Photoluminescence degradation mechanism of $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor by vacuum ultraviolet irradiation*

Zhang Jia-Chi(张加驰)†, Zhou Mei-Jiao(周美娇), and Wang Yu-Hua(王育华)

Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, *China*

(Received 7 February 2012; revised manuscript received 6 June 2012)

A real high power vacuum ultraviolet light source is applied to the investigation on the vacuum ultraviolet irradiation degradation of $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor. The degradations of emission intensity and color quality of the sample are clearly observed after irradiation. It reveals that the oxidation of Eu^{2+} during irradiation is partly responsible for the degradations. The excitation and absorption spectra show that some traps generated during irradiation have negative influence on the luminescence of sample and these traps have been identified as positively charged oxygen vacancies by positron annihilation. The investigations on host emission and decay curve further confirm that these oxygen vacancies are involved in the perturbation of energy transfer from the host to Eu^{2+} and finally result in the degradation.

Keywords: $BaMgAl_{10}O_{17}:Eu^{2+}$, phosphor, luminescence, irradiation degradation

PACS: 41.60.–m, 42.40.My **DOI:** 10.1088/1674-1056/21/12/124102

1. Introduction

As a blue component, the $BaMgAl_{10}O_{17}:Eu^{2+}$ ($BAM:Eu^{2+}$) phosphors have been widely regarded as the best vacuum ultraviolet (VUV) excited phosphors for plasma display panels (PDPs) and Hg-free lamps.[1] However, this phosphor will undergo degradations of brightness and color quality during the baking process in manufacture (thermal degradation) and also during the aging process in operation (VUV radiation degradation).[2] In the past decades, many reports have focused on its thermal degradations and several improvements to reduce the degradation have been proposed.[3,4] On the other hand, some attempts have been also made to study the aging process in operation, however, no explanation of the VUV irradiation degradation mechanism was given.[5,6] Bizarri and Moine[2] have studied the VUV radiation degradation of $BAM:Eu^{2+}$ phosphors by stimulating the irradiation process using 193-nm laser. However, as is well known, the irradiation energy of VUV source (high Xe gas content discharge) is mainly 147-nm beam for a PDP or Hg-free lamp. Thus, the previous reference cannot well clarify the real VUV radiation degradation mechanism of $BAM:Eu^{2+}$ phosphors used in PDPs and Hg-free lamps.[2,7,8]

In this work, we use a high power deuterium lamp (REX-4, 140 W) as the real VUV radiation light source. The VUV radiation degradation of $BAM:Eu^{2+}$ phosphor is investigated in detail and we sum up the essential mechanism, accordingly.

2. Experiment

All $BAM:Eu^{2+}$ samples containing 7 at% Eu^{2+} ions are synthesized by conventional solid state method. A Rigaku D/Max-2400 X-ray diffractometer (XRD) is employed to check the phases of samples. Because the VUV photons can be absorbed by oxygen in the air, the samples are spread over the sample holder and placed in a sealed container which filled with nitrogen. The VUV radiation source is high power deuterium lamp (REX-4, 147 nm, 140 W) and the irradiation duration is 1000 h. The absorption spectra are obtained by a UV-visible spectrophotometer (PE Lambda 950). The photoluminescence (PL) spectra are measured by an FLS-920T fluorescence spectrophotometer. The VUV excitation spec-

*Project supported by the National Natural Science Young Foundation of China (Grant No. 10904057) and the Fundamental Research Funds for Central Universities, China (Grant No. Lzjbky-2011-125).

†Corresponding author. E-mail: zhangjch@lzu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

tra are corrected by dividing the excitation intensity of sodium salicylate. The decay curves are monitored at 450 nm in ns magnitude and measured by the FLS-920T fluorescence spectrophotometer (split=0.5).

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of fresh BAM:Eu^{2+} and sample after VUV irradiation for 1000 h. As shown in Fig. 1, all peaks of patterns can be well indexed and recognized as single phase based on JCPDS Standard Card No 26-0163. Both of the patterns are almost the same except for the slight diffraction peak intensity difference, indicating that the crystal structure of BAM:Eu^{2+} sample is not influenced by VUV irradiation.

