Article ID: 1000-7032(2009)02-0131-04

The Lineshape of Emission Spectra on $BaMgAl_{10}O_{17}:Eu^{2+}$ Phosphor

YIN Yan[1], TANG Yong-bo[1], ZHANG Bao-ping[2], WANG Hai-bo[2]*

(1. *College of Materials Science and Engineering, Nanjing University of Technology, Nanjing* 210009, *China*;
2. *The Research Institute of Electric Light Source Materials of NJUT, Nanjing* 210015, *China*)

Abstract: $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) is the blue phosphor component of three-color fluorescent lamps and plasma display panels(PDP). In present paper the emission spectra lineshape of BAM were investigated by using lattice relation and theory of multiphonon transitions. The result indicated that the broadening emission band of BAM can be fitted by three Gaussian functions very well, the transitions from three different site of Eu^{2+} in the BAM lattice forms the BAM emission spectra, the two of the emission centers are assigned to Eu^{2+} at normal Beevers-Ross sites and anti-Beevers-Ross sites, respectively, but the third luminescence center may be located at mid-oxygen (m_O) sites.

Key words: BAM; lineshape; multiphonon transiton; emission spectrum
CLC number: O482.31 **PACS**: 78.55.Hx **PACC**: 3250F; 7855 **Document code**: A

1 Introduction

Barium magnesium aluminate ($BaMgAl_{10}O_{17}$) activated by divalent europium is a widely used blue phosphor in three-color fluorescent lamps and plasma display panels (PDP)[1,2], so more attention has been paid to it. Under UV or VUV excitation, $BaMgAl_{10}O_{17}:Eu^{2+}$ exhibits a strong emission band at 450 nm corresponding to $4f^65d$ to $4f^7$ transition. In many papers the optical transition process was described by configuration coordinate mode, configuration coordinate mode has its merit, however, it is too simple to interpret the reason why the emission spectra lineshape of $BaMgAl_{10}O_{17}:Eu^{2+}$ is approximately in accordance with Gaussian distribution.

Under UV or VUV excitation, the electron is excited from ground state into a upper state and then the change of the electronic charge density causes displacement of the neighboring atoms, that is, the neighbouring ions will take up new equilibrium positions, compared with the electronic transition this process was shown by Frank Condon approximation[3]. The transition process mentioned above is generally described as configuration coordinate model, in fact, if quantum mechanics is used on the transition process, we will arrive at the theory of multiphonon transitions[4].

2 Experiments

The $BaMgAl_{10}O_{17}:Eu^{2+}$ blue phosphor samples were prepared by solid state reaction method. Mill the blend of $BaCO_3$, Al_2O_3 and Eu_2O_3, then a small amount of BaF_2 was added as flux, all the above materials were of analytical grade exceeding 99.9% purity, subsequently the milled blend was fired at 1 500 ℃ with CO atmosphere for 3 h and slowly cooled down to room temperature at the furnace.

The X-ray powder diffraction data of BAM phosphor were collected in scattering range of 10° ~ 80° with 0.02 interval in 2θ using a Rigaku D/max-

Received date: 2008-08-25; **Revised date**: 2008-11-15
Foundation item: Project supported by Research on the Open of Inorganic and New Composite Materials Key Laboratory of Jiangsu Province (wjjqfhxcl200605)
Biography: YIN Yan, Female, was born in 1985, Jiangsu Province. Her work focuses on inorganic luminescen material. E-mail: epyan85@163.com
*: Corresponding Author; E-mail: wanghaibo88@163.com, Tel: (025)58805619

2000 X-ray diffractometer (CuKα raditation, λ = 0.154 18 nm, with graphite monochromator). The emission spectra were measured by Nichia MPF-4 spectroradiometer.

3 Results and Discussion

3.1 XRD Patterns

The main objective of XRD is to identity the forming of BAM. XRD patterns of the samples are shown in Fig. 1. The XRD patterns indicate that all of the diffraction peaks are assign to the $BaMgAl_{10}O_{17}$ phase and no characteristic peaks of dopants have been observed, the result shows that the solid state solution of BAM is formed and no other phase.

