VNU Journal of Science, Mathematics - Physics 23 (2007) 84-91

Optical transition of Eu^{3+} in $Mg(Al_{1-x} Eu_x)_2O_4$

Trinh Thi Loan[*], Le Hong Ha, Nguyen Ngoc Long

Department of Physics, College of Science, VNU
334 Nguyen Trai, Hanoi, Vietnam

Received 29 November 2007; received in revised form 14 December 2007

Abstract. The powders of $Mg(Al_{1-x}Eu_x)_2O_4$ have been synthesized by sol-gel method. Optical properties of the material were investigated. The nature of lines in luminescence spectra is related to the electron transitions of Eu^{3+} ions corresponding to different sites in the lattice. The influence of Eu concentration on optical spectra was studied.

1. Introduction

The rare-earth in general, and Eu^{3+} ions in particular - doped materials have a large attention because of their potential use in optical devices such as lasers, fiber amplifiers, hole-burning high-density memory, projection color television...[1,2,3]. Besides, the Eu^{3+} ions are well known as an active element for red emitting phosphors. Their spectra may give detailed information about the surrounding of Eu^{3+} ions in a lattice. That is why, it is a very useful structural and optical probe.

In the present work, we report on study of optical properties of trivalent europium ions in powders of $Mg(Al_{1-x}Eu_x)_2O_4$ synthesized by citrate gel method. Our investigation are mainly focused on the nature of lines corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 1,2,3,4) emission transitions of Eu^{3+} ions.

2. Experimental

The powders of $Mg(Al_{1-x}Eu_x)_2O_4$ were synthesized by the method described in [4]. $Mg(NO_3)_2$, $Al(NO_3)_3$ and $Eu(NO_3)_3$ solutions were mixed with molar ratio Mg^{2+}: Al^{3+}: Eu^{3+} = 1: 2(1-x): 2x. Citric acid aqueous solution was added into the above solution with molar ratio CA: ΣM^{n+} = 1.3. The solution was vigorously stirred at room temperature. The pH of solution was adjusted to $6 \div 6.5$ by adding the ammonia solution. These conditions were drawn from our study of the influence of molar ratio CA :ΣM^{n+} and pH of solution on the citrate gel formation. By heating and vigorously stirring the solution at $60 \div 70$ °C, a homogeneous and transparent gel was obtained. After drying in air at $100 \div 110$ °C for a day, the gel was converted to a xerogel more opaque and dense.

The excitation and emission spectra were carried out on FL3-22 Jobin Yvon Spex USA spectrofluorometer with 450W xenon lamp as an excitation source. X-ray diffraction patterns were examined by diffractometer D5005 Brucker Germany.