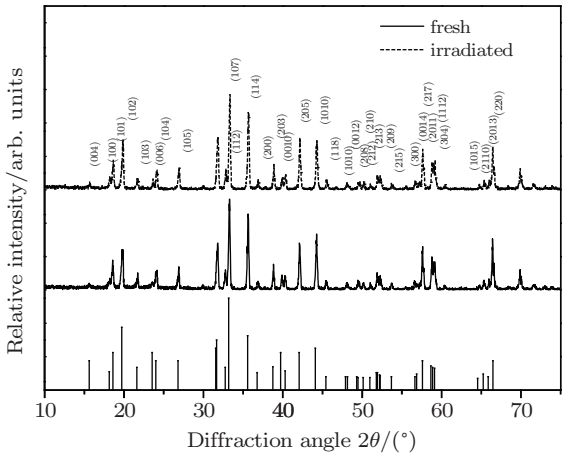


Fig. 1. The X-ray diffraction patterns of fresh BAM:Eu^{2+} (solid line) and sample after VUV irradiation (dotted line) for 1000 h.

Figure 2 shows the emission spectra (λ_{ex} = 147 nm) of fresh BAM:Eu^{2+} and sample after VUV irradiation for 1000 h. The broad dominant blue emission peaked near 450 nm is due to the $4f^6 5d^1$–$4f^7$ transition of Eu^{2+}.[7] It is noted that after VUV irradiation, the emission intensity of Eu^{2+} decreases to about 66% of its original intensity. This result suggests that the VUV excited luminescence intensity of Eu^{2+} in BAM:Eu^{2+} sample is seriously damaged by VUV irradiation. In addition, it is also found that the emission band becomes wider in long wavelength region after VUV irradiation. As a result, the chromaticity of BAM:Eu^{2+} sample is obviously influenced and the color coordination which can be calculated by "Zolix Color Convert" program changes from original value (0.148, 0.072) to present value (0.145, 0.115).

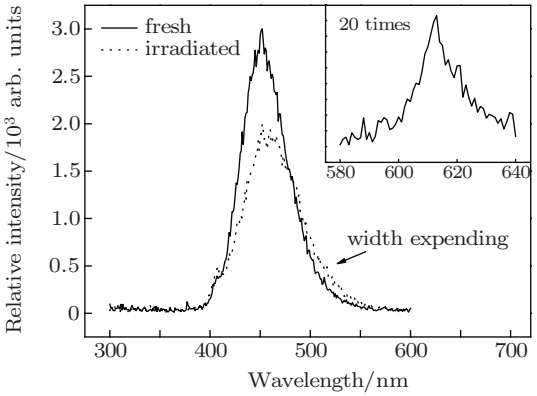


Fig. 2. Emission spectra (λ_{ex} = 147 nm) of fresh BAM:Eu^{2+} (solid line) and sample after VUV irradiation (dotted line) for 1000 h.

On the other hand, as shown in the inset of Fig. 2, a small red emission peak at about 613 nm (magnifying to 20 times) can be observed in sample after VUV irradiation. This result indicates that some Eu^{2+} ions in BAM:Eu^{2+} have been oxidized to Eu^{3+} during VUV irradiation. The emission of Eu^{3+} is usually observed in BAM:Eu^{2+} sample after baking in air, and the oxidation of Eu^{2+} by oxygen in air is generally regarded as the main reason for the thermal degradation of BAM:Eu^{2+}.[3,4,7,8] However, because the VUV photons can be absorbed by oxygen in air, the BAM:Eu^{2+} sample in this case is irradiated in a sealed container filled with nitrogen. This result also suggests that the oxidation mechanism of Eu^{2+} by VUV irradiation is not related to the oxygen in atmosphere and may originate from a self-oxidation process. Under the VUV irradiation in nitrogen, some oxygen atoms in mirror plan (conduction layer) can disappear and thus some oxygen vacancies are created. These oxygen vacancies which are close enough to Eu^{2+} centres can capture electrons from Eu^{2+} centres and subsequently the Eu^{3+} centres are created.[9,10] This process can be expressed by the following equation:

$$V_o + 2Eu^{2+} \rightarrow V_o^{\times} + 2Eu^{3+}. \quad (1)$$

According to the above results, the oxidation of Eu^{2+} can lead to the decrease of blue emission centre (Eu^{2+}) and may be partly responsible for the VUV irradiation degradation of BAM:Eu^{2+} sample.

Figure 3 exhibits the excitation spectra (λ_{em} = 450 nm) of fresh BAM:Eu^{2+} and sample after VUV irradiation for 1000 h. The excitation curves show two different areas: a band at high energies (< 200 nm) corresponding to the host lattice absorption and the bands above 200 nm due to the direct absorption in

the energetic levels of Eu^{2+}.[2] It is surprisingly found that after VUV irradiation, the BAM:Eu^{2+} only shows the clear degradation in 120 nm–180 nm and the excitation intensity above 200 nm, which is ascribed to the fact that the direct levels of Eu^{2+} seems not to be decreased as seriously as the host absorption. This result demonstrates that the amount of Eu^{2+} involved in oxidation during VUV irradiation is very small in fact and the oxidation of Eu^{2+} should be not the main reason for the VUV irradiation degradation of BAM:Eu^{2+}.

