Advances in Natural Sciences, Vol. 7, No. 1 & 2 (2006) (63 – 69)

Materials Science

PREPARATION, OPTICAL PROPERTIES AND ENERGY TRANSFER OF Y_2O_3: RARE EARTH (RE: Tb,Eu, Er, Yb) NANOPHOSPHORS

Tran Kim Anh, Nguyen Vu, Man Hoai Nam, and Le Quoc Minh

Institute of Materials Science, VAST

18 Hoang Quoc Viet Road, Hanoi, Vietnam

E-mail: anhtk@ims.vast.ac.vn

Abstract. This paper describes the preparation, optical properties and the role of the concentration of rare earth ions (RE: Eu, Er, Tb, Yb) as active centers in the energy transfer of Y_2O_3: RE nanophosphors. The materials are prepared by the combustion method using urea or glycine. Nanoparticles can be prepared with sizes ranging from 5 to 100 nm and can be estimated by high resolution TEM. Optimization of Eu and Er content in these nanophosphors was reported. The effect of energy transfer between Tb and Eu and the up-conversion between Er and Yb were studied. We will survey recent advances in nanophosphor development and discuss their future application potential.

1. INTRODUCTION

The Y_2O_3 is characterized by low phonon frequencies causing the inefficient non-radiactive relaxation of the excited states. The Y_2O_3: Eu have been known as excellent phosphor materials used in both trichromatic lamps, and projection colour television with high brightness. Rare earth ions Tb, Eu, Yb and Er doped materials have attracted considerable interest not only from the energy transfer and the up-conversion effects but also due to their technological applications. The high-definition displays call for sub-micron particle sizes to maximize screen resolution and screen efficiency [1-4]. Optical properties and up-conversion studies of Er^{3+} doped Y_2O_3 nanocrystals were presented [5]. Many different techniques such as rapid exothermic reaction [1], spray pyrolysis method [2], epitaxial growth [3], chemical vapor technique [4], co-precipitation method [5] have been used for preparation of Y_2O_3: Eu nano particles and thin films. Nanophosphors can exhibit enhanced structures and an increase in the luminescent efficiency as compared to their bulk material. The energy transfer between Tb and Eu in the Y_2O_3:Tb,Eu nanophosphors will be investigated. The synthesis, properties and the up-conversion effect of Y_2O_3: Yb-Er will be presented. The luminescent spectra as well as the lifetime of Tb and Eu were measured. A special attention is paid to the up-conversion mechanism in Y_2O_3:Yb,Er nanophosphors.

2. EXPERIMENTAL

The Y_2O_3: Tb, Eu and Y_2O_3: Yb, Er samples were prepared by using a combustion synthesis procedure (Eu,Tb, Er, Yb 5-10 mol %). Eu^{3+}, Er^{3+}, Yb^{3+} and Tb^{3+}(RE) ions

are easily hydrolysed and then form the precipitation of basic carbonate in an aqueous solution of urea according to following reaction:

$$(1-x)Y(NO_3)_3 + xRE(NO_3)_3 + CO(NH_2)_2 + H_2O \Longrightarrow [Y_{1-x}RE_x](OH)CO_3.H_2O$$

The combustion method was used for preparation of Y_2O_3: Eu nanophosphors. The Eu concentration are 1, 3, 5, 7% mole. Reaction of an aqueous solution containing NH_2CH_2COOH, $Eu(NO_3)_3$ and $Y(NO_3)_3$. Glycine and salts are easily soluble. The synthesis reaction is:

$$6RE(NO_3)_3 + 10NH_2CH_2COOH + 18O_2 \Longrightarrow 3RE_2O_3 + 5N_2 + 18NO_2 + 20CO_2 + 25H_2O$$

A glycine-to-metal nitrate molar ratio of 1.0:1, 1.2:1, 1.4:1, 1.6:1, 1.67:1 was employed to prepare the precursor solution. After combustion, the powder was heated for an hour at 600^oC. For the samples with Glycine-to-metal nitrate molar ratio of 1.67:1, the treatment temperatures were chosen from 500^oC to 700^oC. Y_2O_3:Tb,Eu with the mole ratio of Eu/Tb: 7/3, 8/2, 9/1 and Y_2O_3:Yb, Er with the mole ratio of Er/Yb: 1/5,1/4, 2/3 were prepared by the combustion method [6]..