---

[*] Corresponding author. Tel.: 84-4-8587344
E-mail: loantt@vnu.edu.vn

3. Results and discussion

3.1. Photoluminescence spectra

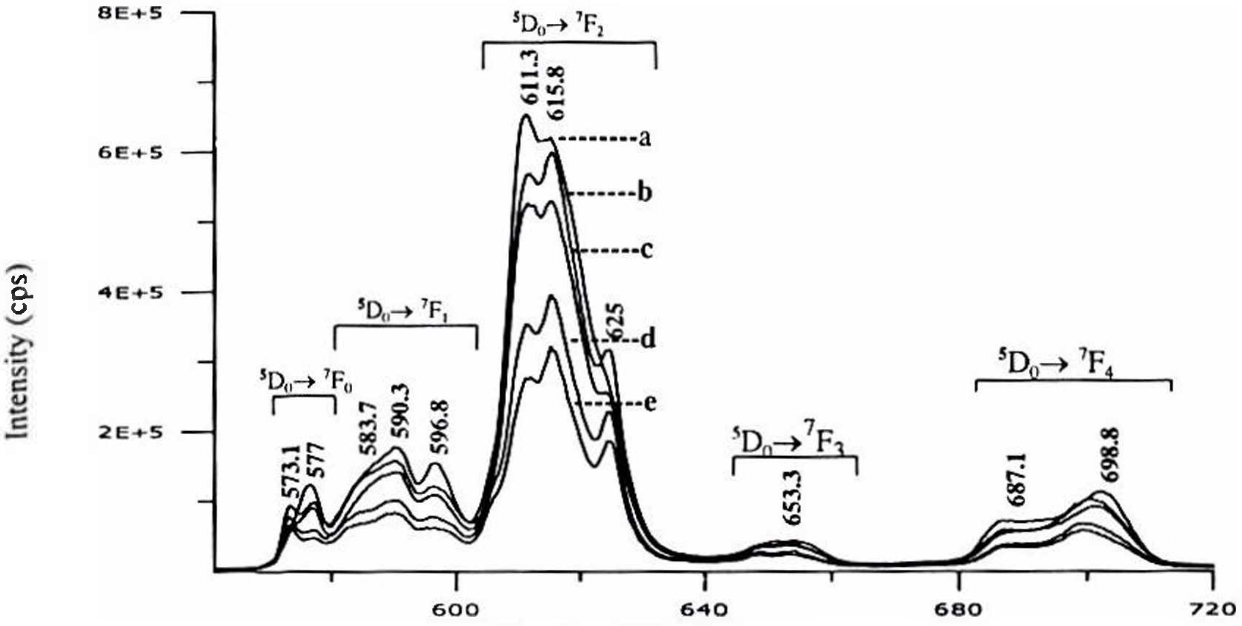

Fig. 1. Emission spectra of $Mg(Al_{1-x}Eu_x)_2O_4$ with different contents x, λ_{exc}= 399 nm.
a- x = 0.01; b- x = 0.04; c- x = 0.08; d- x = 0.15; e- x = 0.2.

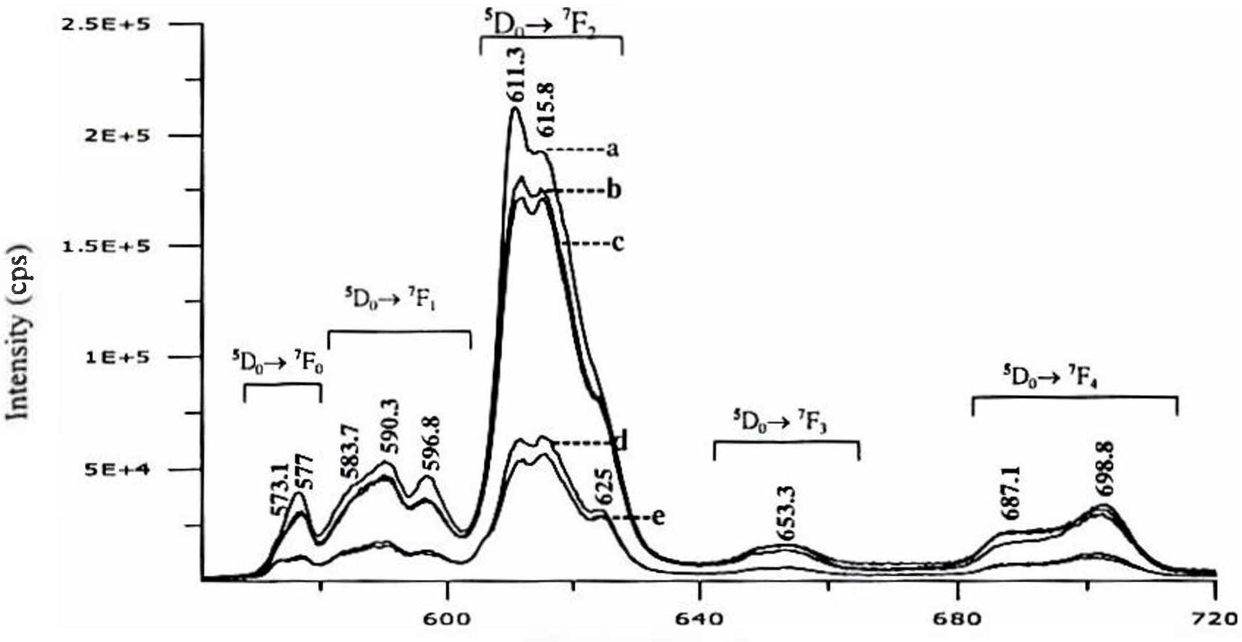

Fig. 2. Emission spectra of $Mg(Al_{1-x}Eu_x)_2O_4$ with different contents x, λ_{exc}= 469 nm.
a- x = 0.01; b- x = 0.04; c- x = 0.08; d- x = 0.15; e- x = 0.2.

The room temperature fluorescence spectra excited by 399 nm and 469 nm wavelengths of the synthesized $Mg(Al_{1-x}Eu_x)_2O_4$ with different contents (x = 0.01 - 0.2) of Eu^{3+} ions are presented in Fig.1 and 2, respectively. The peak positions of lines assigned to $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions are given in Table 1.The results indicate that the intensity of emission lines corresponding to $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) transitions decreased with increasing concentrations of Eu^{3+} ions. It is seen from Fig.1 that in the case of $^5D_0 \rightarrow {}^7F_0$ nondegenerate transition in emission spectra of $Mg(Al_{1-x}Eu_x)_2O_4$ with the lowest content (x = 0.01) only one line at 577 nm is observed. For samples with higher concentrations of Eu^{3+} ions, besides the line at 577 nm we could find other one at 573.1 nm, which also belongs to $^5D_0 \rightarrow {}^7F_0$ transition. These results strongly suggest the existence of two sites of Eu^{3+} ions located at 577 nm (labeled A-site) and at 573.1 nm (labeled B-site) in the powders of $Mg(Al_{1-x}Eu_x)_2O_4$, the nature of which will be discussed later.