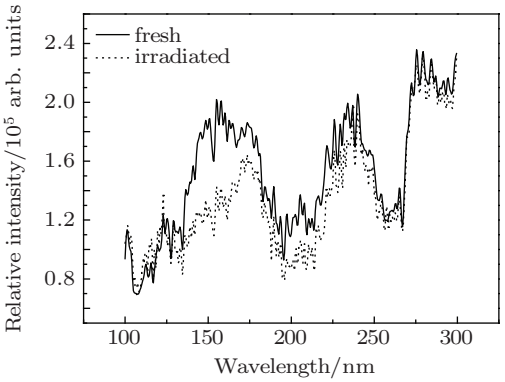


Fig. 3. Excitation spectra (λ_{em} = 450 nm) of fresh BAM:Eu^{2+} (solid line) and sample after VUV irradiation (dotted line) for 1000 h.

Now, an interesting question arises: what should be mainly responsible for the serious VUV irradiation degradation of BAM:Eu^{2+}? The BAM is known to have many traps in the conduction layer for its high ion conductivity. Accordingly, some oxygen vacancies ($V_o^{\bullet\bullet}$) can be created under VUV irradiation in nitrogen and we consider that these oxygen vacancies ($V_o^{\bullet\bullet}$) may play an important role in the VUV irradiation degradation. In order to prove this point, it is necessary to provide the data of positron annihilation experiments, absorption spectra and decay curves as proofs.

Table 1 exhibits the positron annihilation lifetimes of fresh BAM:Eu^{2+} and sample after VUV irradiation for 1000 h. The average lifetime (τ) can be calculated by the following equation:

$$\tau = \tau_1 I_1 + \tau_2 I_2. \quad (2)$$

It is found that after VUV irradiation for 1000 h, the values of average τ clearly decreases from 291.3 ps to 284.4 ps. For the positron annihilation experiments, positrons in solid are trapped at negative vacancy defects because of the missed positive charges of the ion cores, and thus the increased electron density at a positively charged vacancy such as oxygen vacancy ($V_o^{\bullet\bullet}$) could reduce its positron lifetime.[11,12] Therefore, it is understandable that the vacancy which is created during VUV irradiation is positively charged and thus it could be attributed to oxygen vacancy ($V_o^{\bullet\bullet}$).

Table 1. The positron annihilation lifetimes of fresh BAM:Eu^{2+} and BAM:Eu^{2+} samples after VUV irradiation.

	τ_1/ps	τ_2/ps	I_1/%	I_2/%	τ/ps
Fresh BAM:Eu^{2+}	196.8	67.7	489.3	32.3	291.3
Irradiated BAM:Eu^{2+}	193.1	68.4	481.5	31.6	284.4

Figure 4(a) represents the comparison between absorption spectra of fresh BAM:Eu^{2+} and sample after VUV irradiation for 1000 h. The absorption band in 215 nm–400 nm is mainly attributed to the direct absorption of Eu^{2+} ions and the band in 200 nm–210 nm has been proved to be trap absorption (oxygen vacancies in this case).[2,3] It can be seen that after VUV irradiation, the trap absorption in 200 nm–210 nm of the sample increases obviously, suggesting the increase of the trap centre ($V_o^{\bullet\bullet}$) in sample.

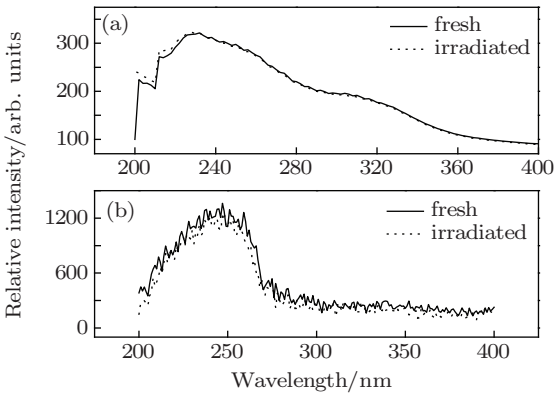


Fig. 4. Comparison between absorption spectra of fresh BAM:Eu^{2+} (solid line) and sample after VUV irradiation (dotted line) (a), and comparison between emission spectra (λ_{ex} = 170 nm) of the fresh non-doped BAM host (solid line) and the sample after VUV irradiation (dotted line) (b).