The morphology and particle sizes of Y_2O_3: Eu were observed by using high resolution transmission electron microscopy (TEM) Philips CM 200 160KV. The Y_2O_3: Eu powder was analyzed by X-ray diffraction D5000 (Siemens). The DTA, DTG spectra were measured in air at a heating rate of 10 $^\circ$C/min from room temperature to 700 $^\circ$C by using Shimadzu-50 (Japan) in order to find optimal conditions for synthesis and annealing samples. The excitation and emission spectra were obtained on spectrometer FL3-22 with double monochromater or Spex 1250 M. The excitation source is a Xenon lamp XBO 450 W or He-Cd Laser. The decay times were measured with monochromator HDR1, Oscilloscope Lecroy 9362, Nitrogen laser 1ns, 20 Hz, 11 J. The luminescent spectra were measured by using Jobin Yvon HR 460 and multichanel CCD detection from Instruments SA model Spectraview-2D, Ti-Sapphire, N_2, He-Ne, Argon or emitting diode lasers.

3. RESULTS AND DISCUSSION

The influence of the technological condition on the optical and structural properties was investigated. The transmission electron microscopy (TEM), and X - ray diffraction were measured for the Y_2O_3: RE powders. For Y_2O_3: Eu at different annealing conditions such as 550^oC, 60 min., 600^oC, 30 min., 700^oC, 30 min., 900^oC, 30 min. and 900^oC, 60 min., the average sizes are of about 4.4 nm, 5.6 nm, 15.2 nm, 46.1 nm and 72.2 nm, respectively [6]. The technology conditions influence the size of particles Y_2O_3: RE. The average sizes are of 20nm-80 nm for the samples in the optimal annealing temperature is 550 $^\circ$C- 600 $^\circ$C, the optimal annealing time is 30 minutes. Fig. 1 shows the luminescent spectra of Y_2O_3:Tb, Eu ($Y_{0.95}Eu_xTb_y$, $x+y=0.05$) for the ratio of Eu/Tb: 7/3, 8/2, 9/1 600 $^\circ$C annealing, 30 min. The energy transfer is clearly observed in the case of Eu/Tb= 8/2 (b) with high Eu red emission.

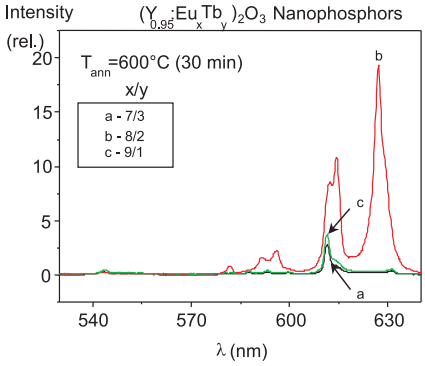

Fig. 1. The luminescent spectra of Y_2O_3: Tb, Eu with the mole ratio of Eu/Tb: 7/3(a), 8/2(b), 9/1(c)

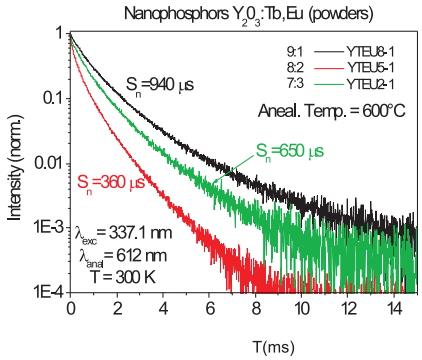

Fig. 2. The decay times of Y_2O_3: Tb, Eu 5 mole % with the mole ratio of Eu/Tb: 7/3 (650 μs), 8/2(360 μs), 9/1(940 μs)

