OPTICAL PROPERTIES OF Eu^{3+} IONS DOPED ALUMINOSILICATE GLASS

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ABSTRACT

Eu^{3+} -doped aluminosilicate (AlSi) glass with the concentrations of 1.0 wt % was prepared by Sol-gel method. Optical excitation and emission spectra of Eu^{3+} ions have been investigated. The phonon sideband (PSB) associated with the $^7F_0$-$^5D_2$ excitation transition is used to determine the electron–phonon coupling constant and the local structure of the local environment around Eu^{3+} ions. The luminescence intensity ratio of the $^5D_0$-$^7F_2$ to $^5D_0$-$^7F_1$ transition has been calculated to estimate the local site symmetry around the Eu^{3+} ions. The Judd–Ofelt (JO) intensity parameters Ω_λ (λ=2, 4, 6) are calculated from the emission spectra and are used to estimate the transition probability (A), branching ratios (β), the stimulated emission cross-sections ($\sigma_{\lambda p}$) for the excited levels $^5D_0$ of the Eu^{3+} ions.

Key word: *Sol-gel method, aluminosilicate glass, Judd- Ofelt theory*

INTRODUCTION

Rare earth (RE) doped glasses have been attracted the attention of scientists due to their wide applications in many optical devices like lasers, light converters, sensors, high-density memories and optical amplifiers [1, 2]. Among the RE^{3+} ions used to optically activate materials, the Eu^{3+} ions are mostly chosen due to Eu^{3+} ions emit narrow-band, almost monochromatic light and have long lifetime of the optically active states [2, 3]. Further, the structure and the relative intensities of the optical transitions in Eu^{3+} ion strongly depend on the its local environment, so this ion is used as a probe to study the point group symmetry of the Eu^{3+} site and sometimes also information on the coordination polyhedron [1-3].

As for the hosts, alumina is a good network modifier for dispersing RE^{3+} ions in silica gel and silicate glass matrices, in which RE^{3+} ions were preferably partitioned by alumina, forming Al-O-RE bonds rather than clustering and forming RE-O-RE bonds [4, 5]. Monteilet al [6] have shown that when Eu^{3+} ions doped aluminosilicate glasses, these ions are preferentially located in alunimum-rich domains, while the local structure around Eu^{3+} ions is affected by aluminum through a structuring effect. M. Nogami and Y. Abe have reported that the aluminum was effective to gives intense photoluminescence from aluminosilicate glasses doped with the Sm^{2+} ions [7].

However, the optical properties of Eu^{3+} ions in aluminosilicate (AlSi) glass have been studied less than other matrixes. In this paper, Eu^{3+} ions are used as probe to study the ligand field around RE^{3+} in aluminosilicate (AlSi) glass. In addition, optical properties of AlSi:Eu^{3+} glass are analyzed using Judd–Ofelt (JO) theory.

EXPERIMENTAL

Aluminosilicate ($90SiO_2$+$10Al_2O_3$) glass doped with 1.0 wt % of Eu^{3+} ions have been prepared by sol-gel method [4, 5, 6]. The glass nature of samples was confirmed by X-ray diffraction (XRD) pattern using a Bruker D8-Advance. Raman spectra were carried out by Micro Raman spectroscopy (XploRA-Horiba). The photoluminescence (PL) and photoluminescence excitation (PLE) were recorded by Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. All the measurements were carried out at room temperature.

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RESULTS AND DISCUSSION

Structural analysis

XRD pattern: The X-ray diffraction pattern of the Eu^{3+} doped AlSi glass recorded in the range 10 to 70^o exhibits broad diffusion at lower scattering angles which in turn confirm the amorphous nature of the title glasses and as a representative case XRD pattern of the AlSi glass is shown in Fig. 1.