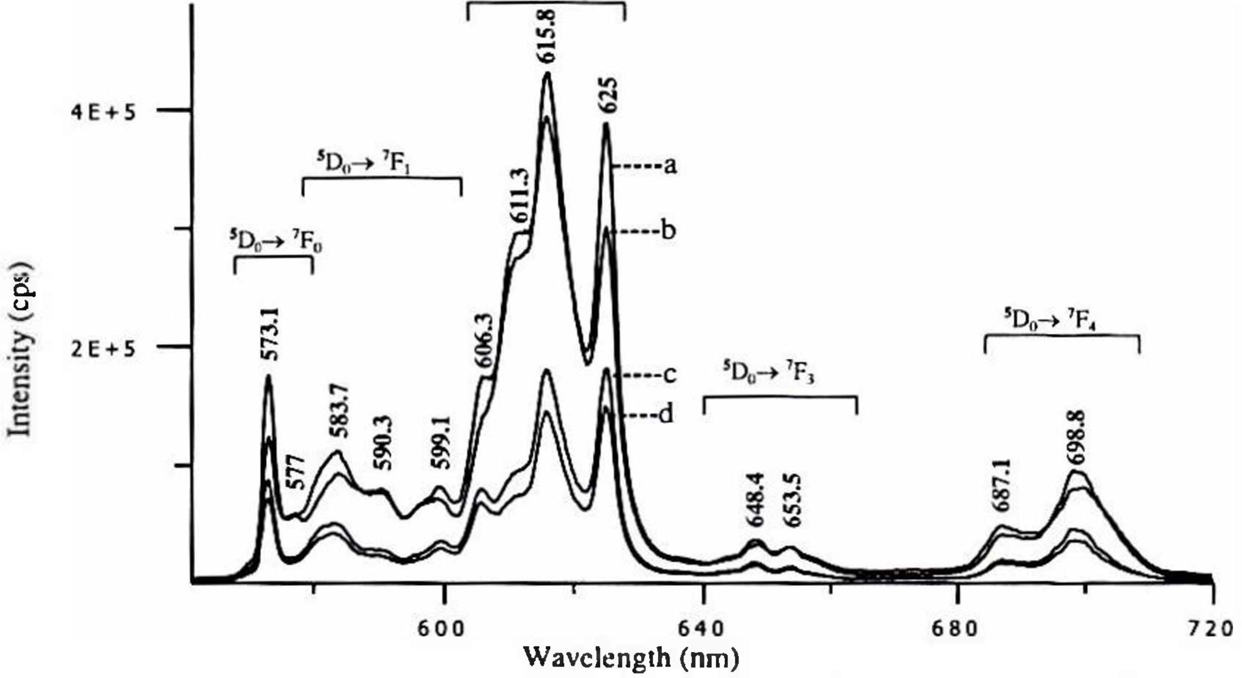

Fig. 3. Emission spectra of $Mg(Al_{1-x}Eu_x)_2O_4$ with different contents of Eu^{3+}, λ_{exc}= 396 nm. a- x = 0.04; b- x = 0.08; c- x = 0.15; d- x = 0.2.