The Fig. 2 shows the decay times of Y_2O_3:Tb,Eu 5 mol % with the mole ratio of Eu/Tb: 7/3, 8/2 and 9/1. The life time of $^5D_0$-$^7F_2$ transitions of Eu^{3+} (612 nm) were 940, 650 and 360 μs for the mole ratio of Eu/Tb: 9/1, 7/3, 8/2, respectively. The life time of Tb (545 nm) were 400, 220 and 175 μs for the mole ratio of Eu/Tb: 9/1, 8/2 and 7/3, respectively.

The concentration dependences of Yb and Er in Y_2O_3:Yb,Er were studied. The ratio of Yb/Er are 1/5, 1/4 and 2/3. The luminescent spectra in the infrared region of 4 samples Y_2O_3:Yb, Er(1/4), 5 mol % and 10 mol % in annealing temperature of 600 ° C and 700 ° C were presented in Fig. 3. The up-conversion effect depends on excitation wavelength of 972 nm, 800 nm or 632.8 nm as well as Er and Yb concentration.

The Erbium ion finds uses in laser 980 nm materials and optical amplifiers by ground and excited state transitions near 800 and 980 nm, where high power diodes are available there by facilitating the up-conversion process. In the case of 15 mol % RE dopped, luminescent intensity is decreased by the concentration quenching effect. In order to compare the influence of ratio between Er and Yb, the up conversion spectra were measured for the samples of Yb 10 mol %, Er/Yb=1/5, 1/4 and 2/3. For the case only have Er doped in Y_2O_3 nanophosphor the up-conversion effect could be occurred by the following mechanism: the laser light (800 nm) brings the Er^{3+} ion into the $^4I_{9/2}$ level, which then non-radiatively decays to the $^4I_{11/2}$ and $^4I_{13/2}$. Energy transfer processes bring the ion to the $^4F_{3/2}$ and $^2H_{11/2}$ levels. The ion then non-radiatively decays to the lower lying levels and the $^2H_{11/2}$, $^4S_{3/2}$ to $^4I_{15/2}$ (550 nm) transition occur. The other transition $^4F_{9/2}$ to $^4I_{15/2}$ (650 nm) is rather strong when excited by 488 nm but is very weak when pumped by 972 nm emitting laser diode. In some Er^{3+} doped phosphors, red emission from $^4F_{9/2}$ level predominates over the green emission, this is specially the case for the oxyhalides, which have larger phonon cut-off energies as compared to fluoride materials. Several possible excitation routes have been postulated for the red emission. All of these routes require multiphonon nonradiative decay to bridge large energy gaps or energy transfer steps assisted by the simultaneous emission of phonons to surmount the energy mismatch between two transitions [7] and [8].

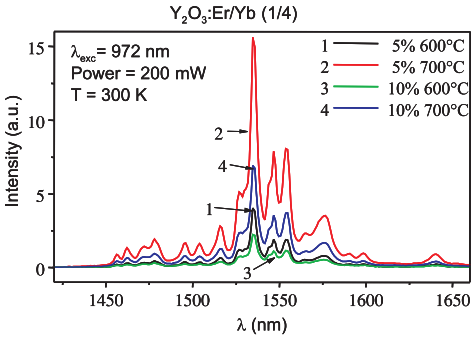

Fig. 3. The luminescent spectra in the infrared region (transition $^4I_{13/2}$ - $^4I_{15/2}$ Er^{3+}) of Y_2O_3: Er,Yb with Er/Yb=1/4 , RE= 5 mol % and 10 mol %, 600 ° C and 700 ° C annealing.

