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INTERACTION MECHANISM OF ENERGY TRANSFER FROM Ce TO Tb IONS IN SILICA AND LaF_3.

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Abstract

The phenomenon of energy transfer plays an important role in the development of luminescent materials, especially materials used for manufacturing white LED.The process of luminescence at wavelength 542nm from Tb3+ doped in silica or LaF3 can be stimulated by ultraviolet light near 227 nm. However, the excitation wavelength can be shifted to a more accessible value of 325 nm by co- doping Tb3+ with Ce3+ ions. At this wavelength Ce3+ ions absorb and then transfer the energy to the Tb3+ ions. This process involves the stimulation of the donor followed by energy transfer to acceptor excitation radiation. System co-doped samples Ce, Tb in Silica is made sol-gel method, system co-doped sample ions Ce, Tb in LaF3 is made by hydrothermal method. After surveying the excitation spectrum, fluorescence, measured lifetimes empirical, applied theory Forster, Dexter and computational models of Inokuti and Hirayama or approximate Reisfelds. We determined the mechanism of energy transfer from Ce to Tb in Silica and in LaF3.

Keywords: *energy transfer, Silica, LaF_3, co-doped Ce, Tb.*

1. Introduction

Many theoretical and experimental studies have been done on non-radiative energy transfer since Forster first treated it theoretically [1], [4]. The process involves excitation of a donor followed by transfer of the excitation energy to an acceptor.

Forster developed a theory for the rate of non-radiative energy transfer by electric dipole-dipole interaction [1]. This was later extended by Dexter to involve the higher multipole interactions [2]. Dexter also created a model for shorter donor-acceptor distances based on the exchange interaction [2]. The transfer mechanisms differ according to the dependence of the transfer rate on the donor-acceptor distance. Inokuti and Hirayama [3] developed numerical methods on energy transfer that determine the mechanism responsible. In this study, the theoretical calculations of Inokuti and Hirayama [3] are implemented in MATLAB and compared to experimental data to investigate the mechanism of the energy transfer from Ce to Tb in sol-gel silica fabricated by sol-gel method and in LaF_3 by hydrothermal.

2. Theory

The non-radiative transfer of an electronic excitation from a donor to an acceptor can be represented by:

$$D^* + A \rightarrow D + A^*$$

The transfer rate between the initial and final states is given by:

$$W_{DA} = \frac{2\pi}{h}\left|\langle DA^* \mid \mathbf{H}_{DA} \mid D^*A\rangle\right|^2 \int f_D(E) f_A(E) dE$$

The integral represents the overlap between the universal donor (D) spectrum transmitter, acceptor (A) the absorption spectrum. The emission spectrum of the donor's normal $f_D(E)$ and normal absorption spectrometry acceptor was $f_A(E)$. The mechanism of energy transfer depends on the interaction Hamiltonian.

If the donor and acceptor wavefunction overlap, the quantum mechanical interactions cause the delivery rate [5].

$$W_{DA} = \frac{1}{\tau_0}\exp\left(\frac{2R_0}{L}\left[1 - \frac{r}{R_0}\right]\right)$$

Inside, τ0 life expectancy in the absence of donor acceptor, r is the distance between donor and

acceptor, R0 the separation distance is important that the energy is transmitted at the same rate it reduces the luminescence in the absence of acceptor, and L is a scaling factor corresponding to an effective Bohr radius. The corresponding decay function Φ(t) after excitation pulse is given by:

$$\phi(t) = \exp\left[\frac{-t}{\tau_0} - \gamma^{-3}\frac{c}{c_0}g\left(\frac{t}{\tau_0}e^{y}\right)\right]$$

For greater separation distance radiation energy transfer can not occur through interactive multi-electrode, resulting in energy transfer rate [2]:

$$W_{DA} = \frac{1}{\tau_0}\left(\frac{R_0}{r}\right)^{s}$$

S = 6 for dipole - dipole, quadrupole 8 and 10 to interact quadrupole-quadrupole.