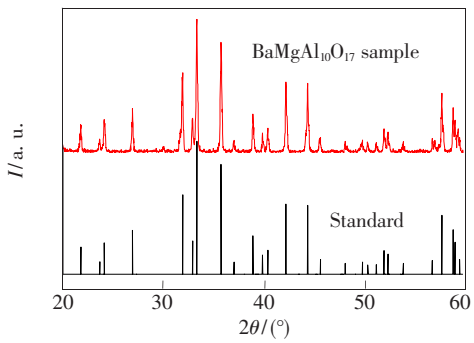

Fig. 1 X-ray diffraction patterns of $BaMgAl_{10}O_{17}$: Eu phosphor

3.2 Theory

Denoting the initial state and final state by $|jn\rangle$ and $|in'\rangle$ respectively, the transition probability between $|jn\rangle$ and $|in'\rangle$ has the following form[5]:

$$I_{ba}(E)=A_nV\sum_{n'}|\langle in'|M|jn\rangle|^2\delta(E_{jn}-E_{in'}-E) \tag{1}$$

where symbol A_nV means the "thermal average" over initial lattice vibrational states weighting each with the Boltzmann factor $\exp[-E_{jn}/kT]$. It is more convenient to calculate the Fourier transform of equation (1)[6]

$$f(u)=\int_{-\infty}^{\infty}I(E)\mathrm{e}^{-iuE}\mathrm{d}E \tag{2}$$

With (1), we have from (2):

$$f(u)=\left(\sum_n \mathrm{e}^{-\beta E_{jn}}\right)^{-1}\sum_n\sum_{n'}\int_{-\infty}^{\infty}|\langle in'|M|jn\rangle|^2\delta[E-(E_{jn}-E_{in'})]\mathrm{e}^{-iuE}\mathrm{d}E \tag{3}$$

where $\beta = 1/kT$, the Frank Condon approximation asserts that the electronic dipole operator M does not depend significantly on q, so one can obtain the following equation:

$$\int\varphi_i(r,q)M\varphi_j(r,q)\mathrm{d}x = M_{ij} \tag{4}$$

in which r and q is the coordinate of electron and the lattice, respectively.

If E_{jn} and E_{in} were replaced by the corresponding Hamiltonian operators H_i and H_j, we can express the manipulating result in terms of traces[7]:

$$f(u)=tr[M_{ij}^*\mathrm{e}^{iH_j}M_{ij}\mathrm{e}^{-(iu+\beta)H_j}]/tr[\mathrm{e}^{-\beta H_j}] \tag{5}$$

Making use of Mehler's formula[8] and the method of moments, equation (5) can be factorized, the factorization processes is complicated and lengthy, in order to save space we here represent the final result that was published in Huan Kun's paper[9]:

$$I(E)=\frac{|M_{ij}|^2}{[2\pi S(T)(\overline{\hbar\omega_s})_T^2]^{1/2}}\exp\left[-\frac{(E-\bar{E})^2}{2S(T)(\overline{\hbar\omega_s})_T^2}\right] \tag{6}$$

where $S(T)$ and $\overline{(\hbar\omega_s)}$ is defined by (7) and (8), respectively.

$$S(T)=\sum_s\left(\frac{\omega_s}{2\hbar}\right)\Delta_{js}^2 \tag{7}$$

$$\overline{(\hbar\omega_s)}=\frac{1}{S(T)}\sum_s\left[\left(\frac{\omega_s}{2\hbar}\right)\Delta_{js}^2\right](\hbar\omega_s) \tag{8}$$

Obviously, the emission spectrum of phosphors which have a strong electron-phonon interaction should be Gaussian lineshape as shown by Eq. (6).

3.3 Fitting

BAM has a broad emission band with an asymmetric line shape, but according to multiphonon transition theory in section 3.2, the lineshape of emission spectrum of BAM should be Gaussian and symmetric, the non-Gaussian shape might be caused by several reasons independently or together: small Stokes shift (small Huang-Kun factor), reabsorption of emission of phosphor, or it is due to multiple luminescent sites.

The wider emission band of BAM implies that Huang-Kun factor was large and it was transparent for its emitting phonons; so small Stokes shift and reabsorption should be eliminated. By examining

these reasons that result in the asymmetry of BAM's emission spectrum, multiple luminescence sites can be used to explain the asymmetry of BAM's emission spectrum satisfactorily.