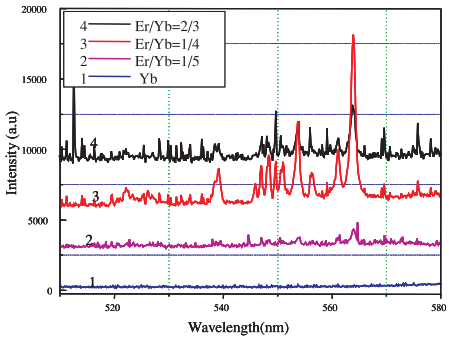

Fig. 4. Up-conversion effect of Y_2O_3: Er, Yb (10 mol%) 600 ° C, 30 min. (λ_{EXC} = 632.8 nm) with relative concentration Y_2O_3:Yb 10% mol Yb (1), Y_2O_3: Er/Yb =1/5(2), Er/Yb=1/4(3), Er/Yb=2/3 (4)

Efficient up-conversion emission is observed in Y_2O_3: Yb, Er, the green emission at 550 nm is generated as a result of two successive resonant energy transfers from Yb^{3+} to Er^{3+} ion, followed by nonradiative decay to the green emitting level. Fig. 4 present the up-conversion effect of Y_2O_3: Er, Yb (10 mol%) 600 ° C, 30 min.(λ_{EXC} = 632.8 nm) with relative concentration Y_2O_3: Yb 10% mol Yb(1), Y_2O_3:Er/Yb=1/5(2), Er/Yb=1/4(3), Er/Yb=2/3 (4). One can notice that the case excited by He-Ne laser luminescent intensity of the sample Y_2O_3: Er, Yb (10 mol%) 600 ° C, 30 min with ratio of Er/Yb=1/4 is maximum. The emission intensity of the up- conversion at 564 nm and 1538 nm were measured versus power laser with the excitation wavelength 803.7 nm for the Y_2O_3:Er. One can notice that the emission intensity is increased when the power increased from 50 mW to 750 mW.

Emission intensity at 612 nm with the concentration of Eu, 1, 3, 5, 7% mol were presented in the Fig. 5. The transmission electron microscopic (TEM) and X-ray diffraction was measured for Y_2O_3: Eu powder. Fig. 6 shows the transmission electron microscopic (TEM) of the Y_2O_3 powder obtained by the calcinations at 600 ° C for 1h. We can see that the particles size is smaller than 20 nm.

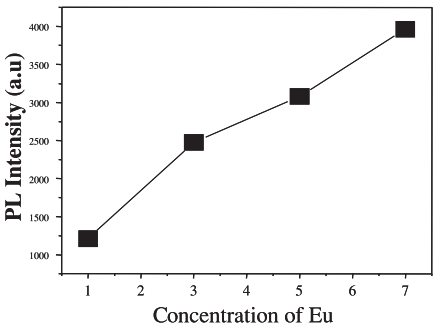

Fig. 5. Emission intensity at 612 nm with the concentration of Eu, 1%mol, 3%mol, 5%mol, 7%mol

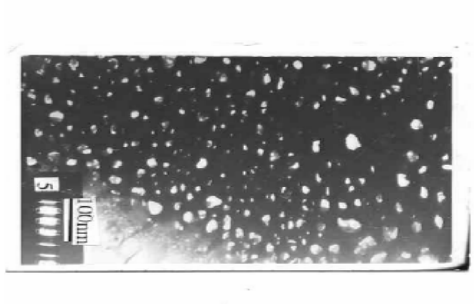

Fig. 6. The transmission electron microscopic (TEM) photograph of the Y_2O_3 powder (G:M=1.67), which was annealed at 600 ° C for 1h in air.

The Fig. 7 shows the images of high resolution TEM of Y_2O_3: Eu 5%mol heat treatment at 600 ° C for an hour.