3. Results and discussion

3.1. Interaction Mechanism of Energy Transfer from Ce to Tb Ions in Silica

A series of 10 Ce, Tb co-doped silica samples with a fixed concentration of Ce (0.5mol%) and varying concentration of Tb from 0 up to 1 mol% were produced by the sol- gel method. Tetraethylorthosilicate (TEOS), water, $Ce(NO_3)_3.6H_2O$, and $Tb(NO_3)_3.6H_2O$ were used as starting materials, ethanol (C_2H_5OH) as a solvent, and nitric acid (HNO_3) as a catalyst. An amount of 11.15 ml of TEOS (0.05 M) was mixed with 10 ml of ethanoland stirred for 30 minutes, after which 9 ml of water (containing 0.15 M HNO_3) was added. Stirring then continued for another 30 minutes, after which the appropriate amount of dissolved $Ce(NO_3)_3.6H_2O$ and $Tb(NO_3)_3.6H_2O$ in ethanol was added to the mixture, which was stirred for a further 4 h. The mixture was then stored in a closed container and transferred to a water bath at 50°C until a gel was formed. The gel was dried, crushed and annealed at 1000°C. Photoluminescence (PL) measurements were made at room temperature at the University of Da nang Duy Tan. Figure 1(a) presents the PL emission of Ce and Tb for the samples having Tb concentrations of 0.01 and 1 mol%. The reduction of the Ce emission and increase of the Tb emission while exciting the Ce shows that energy transfer occurs figure 1(b).

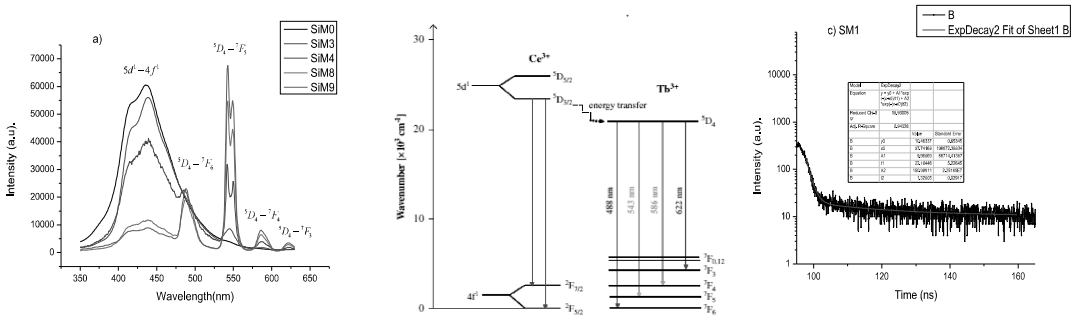


Figure 1: Sample fluorescence spectra of Ce-Tb-doped copper fabricated by sol-gel method(a); schematic energy tranfer from Ce to Tb(b), decay lifetime (c)

Results INOKUTI theoretically calculate and HIRAYAMA.

The reduced emissions and increased emissions Ce Tb while stimulating Ce showed energy transfer occurs. Table 1 shows the emission intensity (I), the relative emission intensity I/Io, lifetime τm and lifetime of the donor Ce relative to the silica template system manufactured by sol-gel method

Table 1: Concentrations donor acceptor emission intensity, the lifetime of the silica.

sample	*Donor (mol%*	*Acceptor (%mol)*	*Emission intensity donor*		*Donor lifetime*	
			I(a.u)	I/Io	$\tau_m(ns)$	τ_m/τ_0
SiM0	0.5	0	51129.1	1	22	1
SiM1	0.5	0.01	48100.3	0.94076172	21.6	0.981818182
SiM2	0.5	0.02	44151.5	0.86352977	20.8	0.945454545
SiM3	0.5	0.04	40600.1	0.7940703	19.6	0.890909091
SiM4	0.5	0.08	30766.6	0.60174343	18.8	0.854545455
SiM5	0.5	0.1	33686	0.65884203	18.2	0.827272727
SiM6	0.5	0.2	25116	0.49122711	17.66	0.802727273
SiM7	0.5	0.4	17568	0.34360081	15.86	0.720909091
SiM8	0.5	0.8	9070.6	0.17740582	12.4	0.563636364
SiM9	0.5	1	7510.8	0.14689873	9.99	0.454090909

Figure 2 theoretical curves for the different types of multipole interaction, and from this data one shows the plot of the experimental values of I/Io versus τ_m/τ_0 compared to the can also see that the dipole-dipole interaction mechanism is the most probably mechanism for energy transfer between Ce and Tb in silica [6].

