow materials and the results of thermoluminescence spectra, two maximum values corresponded to the destruction of two trap levels at different temperatures. X-ray photoelectron spectroscopy results showed that the element composition of Sr and O on the phosphor surface increased with the increasing heat-treatment temperature, confirming that a SrO layer formed on the surface. Based on above results, we proposed a surface corrosion and expansion mechanism on the thermal degradation of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}.

1. Introduction

In recent years, $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, as a new type of long afterglow phosphors, has been widely used in signs on buildings or highways, painting, art works, and other fields [1–5]. Compared with the conventional luminescent materials, it has high fluorescence intensity, long afterglow time, non-radioactivity and other advantages.

However, $SrAl_2O_4:Eu^{2+}$, Dy^{3+} has a bad thermal stability [6], which limits its application in high temperature products. There is little research concerning about the thermal degradation mechanism of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor. Referring to the thermal degradation mechanism of other phosphors, the oxidation of Eu^{2+} to Eu^{3+} may be the cause for the thermal degradation [7]. However, several researches showed that micro-structural distortion also resulted in the thermal degradation of phosphors, in addition to the oxidation of activator ions [8]. Hence, the thermal degradation mechanism of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors should be further discussed.

To clarify the thermal degradation mechanism of $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, the changes on luminescent properties and surface chemical compositions after a heat-treatment at different temperatures were investigated. The relationship between afterglow property degradation and emission intensity changes was discussed by the law of energy conservation. The interrelation of luminescent degradation, surface chemical composition and heat-treatment temperature was also discussed. According to the obtained results, a surface corrosion and expansion mechanism on the thermal degradation of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} was proposed.

2. Experimental

Commercial $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphors were provided by Guangzhou Research Institute of Non-ferrous Metals. The annealing process was carried out at different temperatures (ranging from 400 to 1200 °C) for 0.5 h in air. All pre-annealed and post-annealed samples were measured by powder X-ray diffraction (D8 Advance, Germany) to analyze their crystal phases. Emission and excitation spectra were measured by a fluorescence spectrophotometer (Cary Eclipse, America). A thermoluminescent dosimeter (FJ-427A1, China) was used to observe the trap levels of samples. Afterglow

* Corresponding author. School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, PR China.
E-mail address: zzhlzu@163.com (Z. Zhang).

https://doi.org/10.1016/j.jallcom.2018.04.211
0925-8388/

decay curves were measured by a screen brightness meter (ST-86LA, China) after the phosphors were excited by a 150 W Xe lamp at 365 nm for 15 min. The changes of surface composition and microstructure of samples were analyzed by an X-ray photoelectron spectroscopy (XSAM800, Britain), and the pollution carbon standard was 284.6eV.

3. Results and discussion

3.1. XRD patterns analysis

Fig. 1 presented the XRD patterns of samples with different heat-treatment temperatures. According to Fig. 1, with the increasing heat-treatment temperature, the diffraction peak position of phosphors did not shift and kept matching with the standard card JCPD34-0379 perfectly. These results suggested that the crystal phases of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} had no change and belongs to monoclinic system.

Fig. 2 gave the cell parameters of samples with different heat-treatment temperatures. We found that the cell parameters (a, b, c) values presented a rising trend as a whole with the increasing heat-treatment temperature from Fig. 2. It indicated that the lattice distortion took place in the crystal because of the heat-treatment. According to Figs. 1 and 2, we concluded that heat-treatment did not change the crystal phases but caused lattice distortion.

3.2. Analysis of luminescent properties

Figs. 3 and 4 showed the excitation and emission spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors with different heat-treatment temperatures. The excitation spectrum of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphor was a continuous band distributing from 250 nm to 450 nm. It peaked at 340 nm and belonged to $4f^7 \rightarrow 4f^6 5\,d^1$ characteristic transition of Eu^{2+}. And the emission spectrum of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphor was a continuous band distributing from 450 nm to 600 nm. It peaked at 514 nm and belonged to $4f^6 5\,d^1 \rightarrow 4f^7$ [9] characteristic transition of Eu^{2+}. As we found from Figs. 3 and 4, the peak shapes of samples with different heat-treatment temperatures stayed the same. It also indicated that heat-treatment did not change the crystal phases. Moreover, it seemed to be no trend about the emission intensities of samples with the increasing heat-treatment temperature. However, we found some interesting phenomena in following Fig. 5.