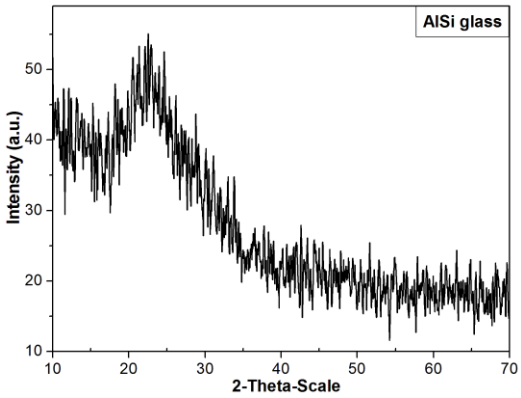

Fig 1. *XRD pattern of AlSi glass*

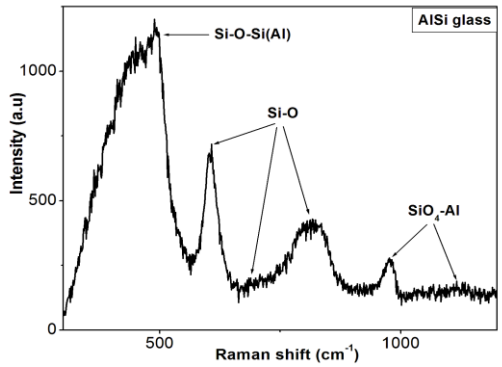

Fig.2. *Raman spectrum of AlSi glass*

Raman spectrum: Figure 2 shows the Raman spectrum of the AlSi glass. It is found that the maximal phonon mode frequency is 1120 cm^1. Among observed bands, the Raman band about 480 cm^{-1} has the most intense intensity. This band relates vibration of the Si-O-Si (Al) bond. The bands about 970 and 1120 cm^{-1} are assigned to stretching vibrations of SiO_4 tetrahedra bound to one and two Al atoms, respectively. Three bands near 600, 706 and 800 cm^{-1} are due to stretching vibration of the Si-O bond in SiO_4 tetrahedral groups with various number of non-bridging oxygens [8, 9].

Photoluminescence excitation spectrum and sideband phonon energy

The excitation spectrum of SiAl:Eu^{3+} glass was recorded in the spectral region 330-560 nm by monitoring the emission at 617 nm ($^5D_0$-$^7F_2$ transition) and shown in Fig 3. The excitation spectrum consists the sharp bands due to the f-f transitions from $^7F_0$ of ions Eu^{3+} to the excited levels. The most intense excited band at wavelength of 397 nm corresponds to the $^7F_0 \rightarrow {}^5L_6$ transition, which is often used in fluorescence excitation for Eu^{3+}. The should reappears at wavelength around 508 nm can be related to the phonon sideband (PSB), which is used to understand the vibration modes around the Eu^{3+} ions[9]. The PSB of Eu^{3+} in SiAl glass is associated with the $^7F_0 \rightarrow {}^5D_1$ transition and shown in inset of Fig 3, in which the $^7F_0 \rightarrow {}^5D_1$ excited transition is the pure electronic transition (PET). The PET is set as zero energy shift, the sideband phonon energy in SiAl glass can be calculated to be 805 cm^{-1}. This phonon energy is related to stretching vibration of the Si-O bond in SiO_4 tetrahedral groups [8,9].

The electron phonon coupling constant (g) have been calculated by [3]:

$$g = \frac{\int I_{PSB}(\lambda)d\lambda}{\int I_{PET}(\lambda)d\lambda} \quad (1)$$

where I_{PSB} is the intensity of the phonon sideband and I_{PET} is the intensity of the pure electric transition. In SiAl:Eu^{3+} glass, the g value is found to be 0.021. This value is much lower than that in lead fluoroborate (LFB) glasses [3] and borotellurite glasses [11]. This behavior shows that the electron phonon coupling in SiAl:Eu^{3+} glass is weaker than that in lead fluoroborate and borotellurite glasses.