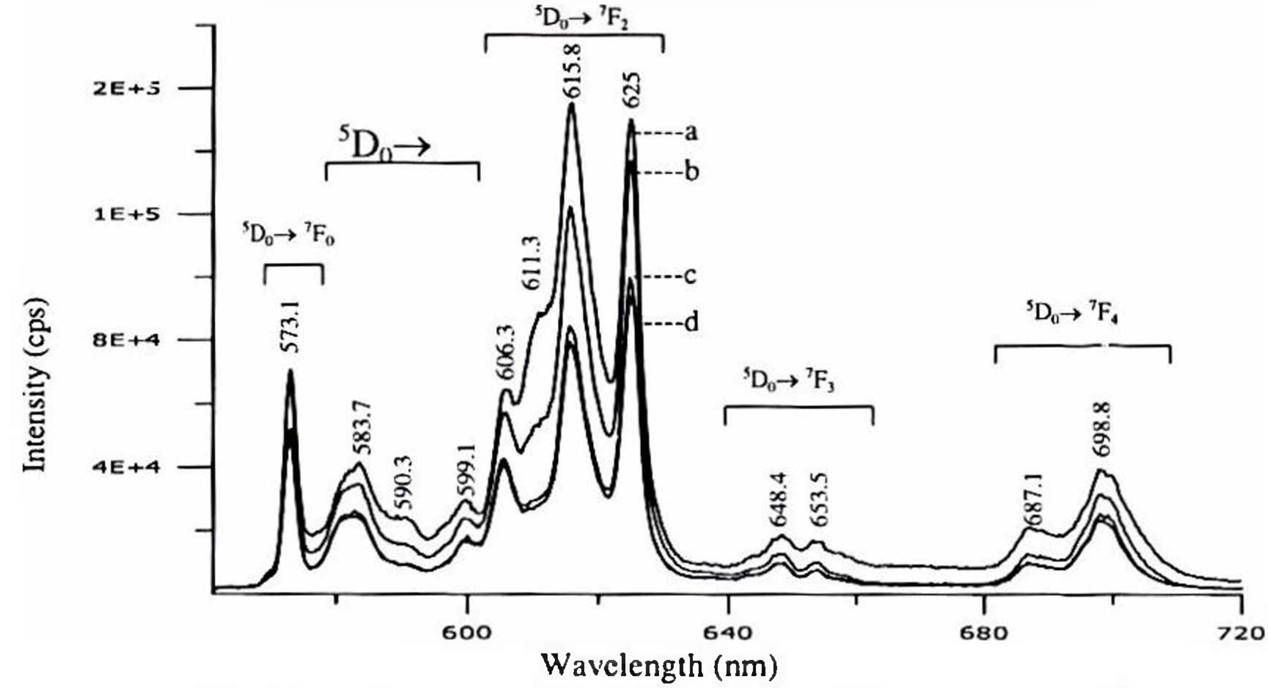

Fig. 4. Emission spectra of $Mg(Al_{1-x}Eu_x)_2O_4$ with different contents of Eu^{3+}, λ_{exc}= 466 nm . a- x = 0.04; b- x = 0.08; c- x = 0.15; d- x = 0.2.

Moreover, in the observed emission spectra dominant peaks lying at 611.3 nm and 615.8 nm belong to $^5D_0 \rightarrow {}^7F_2$ transition. It means that there is an asymmetry in the sphere surrounding the Eu^{3+} ions in synthesized material [5]. When the samples Mg(Al$_{1-x}$Eu$_x$)$_2$O$_4$ with contents of Eu^{3+} ions $x \geq$ 0,04 were excited by 396 nm and 466 nm, significant differences in the spectral structure are shown in Fig. 3 and 4. For comparison, the peak positions corresponding to $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions in these cases are also given in the Table 1. It means that, with the selective excitation wavelengths we could obtain only one luminescence line at 573.1 nm for $^5D_0 \rightarrow {}^7F_0$ transition related to B-site of the Eu^{3+} ions in the lattice. The presence of the strongly forbidden $^5D_0 \rightarrow {}^7F_0$ transition indicates that, the local site is the lack of inversion symmetry [6]. Moreover, the existence of B-site here creates not only the peak at 573.1 nm associated to $^5D_0 \rightarrow {}^7F_0$ transition, but also the other new ones at 599.1 nm ($^5D_0 \rightarrow {}^7F_1$) and at 606.3 nm ($^5D_0 \rightarrow {}^7F_2$). Besides, in the wavelength range corresponding to $^5D_0 \rightarrow {}^7F_2$ transition the luminescence lines are different from those showing in Fig. 1 and 2. Here we can see a strong intensive sharp line lying apart at 625 nm, its intensity is compared with 615.8 nm line, while peak at 611.3 nm in this case is weaker.

Table 1. The peak positions assigned to $^5D_0 \rightarrow {}^7F_{0,1,2}$ emission transitions in synthesized Mg(Al$_{1-x}$Eu$_x$)$_2$O$_4$.

Content of Eu^{3+} (x)	Transitions $^5D_0 \rightarrow {}^7F_j$ (j = 0,1,2)	Peak positions (nm)	
		λ_{exc} = 399 nm or 469 nm	λ_{exc} = 396 nm or 466 nm
0.01	J = 0	577.0 (site-A)	–
	J = 1	590.3 (site-A)	–
		596.8 (site-A)	–
	J = 2	611.3 (site-A)	–
		615.8 (site-A+B)	–
0.04 - 0.08	J = 0	573.1 (site-B)	573.1 (site-B)
		577.0 (site-A)	–
	J = 1	–	581.0 (site-B)
		583.7 (site-B)	583.7 (site-B)
		590.3 (site-A)	590.3 (site-A)
		596.8 (site-A)	–
		–	599.1 (site-B)
	J = 2	–	606.3 (site-B)
		611.3 (site-A)	611.3 (site-A)
		615.8 (site-A+B)	615.8 (site-A+B)
		625.0 (site-B)	625.0 (site-B)
0.15 - 0.2	J = 0	573.1 (site-B)	573.1 (site-B)
		577.0 (site-A)	–
	J = 1	–	581.0 (site-B)
		583.7 (site-B)	583.7 (site-B)
		590.3 (site-A)	590.3 (site-A)
		596.8 (site-A)	–
		599.1 (site-B)	599.1 (site-B)
	J = 2	–	606.3 (site-B)
		611.3 (site-A)	611.3 (site-A)
		615.8 (site-A+B)	615.8 (site-A+B)
		625.0 (site-B)	625.0 (site-B)