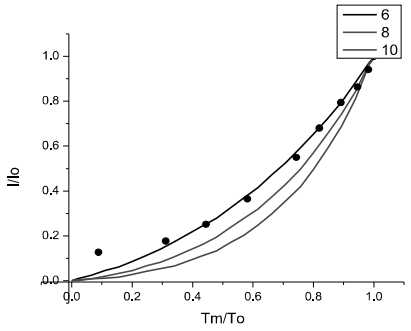
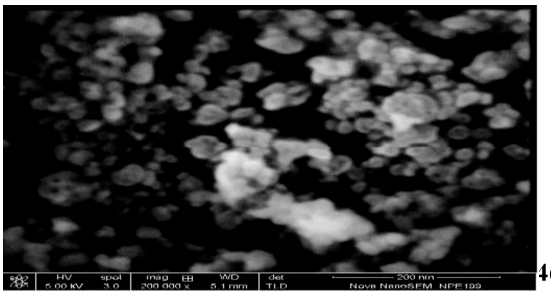


Figure 2: Relative emission intensity I/I_0 vs lifetime decay τ_m/τ_0 of the donor.

3.2. The mechanism of energy transfers of Ce, Tb-doped copper in LaF_3.

A series of 10 Ce, Tb co-doped LaF_3 samples with a fixed concentration of Ce (1mol%) and varying concentration of Tb from 0 up to 10 mol% were produced by hydrothermal. $La(NO_3)_3.6H_2O$ and NaF was used as the starting material $Ce(NO_3)_3.6H_2O$ and $Tb(NO_3)_3.6H_2O$ has been added to doping. $C_{19}H_{42}BrN$ (CTAB) additive precipitation to control particle size. We take photos with machine JEOL SEM (SEM) JSM-5401LV in materials science center Hanoi National University. LaM4 samples were incubated for 12 hours with 600 ^0C.



4(b) samp

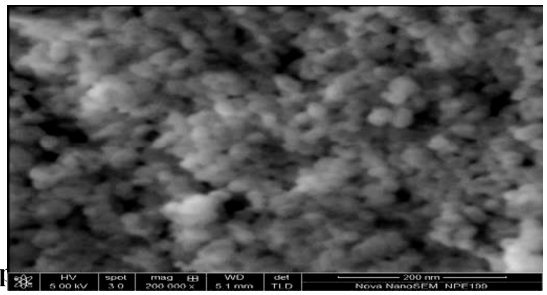


Figure 3 presents a SEM image of LaM2 and LaM4. Charging on the insulating samples limits the resolution of the images, so the particle shape is not clear, but it can be seen that that the particle size is less than 40 nm. Fluorescence spectra Ce, Tb-doped copper in LaF_3 similar Ce, Tb-doped copper in silica figure 4.

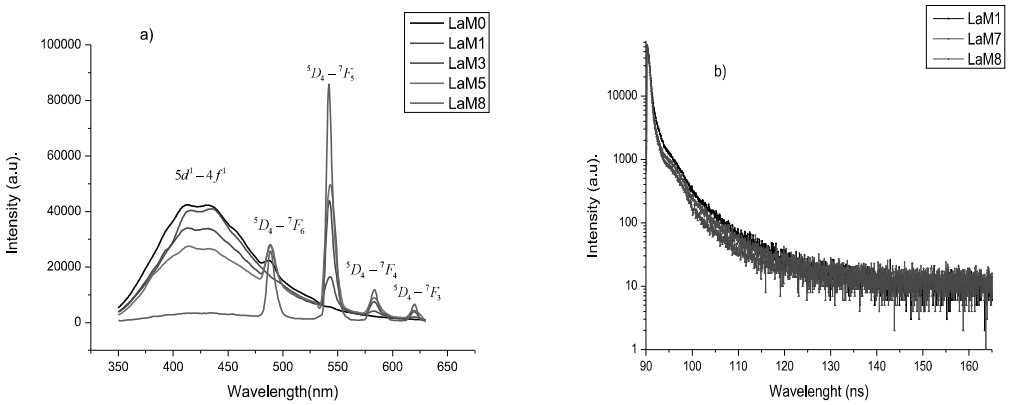


Figure 4: Fluorescence spectra (a) decay lifetime, LaM1;LaM7;LaM8(b).

Results INOKUTI theoretically calculate and HIRAYAMA.