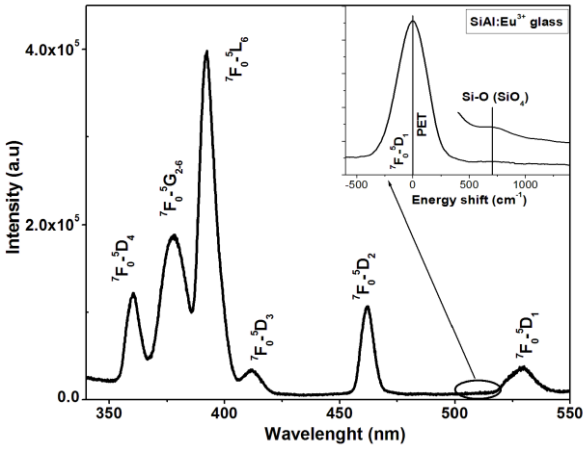

Fig 3. *The excitation spectrum of Eu^{3+} in SiAl glass*

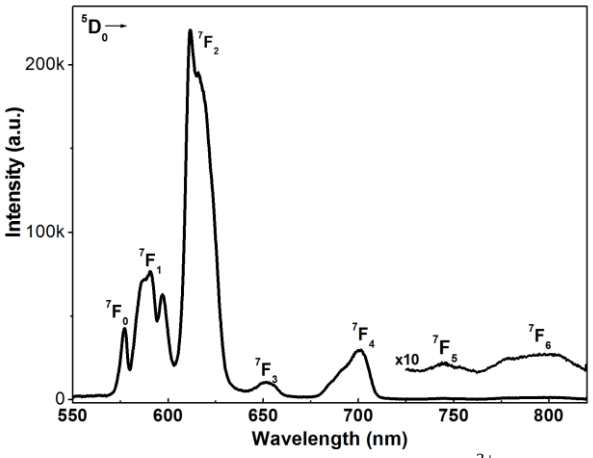

Fig 4. *The emission spectrum of SiAl:Eu^{3+} glass*

Emission spectrum

Fig. 4 illustrates the emission spectrum of AlSi:Eu^{3+} glass using the 397 nm excitation wavelength of xenon lamp source. The luminescence lines are assigned according to Carnall's paper [10]. The emission spectrum consists seven observed emission bands at wavelengths of 577, 590, 611, 651, 700, 745 and 802 nm corresponding to the $^5D_0 \rightarrow {}^7F_{0\text{-}6}$ transitions, respectively. Among emission transitions, the $^5D_0 \rightarrow {}^7F_2$ transition has the most intense intensity whereas the $^5D_0 \rightarrow {}^7F_5, {}^7F_6$ transitions are very weak in intensity. The $^5D_0 \rightarrow {}^7F_2$ transition is allowed electric dipole, so the it's intensity strongly depends on asymmetry of ligand and covalency of RE^{3+}-ligand bond. The intensity of the $^5D_0 \rightarrow {}^7F_1$ transition is independent with the asymmetry of ligand, because this is allowed magnetic dipole transition [1-3]. The fluorescence intensity ratio (R) of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transitions of Eu^{3+} ions allows one to estimate the deviation from the site symmetries of Eu^{3+} ions. For AlSi:Eu^{3+} glass, the R values is 2.72. The luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ions in the prepared glasses is stronger than that of $^5D_0 \rightarrow {}^7F_1$ transition and further it suggest that Eu^{3+}ions take a site with inversion anti symmetry [3]. Moreover, these values are higher than those of lead fluoroborate (LFB) glasses [3] and borotellurite glasses [11]. The lower R value is attributed to the higher asymmetry and covalency around the Eu^{3+} ions in AlSi glass than those hosts.

Fig.4 shows that the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition splits into three components, indicating that the crystallographic site of the Eu^{3+} ions in the present glass is as low as orthorhombic, monoclinic or triclinic in a crystalline lattice [2,3].

The Judd-Ofelt intensity parameters (Ω_λ)

The Judd-Ofelt (JO) theory was shown to be useful to characterize radioactive transitions for RE^{3+}-doped solids, as well as aqueous solutions, and to estimate the intensities of the transitions for RE^{3+} ions [12,13]. This theory defines a set of three intensity parameters Ω_λ (λ = 2,4,6), that are sensitive to the environment of the RE ions. Commonly, The JO intensity parameters are usually derived from absorption spectrum. However, owing to the special energy level structure of Eu^{3+} ion, these Ω_λ could be estimated from the emission spectra. Four main emission peaks $^5D_0 \rightarrow {}^7F_{1,2,3,4}$ are used to calculate Ω_λ . The $^5D_0 \rightarrow {}^7F_1$ is a magnetic dipole (MD) transition and its spontaneous emission probability A_{md} is given by [1-8]:

$$A_{md} = \frac{64\pi^4 \nu^3 n^3 S_{md}}{3h(2J+1)} \quad (2)$$

where h is the Planck constant, ν is the wave number of the transition in interest, J is the total angular momentum of the excited state, and n is the refractive index. S_{md} is the MD line strength, which is a constant and independent from the host material. The value of A_{md} can be estimated using the reference value of A'_{md} published somewhere, and using the relationship $A_{md} = (n/n')^3.A'_{md}$ [1-8], where, A'_{md} and n' are spontaneous emission probability and refractive index of the reference material.