3.2. Excitation spectra

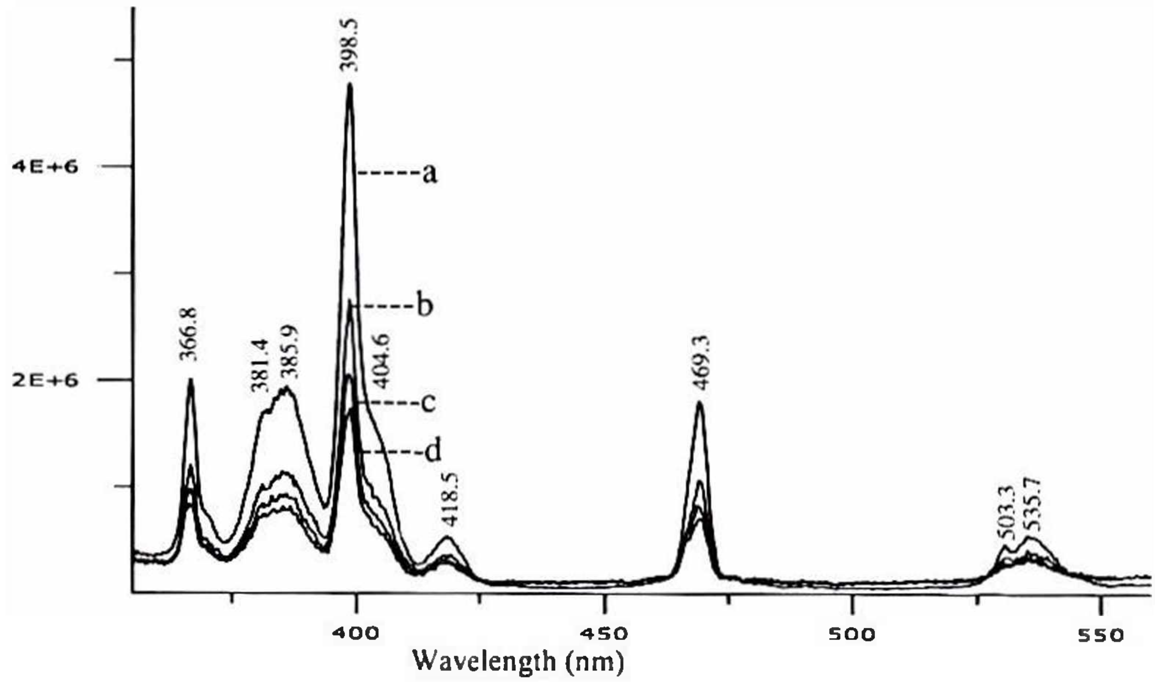

Fig. 5. $^5D_0 \rightarrow {}^7F_{0,1,2}$ excitation spectra of Eu^{3+} for emission line assigned to A-site.
a- λ_{em} = 611.3 nm; b- λ_{em} = 590.3 nm; c- λ_{em} = 596.8 nm; d- λ_{em} =577 nm.