Figure 4(b) exhibits the emission spectra of the fresh non-doped BAM host and the sample after VUV irradiation under 170-nm excitation, which is in line with the band edge of BAM at about 7.0 eV.[13] The host emission occurs as a broad band peaked at 265 nm, which comes from a self-trapped exciton (STE) at Ba-O group.[13] It is observed that after VUV irradiation, the change of the host emission of BAM is found to be very slight. This result indicates that the VUV irradiation degradation is not related to host damage but it is partly linked to the perturbation of host-to-activator energy transfer process.

As is well known, the decay time is an effective means of detection of traps. The decay curves of fresh BAM:Eu^{2+} and sample after VUV irradiation are measured and shown in Fig. 5. Generally, all the curves can be well fitted using the following double-exponential expression:

$$I = A\exp(-t/\tau') + B\exp(-t/\tau''), \tag{3}$$

where τ_1 and τ_2 are the fast and slow components of the decay time and A and B are the fitting parameters. The average decay time (τ) can be determined as $\tau = (A\tau'^2 + B\tau''^2)/(A\tau' + B\tau')$. It is found that the decay time for the sample after VUV irradiation is longer than that of fresh sample, which is beyond the measurement error. It demonstrates that these traps (oxygen vacancies) resulting in a slightly longer decay time are mainly responsible for the VUV irradiation degradation.

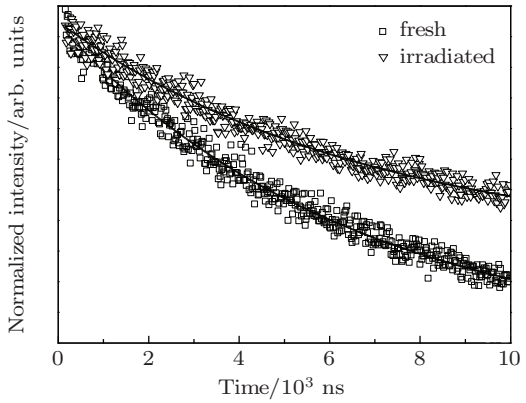


Fig. 5. Decay curves for fresh BAM:Eu^{2+} (empty triangle) and sample after VUV irradiation (empty squares).

4. Conclusions

A real VUV irradiation source is applied to the investigation on the VUV irradiation degradation of BAM:Eu^{2+} phosphor. The results show that the oxidation of Eu^{2+} ions is induced by VUV irradiation and it is partly contributes to the VUV irradiation degradation of BAM:Eu^{2+}. Some traps (oxygen vacancies) are generated during VUV irradiation, thereby inducing a negative perturbation of energy to transfer from the host to Eu^{2+}. It is concluded that the oxygen vacancies should be mainly responsible for the VUV irradiation degradation of BAM:Eu^{2+} phosphors used in PDPs and Hg-free lamps.

References

[1] Deng C Y, He D W, Zhuang W D, Wang Y S, Kang K and Huang X W 2004 *Chin. Phys.* **13** 473

[2] Bizarri G and Moine B 2005 *J. Appl. Phys.* **98** 113528

[3] Bizarri G and Moine B 2005 *J. Lumin.* **113** 199

[4] Yokota K, Zhang S, Kimura K and Sakamoto A 2001 *J. Lumin.* **92** 223

[5] Lehmann W, Ryan F M, Manocha A S and Allister W 1983 *J. Electrochem. Soc.* **130** 171

[6] Justel T, Lade H, Mayr W, Meijerink A and Wiechert D U 2003 *J. Lumin.* **101** 195

[7] Zhang J C, Zhou M J, Liu B T, Wen Y and Wang Y H 2012 *J. Lumin.* **132** 1949

[8] Zhou M J, Zhang J C and Wang Y H 2011 *Acta Phys. Sin.* **61** 074103 (in Chinese)

[9] Liu B T, Wang Y H, Zhou J, Zhang F and Wang Z F 2009 *J. Appl. Phys.* **106** 053102

[10] Peng M, Pei Z, Hong G and Su Q 2003 *J. Mater. Chem.* **13** 1202

[11] Balogh A G, Puff W, Liszkay L and Molnar B 1988 *Phys. Rev.* B **38** 2883

[12] Saarinen K, Nissilä J and Hautojärvi P 1999 *Appl. Phys. Lett.* **75** 2441

[13] Howe B and Diaz A L 2004 *J. Lumin.* **109** 51