The $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are an electric dipole partially allowed. The spontaneous emission probabilities A_{ed} of electric transition is given using the following expression:

$$A_{ed} = \frac{64\pi^4 \nu_J{}^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}\right]\sum_{\lambda=2,4,6}\Omega_\lambda \left\|U^{(\lambda)}\right\|^2 \quad (3)$$

where ν_J is the wave number of transition $^5D_0 \rightarrow {}^7F_J$, e is the electron charge, $\left\|U^{(\lambda)}\right\|^2$ are the squared doubly reduced matrix elements of the unit tensor operator of the rank λ = 2, 4, 6 are calculated from intermediate coupling approximation for a transition $|\psi J\rangle \rightarrow |\psi' J'\rangle$. These reduced matrix elements did not nearly depend on host matrix as noticed from earlier studies. Thus the Ω_λ parameters could be evaluated simply by the ratio of the intensity of the $^5D_0 \rightarrow {}^7F_{J=2,4,6}$ transitions to the intensity of $^5D_0 \rightarrow {}^7F_1$ transition as follow:

$$\frac{\int I_J d\nu}{\int I_1 d\nu} = \frac{A(^5D_0 \rightarrow {}^7F_{2,4,6})}{A(^5D_0 \rightarrow {}^7F_1)} = \left[\frac{e^2}{S_{md1}}\right]\left[\frac{\nu_J}{\nu_1}\right]^3\left[\frac{n(n^2+2)^2}{9}\right]\sum_{\lambda=2,4,6}\Omega_\lambda \left\|U^{(\lambda)}\right\|^2 \quad (4)$$

For $^5D_0 \rightarrow {}^7F_2$ transition, $U^{(2)}$ = 0,0033; $U^{(4)} = U^{(6)} = 0$, $^5D_0 \rightarrow {}^7F_2$ transition, $U^{(2)} = 0$; $U^{(4)}$ = 0,0023; $U^{(6)} = 0$ and $^5D_0 \rightarrow {}^7F_2$ transition, $U^{(2)} = U^{(4)}$, $U^{(6)}$ = 0,003. Using equation (4) and the reduced matrix elements, the JO parameters were calculated. In the AlSi:Eu^{3+} glass, the JO parameters are: $\Omega_2 = 4.31\times10^{-20}$ cm^2, $\Omega_4 = 1.41\times10^{-20}$ cm^2 and $\Omega_6 = 1{,}19\times10^{-20}$ cm^2.

The Ω_λ parameters are important to study the symmetry of local structure around RE^{3+} ions and nature of RE–X (X = F, O) bonding. The Ω_4 and Ω_6 are related to the bulk properties such as viscosity and rigidity whereas the Ω_2 is more sensitive to the local environment of the RE^{3+} ions and is often related with the asymmetry of the local crystal field. The Ω_2 and Ω_6 parameters in AlSi:Eu^{3+} is larger than those of lead fluoroborate (LFB) glasses [3] and borotellurite glasses [11].The large value of Ω_2 can be attributed to higher asymmetry of the ligand field and covalent in Eu^{3+}-ligand bond than other hosts, whereas the larger of Ω_6 parameter shows that the rigidity of the media in which RE ions put into other hosts is lower.

Radiative properties

Table 1. *The radiative properties of SiAl:Eu^{3+} glass*

$^5D_0 \rightarrow$	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$	$^7F_5$	$^7F_6$
A_R (s^{-1})	0	51	161	0	27.4	0	18
β_{cal} (%)	0	19.8	62.5	0	10.6	0	7.1
β_{mes} (%)	4.6	21.7	60.5	2.8	9.4	0.3	0.7
$\sigma(\lambda_P)$ (x10^{-22} cm^2)	0	2.1	7.9	0	1.7	0	1.3
$\sigma(\lambda_P)\times\Delta\lambda_{eff}$ (10^{-28} m^3)	0	23.4	65.7	0	26.5	0	24.7
$\sigma(\lambda_P)\times\tau_{cal}$ (cm^2.s)	0	8.87	30.5	0	6.68	0	5.1

The JO parameters have been used to estimate the radiative properties such as the radiative transition rates (A_R,s^{-1}), branching ratios (β_{cal}, %) and stimulated emission cross-section ($\sigma(\lambda_P)$,10^{-22} cm^2) for $^5D_0 \rightarrow {}^7F_J$ transitions and radiative lifetime (τ_R) of $^5D_0$ level of Eu^{3+} in AlSi glass by using Eqs in Ref [14]. In addition, the gain band width ($\sigma(\lambda_P)\times\Delta\lambda_{eff}$, 10^{-28} cm^{-3}) and optical gain

($\sigma(\lambda_P)\times\tau_R$, 10^{-25} cm^2s^{-1}) also calculated for $^5D_0\rightarrow{}^7F_J$ transitions. The results are presented in Table 1.The predicted branching ratio (β_{cal}) of $^5D_0 \rightarrow {}^7F_2$ transition get a maximum value 62.5 % whereas the measured ratio (β_{mes}) is 60.5 %, thus there is a good agreement between experimental and calculated branching ratios.