Previously, Ellen[10], using fluorescent probe, determined that there are at least two unique Eu^{2+} sites in BAM lattice, whereafter XRD experiment on single crystals indicated that there are three different types of sites for Eu^{2+} in BAM[11]. The emission spectrum cannot reasonably be fit with two centers, the residual distribution of Fig. 2 is not stochastic. The best fitting of the normalized Eu emission spectra in BAM with three Gaussian profile are shown in Fig. 3, the peaks at 2.739 eV (452.6 nm), 2.836 eV (437.2 nm), 2.616 eV (474.0 nm) are labeled Eu1, Eu2, and Eu3, Eu1 is assigned at a normal

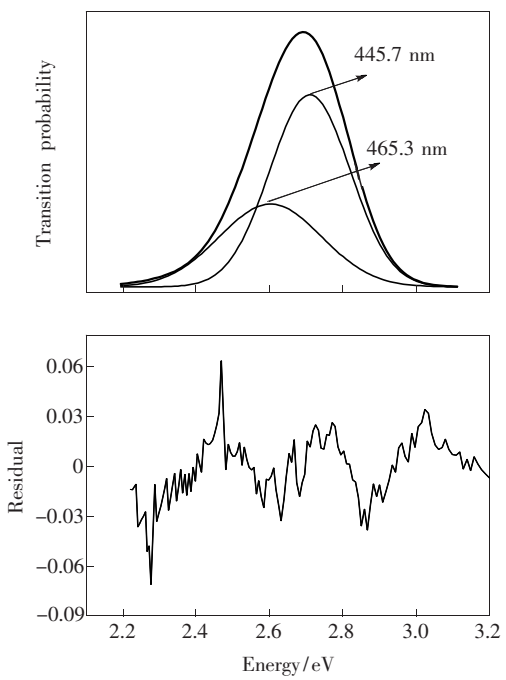

Fig. 2　The fitting of line profile of BAM's emission spectrum by using two Gaussians

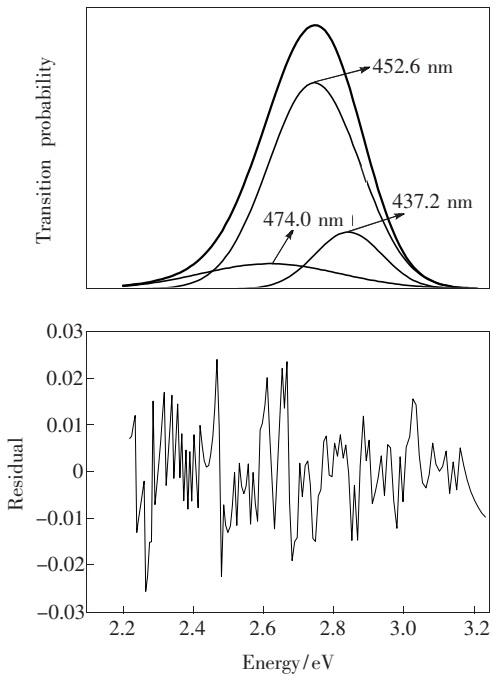

Fig. 3　The fitting of line profile of BAM's emission spectrum by using three Gaussians

Ba site in BAM lattice (Beevers-Ross site), and Eu2 displaced to an anti-Beevers-Ross at site[12], the assignment of Eu3 may be at mid-oxygen m_O site.

4　Conclusion

Theory of multiphonon transitions predicts that emission spectrum of phosphor that has a strong electron-lattice coupling is approximately Gaussian lines.

The emission spectrum of BAM phosphor can be fitted with three gaussian functions statisfactory, the emission peaks occur at 2.739 eV(452.6 nm), 2.836 eV (437.2 nm), 2.616 eV(474.0 nm) and these three different emission peaks are caused by three types of luminescence center, that is Beever-Ross sites, anti-Beevers-Ross sites and mid-oxyden sites.