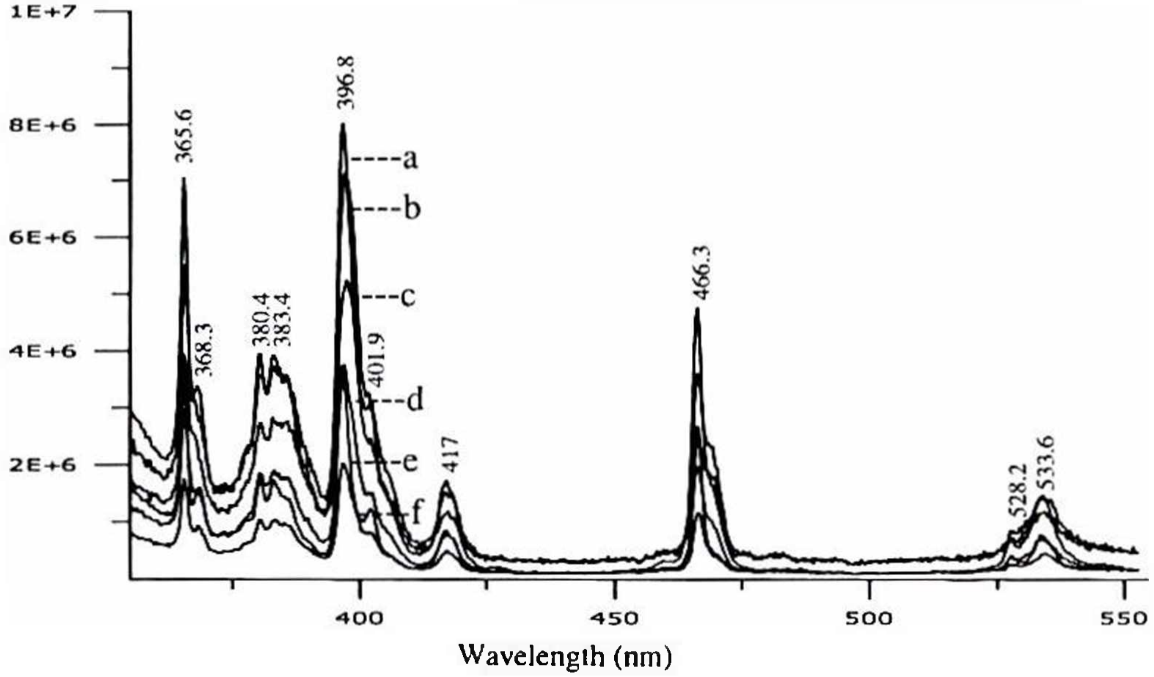

Fig. 6. $^5D_0 \rightarrow {}^7F_{0,1,2}$ excitation spectra of Eu^{3+} for emission line assigned to B-site.
λ_{em} = 625 nm; b- λ_{em} = 583.1 nm; c- λ_{em} = 599.1 nm; d- λ_{em} = 606.3 nm; e- λ_{em} = 573.1 nm; f- λ_{em} = 581 nm.

The excitation spectra for luminescence lines around $^5D_0 \rightarrow {}^7F_j$ transitions in the wavelength region from the near UV to visible (350 nm - 560 nm) including lines associated to intra - 4f^6 absorption transitions from the ground level $^7F_0$ to the excited levels $^5D_{1-5}$, $^5G_2$, $^5L_6$ [7] were examined at room temperature. From series of similar lines, the observed excitation spectra could be classified into two groups, which are displayed in Fig. 5 and 6. For the first group, there are spectra recorded by monitoring the fluorescence of transitions $^5D_0 \rightarrow {}^7F_j$ at 577 nm (j = 0), 590.3 - 596.8 nm (j = 1) and 611.3 nm (j = 2), while the second ones are associated to 573.1 nm (j = 0), 581 - 583.7 - 590.3 - 599.1 nm (j = 1) and 606.3 - 625 nm (j = 2). The similar of the excitation spectra indicates that, each group of lines belongs to Eu^{3+} ions occupying the same site in the lattice of $Mg(Al_{1-x}Eu_x)_2O_4$. For comparison between two groups, the excitation spectra for the emission lines assigned to the nondegenerate transition $^5D_0 \rightarrow {}^7F_0$ at 577 nm and 573.1 nm are shown in Fig.7. Here we can see the different spectra with a pair of corresponding peaks, which are shifted each other about 2 - 3 nm. This result also is an obvious evidence about presence of two different sites of Eu^{3+} ions in $Mg(Al_{1-x}Eu_x)_2O_4$.