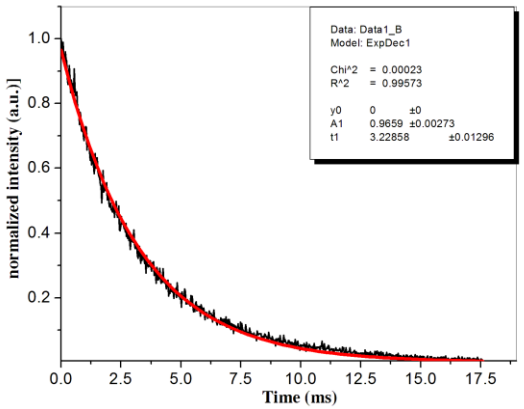

Fig. 5. *Decay profiles of $^5D_0$ level of Eu^{3+} doped aluminosilicate glass*

The decay curve of $^5D_0$ state of Eu^{3+} in AlSi glass is shown in Fig. 5. The measured lifetime is 3.23 ms, whereas the calculated lifetime is 3.88 ms. It is observed that the experimental lifetime is smaller when compared with the calculated lifetime. The deviations between measured and calculated lifetime may be owing to the nonradiative relaxation rates of excited Eu^{3+} ions. The quantum efficiency of the excited state $^5D_0$ is given by the equation: $\eta = \tau_{exp}/\tau_{cal}$. For the AlSi:$Eu^{3+}$ glass, η = 83.24 %. Table 1 presents that the branching ratio, stimulated emission cross-section, gain band width and optical gain of $^5D_0\rightarrow{}^7F_2$ transition are larger than those of other transitions. Further the quantum efficiency of sample is high. These results suggest that the $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} ions in AlSi glass is found to be suitable for developing the optical devices such as laser and optical amplifier.

CONCLUSIONS

Aluminosilicate glass doped with 1.0 wt% of Eu^{3+} ions have been prepared by sol-gel method. The XRD indicates that the glass has an amorphous structure. Raman spectrum presents the existence of specific structural groups in silicate glass and the maximal phonon mode frequency is 1120 cm^{-1}. From the excitation spectrum, the PSB was found at the energy phonon about 805 cm^{-1}. This PSB relates to stretching vibration of the Si-O bond in SiO_4 tetrahedral groups. The optical properties of Eu^{3+}-doped aluminosilicate glass have been investigated. The large value of *R* and Ω_2 parameter shows that the coordination structure surrounding the Eu^{3+} ions has high asymmetry and Eu^{3+}-O^- bond in AlSi glass has high polarizability. The radiative parameters show that the $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} ions in AlSi glass is very useful for optical devices.

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TÓM TẮT

TÍNH CHẤT QUANG CỦA ION Eu^{3+} PHA TẠP TRONG THỦY TINH ALUMINOSILICATE

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Thủy tinh aluminosilicate (AlSiO) pha tạp Eu^{3+} với nồng độ 1,0 % khối lượng, được chế tạo bằng phương pháp sol-gel. Phổ kích thích và phát xạ của mẫu đã được khảo sát. Phổ phonon-sideband (PSB) gắn với chuyển dời kích thích $^7F_0$-$^5D_2$ được sử dụng để đánh giá hằng số liên kết điện tử - phonon và cấu trúc của môi trường cục bộ xung quanh ion Eu^{3+}. Tỉ số cường độ của chuyển dời $^5D_0$-$^7F_2$ và $^5D_0$-$^7F_1$ được sử dụng để đánh giá độ bất đối xứng của môi trường xung quanh ion Eu^{3+}. Các thông số cường độ Judd–Ofelt (JO) được tính từ phổ huỳnh quang và được sử dụng để đánh giá xác suất chuyển dời, (A), tỉ số phân nhánh (β), tiết diện phát xạ cưỡng bức ($\sigma_{\lambda p}$) cho mức kích thích $^5D_0$ của ion Eu^{3+}.

Từ khóa: *Phương pháp sol-gel, thủy tinh aluminosilicate, lý thuyết Judd-Ofelt*

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