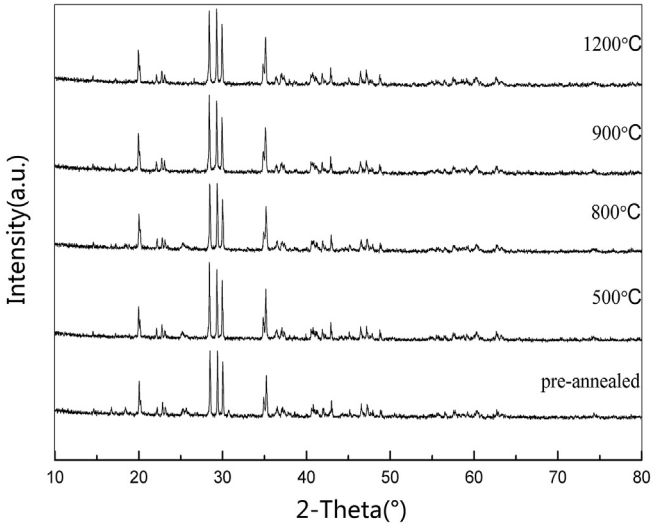

Fig. 1. XRD patterns of samples with different heat-treatment temperatures.

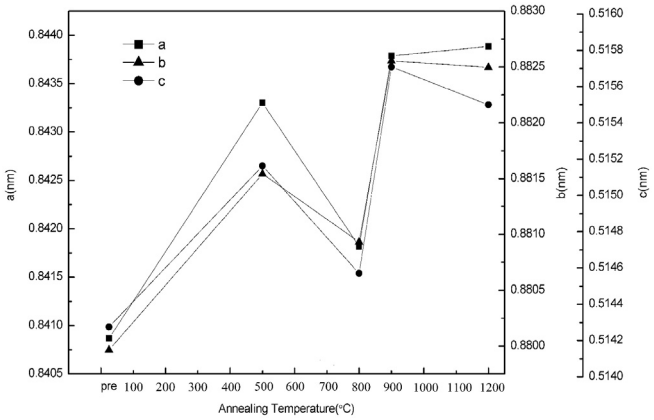

Fig. 2. The unit cell parameters, a, b and c of pre-annealed and annealed samples.

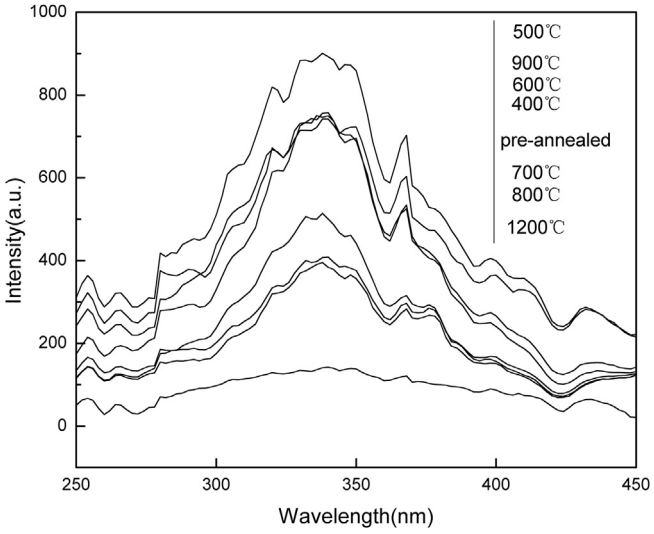

Fig. 3. Excitation spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors ($\lambda_{em} = 514$ nm).

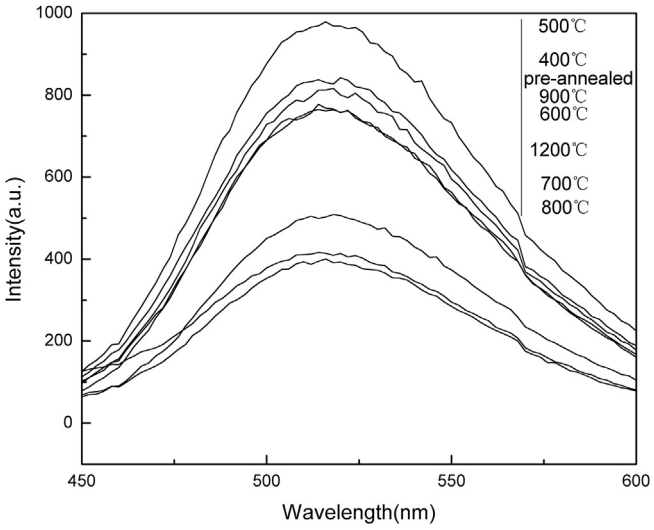

Fig. 4. Emission spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} phosphors ($\lambda_{ex} = 340$ nm).