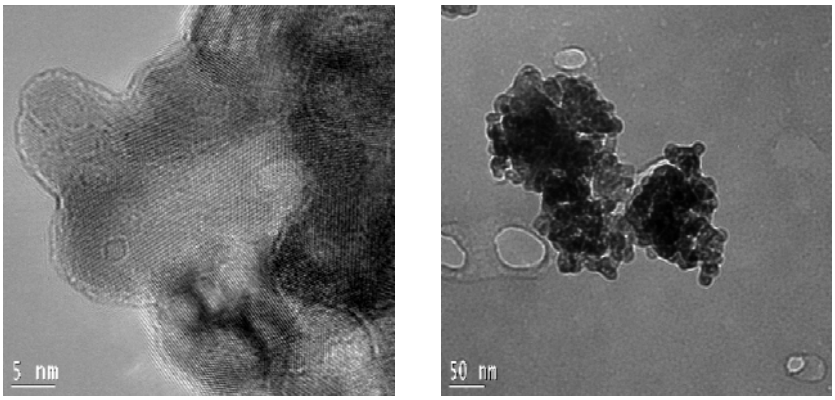

Fig. 7. The high resolution TEM images of Y_2O_3: 5%mol Eu (600 ° C, 60 min)

The luminescent spectra of the nanophosphors in the visible region was studied. Fig. 8 shows the emission spectra of the nano Y_2O_3: Eu (5 mol % Eu) with the difference of glycine-to-metal nitrate molar ratio after excitation at a wavelength of 254 nm into the charge transfer state. The luminescent spectra are described by the well known $^5D_0$ - ^7F_J line emissions ($J = 0, 1, 2$) of the Eu^{3+} ion with the strongest for J=2 at 612 nm. In Fig. 9, the influence of glycine-to- metal nitrate molar ratio on the fluorescence intensity at 612 nm was observed. The intensity is maximum for the sample with G:M^{3+}= 1.6:1.

The excitation spectrum of the 610 nm line of nanocrystalline Y_2O_3: Eu (5 mol% Eu), which is obtained by the calcination at 600 ° C for 1 hour with G:M^{3+}=1, is presented in Fig. 10. The strong excitation positions can be observed at about 399.5, 402.5, 469.5, 471.5 and 537.5 nm.

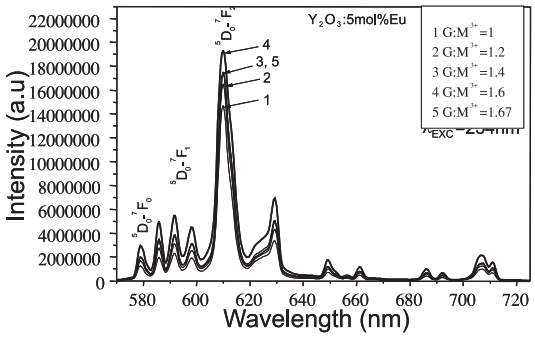

Fig. 8. Emission spectra of the nano Y_2O_3: Eu 5mol%Eu, excuted 254 nm, heat treatment at 400 ° C, 1hours

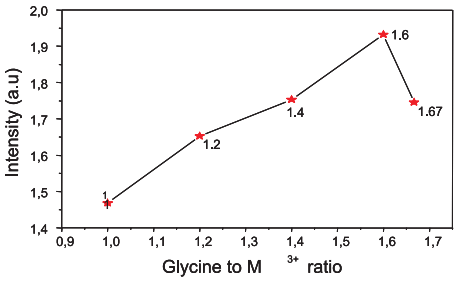

Fig. 9. Emission intensity at 610 nm with various glycine-to-metal nitrate molar

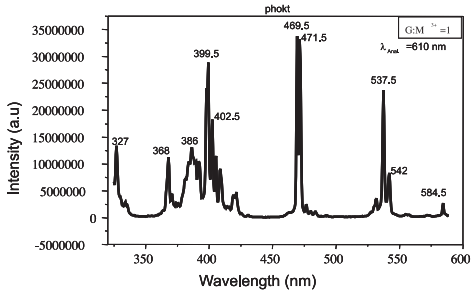

Fig. 10. Excitation spectrum of the nano Y_2O_3: 5mol % Eu with G:M^{3+}=1:1, 600 ° C, λ_{anal} 610 nm.