Table2: Concentrations Donor acceptor emission intensity, the lifetime.

sample	*Acceptor (mol%)*	*Acceptor (mol%)*	*Emission intensity donor*		*Donor lifetime*	
			I(a.u)	I/Io	$\tau_m(ns)$	τ_m/τ_0
LaM0	1	0	42383.3	1	11.815	1
LaM1	1	0.1	39787	0.93874238	11.59	0.980956411
LaM2	1	0.2	34688	0.81843556	11.144	0.943207787
LaM3	1	0.3	33973.9	0.80158695	10.906	0.923063902
LaM4	1	0.4	29686	0.70041738	10.374	0.878036394
LaM5	1	0.8	27299.5	0.64410983	10.152	0.85924672
LaM6	1	1	18986	0.44795946	9.6	0.812526449
LaM7	1	2	6868.3	0.16205203	5.688	0.481421921
LaM8	1	8	3376.2	0.07965873	3.567	0.301904359
LaM9	1	10	1522	0.03591037	2.672	0.226153195

Curve which is redrawn on the graph by means of digitization and to fit the experimental data.

Figure 5 shows a graph of experimental value of I/ I_0 compared to τ_m/τ_0 the theoretical curve for the different types of multi-polar interactions, and from this data one can see that the interaction mechanism quadrupole - quadrupole mechanism of energy transfer between Ce and Tb in LaF_3 matching announced [7].

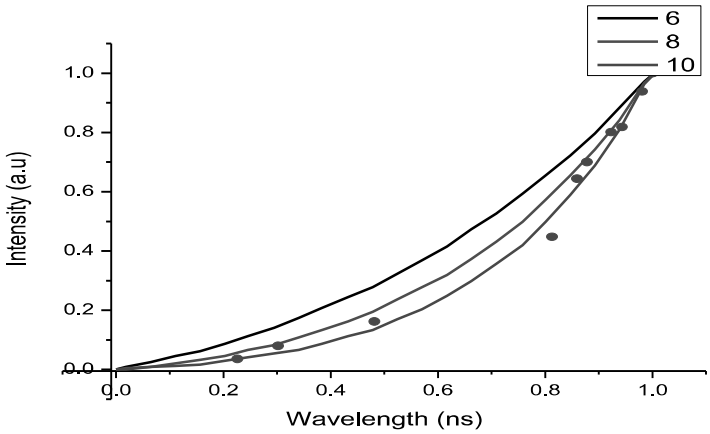


Figure 5: The curve graph theory Inokuti and Hirayama value samples in LaF_3

3.3. Determining the mechanism of energy transfer approximate theoretical Reisfelds.

Based on expressions interaction energy transfer and Dexter multipolar approximation of Reisfeld, the following relationships can view [5]:

$$\frac{\eta_0}{\eta} \alpha C^{n/3}$$

or

$$\frac{I_0}{I} \alpha C^{n/3}$$

The values (I_0 /I) linearly proportional with $C^{n/3}$ with n = 6, 8 and 10 corresponding to that interaction. By examining fluorescence spectra of the two systems to build relationships I_0/I and $C^{n/3}$ then use the appropriate software fit to find the best linear dependence.

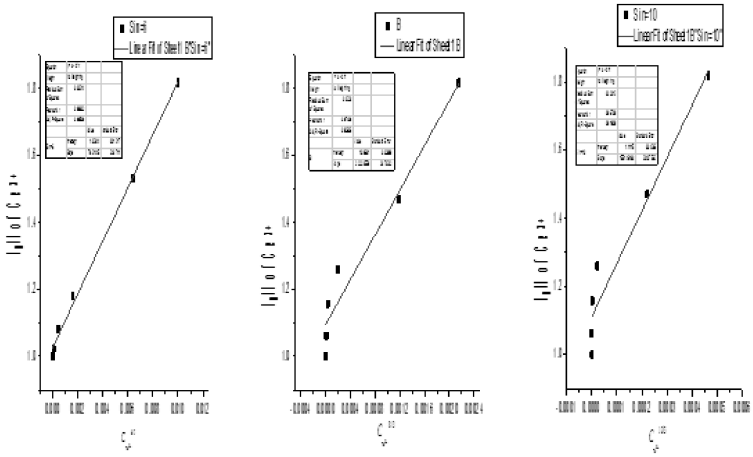


Figure 6: Dependence I_0/I of Ce^{3+} at ($C^{n/3}$) co-doped samples of Tb in Silica.