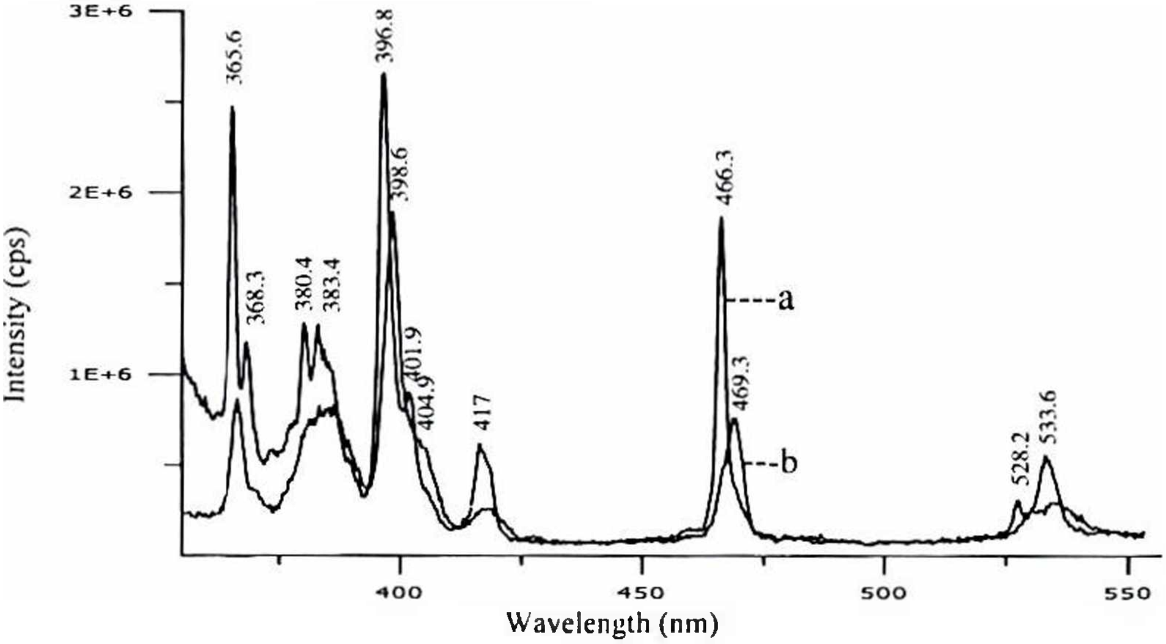

Fig. 7. Site selective $^5D_0 \rightarrow {}^7F_0$ excitation spectra of Eu^{3+} corresponding to a- 573.1 nm of B-site; b- 577 of A-site.

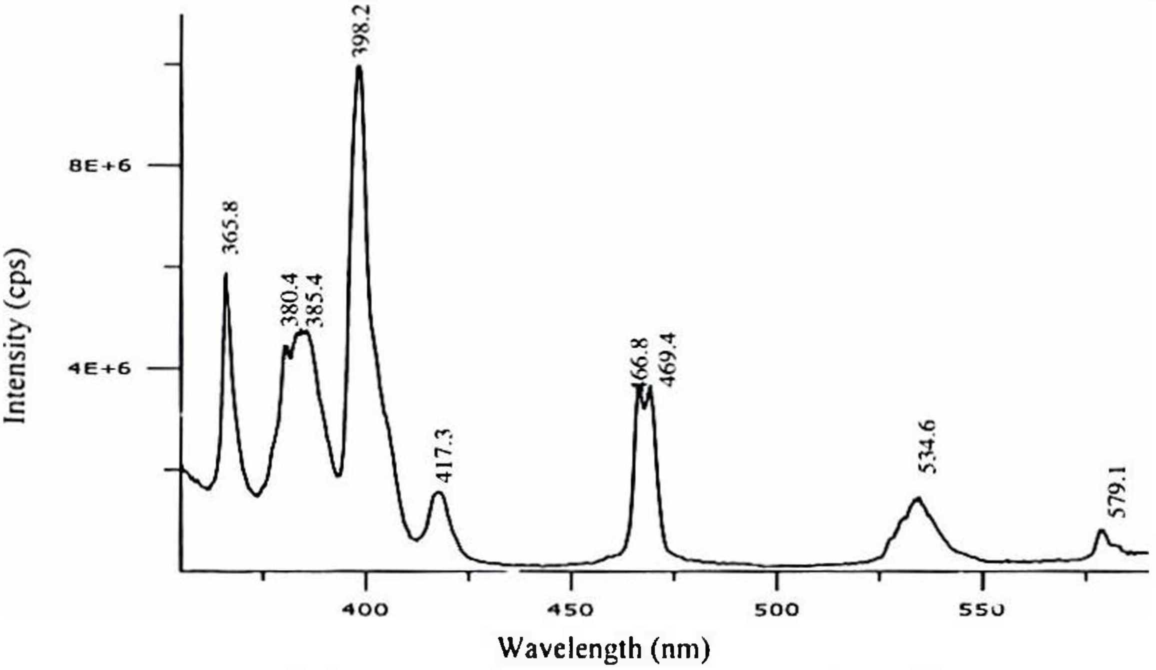

Fig. 8. Excitation spectra of Eu^{3+} ions for emission line $^5D_0 \rightarrow {}^7F_2$ at 615.8 nm.

For the luminescence transition $^5D_0 \rightarrow {}^7F_2$ besides above-mentioned peaks at 611.3 nm belonging to the first group and 606.3 - 625 nm corresponding to the second one, there is a peak at 615.8 nm, the excitation spectra recorded by monitoring the fluorescence of which is displayed in Fig.8. The presence of both of peaks in the spectrum with equal intensity at 466.3 nm and 469.3 nm corresponding to two sites A and B of Eu^{3+} ions indicates their contribution to emission line at 615.8 nm. That is why, in every case, which was represented above, the emission line at 615.8 nm always is presented in the photoluminescence spectra.

In order to find the nature of fluorescence centers Eu^{3+} occupying different sites in $Mg(Al_{1-x}Eu_x)_2O_4$ our attention is focused on the investigation of X-ray diffraction pattern.