References:

[1] Kazuyoshi Yoko, Zhang Shuxiu, Datsuadi Kimura, *et al.* Eu^{2+}-actived barium magnesium aluminate phosphor for plasma displays—Phase relation and mechanism of thermal degradation [J]. *J. Lumin.*, 2001, **92**(3):223-224.

[2] Shen Jingfei, Wang Haibo, Huang Ruxi, *et al.* Surface coating of BAM phosphors with MgF_2[J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(2):264-268 (in Chinese).

[3] Otfried Madelung. *Introduction to Solid-state Theory* [M]. Beijing: World Publishing Corporation, 2003, 413-414.

[4] Kun Huang, Avril Rhys. Theory of light absorption and non-radiative transitions in F-centers [J]. *Proceedings of the Royal*

Society of London. Series A, *Mathematical and Physical Sciences*, 1950, **204**(1078):406-409.

[5] O'Rourke R C. Absorption of light by trapped electrons [J]. *Phys. Rev.*, 1953, **91**(2):265-270.

[6] Pyogo Kubo, Yutaka Toyozawa. Application of the generating function to radiative and non-radiative transitions of a trapped electron in a crystal [J]. *Progress of Theoretical Physics*, 1955, **13**(2):164-167.

[7] Melvin Lax. The Frank-Condon principle and its application to crystals [J]. *J. Chemical Physics*, 1952, **20**(11): 1753-1754.

[8] Jordan Markham J. Interaction of normal modes with electron traps [J]. *Reviews of Modern Phys.*, 1959, **31**(4): 973-976.

[9] Kun Huang. Lattice relation and theory of multiphonon transitions [J]. *Progress in Physics* (物理学进展), 1981, **1**(1): 31-37 (in Chinese).

[10] Ellen A, Zwaschka F, Kummer F, *et al.* Sm^{2+} in BAM: fluorescent probe for the number of luminescence sites Eu^{2+} in BAM [J]. *J. Lumin.*, 2001, **93**(2):147-153.

[11] Mishra K C, Raukas M, Ellens A, *et al.* A scattered wave modes of electronic structure of Eu^{2+} in $BaMgAl_{10}O_{17}:Eu^{2+}$ and associated excitation processes [J]. *J. Lumin.*, 2002, **96**(2-4):95-105.

[12] Valerie Pike, Samuel Patraw, Anthony, *et al.* Defect chemistry and VUV optical properties of the $BaMgAl_{10}O_{17}:Eu^{2+}$-$Ba_{0.75}Al_{11}O_{17.25}:Eu^{2+}$ solid solution [J]. *J. Solid State Chem.*, 2003, **173**(2):359-366.

$BaMgAl_{10}O_{17}:Eu^{2+}$ 发射光谱的谱峰形状

印 琰[1], 唐永波[1], 张宝平[2], 王海波[2*]

(1. 南京工业大学 材料科学与工程学院, 江苏 南京 210009; 2. 南京工业大学 电光源材料研究所, 江苏 南京 210005)

摘要: $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM)是三基色荧光灯和等离子显示用荧光粉中的蓝色组分。用晶格弛豫和多声子跃迁理论研究了BAM发射光谱的谱峰分布。结果表明可以用三个高斯函数很好地拟合BAM的宽带发射。BAM的宽带发射可能由分布在$BaMgAl_{10}O_{17}$晶格中三个不同位置的Eu^{2+}的能级跃迁构成。三个Eu的发光中心分别是Beevers-Ross位和anti-Beevers-Ross位,第三个Eu^{2+}的发光中心可能是位于尖晶石基块中的mid-oxygen(m_o)位。

关 键 词: BAM; 线型状; 多声子跃迁; 发射谱

中图分类号: O482.3 **PACS:** 78.55.Hx **PACC:** 3250F; 7855 **文献标识码:** A

文章编号: 1000-7032(2009)02-0131-04

收稿日期: 2008-08-25; **修订日期:** 2008-11-15

基金项目: 江苏省无机及其复合新材料重点实验室开放研课题(wjjqfhxcl200605)资助项目

作者简介: 印琰(1985-), 女, 江苏南京人, 主要从事无机发光材料的研究。
E-mail: epyan85@163.com

*: 通讯联系人; E-mail: wanghaibo88@163.com, Tel: (025)58805619