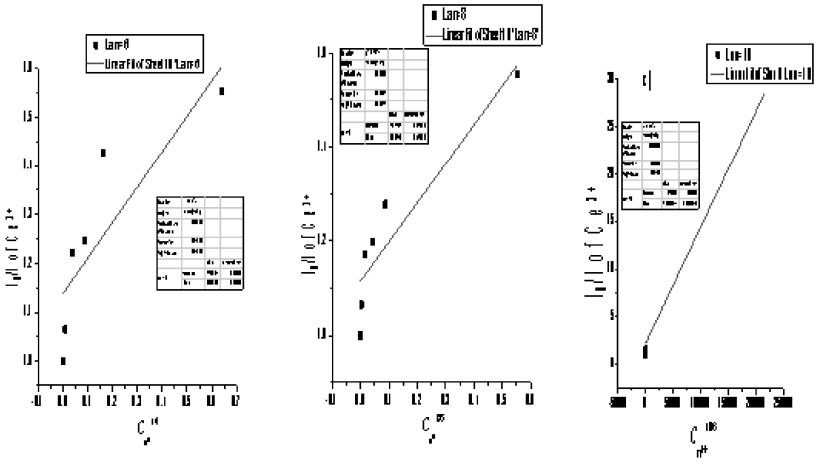


Figure 7: Dependence I_0/I of Ce^{3+} at ($C^{n/3}$) co-doped samples of Tb in LaF_3

On the basis of the Dexter's energy transfer formula of multipolar interaction and Reisfeld's approximation. We have concluded that the mechanism of energy transfer from Ce^{3+} to Tb^{3+} Silica according to the mechanism of bipolar – bipolar and of energy transfer from Ce^{3+} to Tb^{3+} in LaF_3 under the quadrupole – quadrupole.

4. CONCLUSION

The mechanism of the energy transfer from Ce to Tb in sol-gel silica and in LaF3 nanoparticles via the hydrothermal method was investigated using the Inokuti and Hirayama models or approximate Reisfelds model . The relative emission intensity of the donoras a function of the acceptor concentration was found to fit well to the theoretical models associated with the exchange interaction, the dipole-dipole interaction in sol-gel silica and the quadrupole- quadrupole interaction in LaF3 nanoparticles via the hydrothermal method [6], [7].

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SO SÁNH CƠ CHẾ TƯƠNG TÁC ĐỂ TRUYỀN NĂNG LƯỢNG TỪ ION Ce ĐẾN Tb TRONG SILICA VÀ LaF_3.

Ngô Văn Tâm[1], Hà Xuân Vinh[1], Vĩnh Hào[1], Tống Văn Tuất[1], Đoàn Phan Thảo Tiên[1], Võ Tấn Thông[1], Vũ Xuân Quang[2]

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Tóm tắt

Hiện tượng truyền năng lượng đóng một vai trò quan trọng trong sự phát triển của vật liệu phát quang đặc biệt các vật liệu dùng cho chế tạo led trắng.Quá trình phát quang bước sóng 542nm từ Tb^{3+} pha tạp trong silica hoặc LaF_3 có thể được kích thích bằng cách sử dụng ánh sáng tia cực tím bước sóng ngắn gần 227 nm. Tuy nhiên, có thể kích thích huỳnh quang thuận lợi hơn bởi bức xạ có bước sóng 325 nm bằng cách đồng pha tạp các ion Ce^{3+} cùng với Tb^{3+}. Tại bước sóng này các ion Ce^{3+} hấp thụ và sau đó truyền năng lượng cho ion Tb^{3+} . Quá trình này bao gồm việc kích thích của donor sau đó là truyền năng lượng kích thích làm cho acceptor bức xạ . Hệ thống mẫu đồng pha tạp Ce, Tb trong Silica được chế tạo bằng phương pháp Solgel, hệ thống mẫu đồng pha tạp các ion Ce, Tb trong LaF_3 được chế tạo bằng phương pháp thủy nhiệt. Sau khi khảo sát phổ kích thích, phổ huỳnh quang, đo thời gian sống thực nghiệm, áp dụng lý thuyết Forster, Dexter, mô hình tính toán của Inokuti và Hirayama, mô hình gần đúng Reisfelds. Chúng tôi xác định cơ chế truyền năng lượng từ Ce đến Tb trong Silica và trong LaF_3.

Từ khóa: *Truyền năng lượng, silica , LaF_3, đồng pha tạp Ce, Tb.*