3.3. X-ray diffraction pattern measurement

The X-ray diffraction (XRD) pattern measurements in the diffraction angle range of 15^0-80^0 examined on samples of $Mg(Al_{1-x}Eu_x)_2O_4$ containing different concentration of Eu^{3+} ions are shown in Fig. 9. It is found that XRD patterns of $Mg(Al_{1-x}Eu_x)_2O_4$ strongly depend on concentrations of Eu^{3+} ions. As seen from Fig. 9 (a), in the sample with low content (x = 0.01), only strong sharp diffraction peaks corresponding to the structural phase of spinel $MgAl_2O_4$ were observed. With increasing content of Eu^{3+} ions (x = 0.08 – 0.2), these peaks became weaker and entirely new peaks were appeared in the spectra (see Fig. 9-b,c), which are interpreted as peaks associated to a new multiple phase of aluminium - europium oxide ($Al_2Eu_4O_9$/$2Eu_2O_3$-Al_2O_3). Thus, in samples of $Mg(Al_{1-x}Eu_x)_2O_4$ with higher contents of Eu^{3+} ions the host lattice includes two different phases. And the higher content of Eu^{3+} is, the weaker peaks related to spinel phase are and the more intensive ones assigned to phase of the $Al_2Eu_4O_9$ oxide are.

Based on this discussion it is concluded that, trivalent ions europium in powders of $Mg(Al_{1-x}Eu_x)_2O_4$ may be possible to occupy two different sites belonging to a phase of spinel $MgAl_2O_4$ and a phase of aluminium - europium oxide ($Al_2Eu_4O_9$/ $2Eu_2O_3$ - Al_2O_3). Thus, dopant Eu^{3+} ions in synthesized $Mg(Al_{1-x}Eu_x)_2O_4$ maybe also produce new peaks or change their intensity in optical spectra.

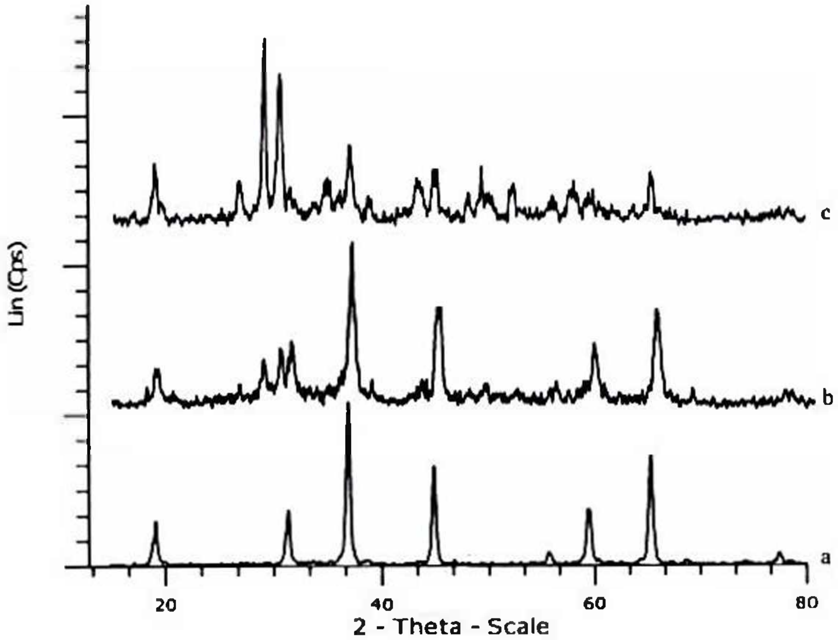

Fig. 9. X-ray diffraction patterns for $Mg(Al_{1-x}Eu_x)_2O_4$ with different content of Eu^{3+}.
a - x = 0.01; b - x = 0.08; c - x = 0.2.

Acknowledgments. This work was completed with financial support from Vietnam National University (N_0 QG 07-05). The authors wish to express their sincere gratitude to the Center for Materials Science, Department of Physics, College of Science for permission to use equipment.

References

[1] Masayuki Nogami, Takehito Nagakura, Tomokatsu Hayakawa, *J. Luminescence* 86 (2000) 117.

[2] D.B.M. Klssen, R.A.M. van Ham, T.G.M. van Rijn, *J. Luminescence* 43 (1989) 261.

[3] J.C. Ronfard-Haret, P. Valat, V. Wintgens, J. Kossanyi. *J. Luminescence* 91 (2000) 71.

[4] Nguyen Ngoc Long, Nguyen Hanh, Le Hong Ha, Trinh Thi Loan, Dao Viet Linh, *Proceedings of the Fifth Vietnamese-German Seminar on Physics and Engineering*, Hue, (2002) 320.

[5] M.A. Zaitoun, D.M. Goken, L.S. Bailey, T. Kim, C.T. Lin, *J. Phys. Chem. B* 104 (2000) 189.

[6] H.R. Li, H.J. Zhang, J. Lin, S.B. Wang, K.Y. Yang, *J. Non-Cryst Solids* 278 (2000) 218.

[7] K. Annapurna, R.N. Dwivedi, S. Buddhudu, *Materials Letter* 53 (2002) 359.