The luminescent spectra of Y_2O_3:Eu (5mol %) nanophosphors in the case of annealing 500 ° C, 600 ° C and 700 ° C for 1h, G:M^{3+}= 1.67:1 were presented in Fig. 11. In general, the fluorescent spectra given by the samples have almost the same shape. The intensity PL increases as the annealing temperature increases.

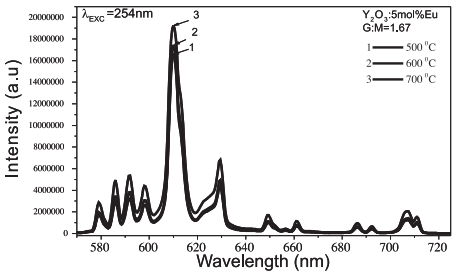

Fig. 11. Emission spectra of the nano Y_2O_3: Eu (5 mol % Eu) with the G:M^{3+}=1,λ_{Exc} = 254 nm, heat treatmen at:1: 500 ° C, 1hr; 2: 600 ° C, 1hr, 3: 700 ° C, 1hr

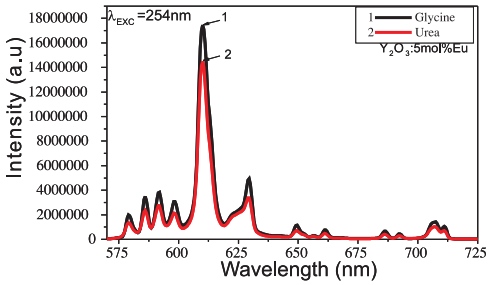

Fig. 12. Emission spectra of the nano Y_2O_3: Eu (5 mol % Eu) prepared by the combustion reaction between Glycine - Yttrium nitrate (1) and Urea - Yttrium nitrate (2)

Fig. 12 shows the emission spectra of the nano Y_2O_3: Eu (5 mol % Eu) prepared by the combustion reaction between Glycine - Yttrium nitrate(1) (G:M^{3+}=1.67) in comparison with the sample prepared by combustion reaction between Urea - Yttrium nitrate(2) after excitation at a wavelength of 254 nm. Two samples were prepared at the same annealing condition (600 ° C, 1 hour).

4. CONCLUSION

We have presented the technology for preparation Y_2O_3: Tb, Eu, Y_2O_3: Er, Yb nanophosphors in the concentration different of 5 mol % and 10 mol%. The size of the nanophosphors are determined by TEM measurements in Vietnam and Germany. Particles are made up of 20 nm- 80 nm in the optimal technology condition of 550 ° C, 30 min. When annealing temperature increases, the particles are biger. The results of luminescent spectra and decay time of Eu and Tb in the series of samples of different concentration of Eu, Tb were presented. The high efficient red emitting Y_2O_3:Tb, Eu nanophosphors are interesting in the field of optoelectronics as well as advanced optical materials by way of optical properties and structural ones. The optimal condition for prepared nanophosphors

was studied. We have also studied the energy transfer between Tb and Eu in the different relative concentrations 7/3, 8/2 and 9/1. The energy transfer is interesting in the case of the mole ratio of Eu/Tb=8/2. The Y_2O_3: Er, Yb nanophosphors with varied concentration of Er and Yb of ratio Er/Yb=1/5, 1/4 and 2/3 were prepared in order to study the up conversion effect. luminescent intensities in the red and infrared regions dependent on concentration of rare earth ions, ratio concentrations between Er and Yb, annealing temperature and selected excitation. The case of 5 mol%, ratio concentration Er/Yb=1/4, 700 $^\circ$C and annealing He-Ne excitation 632.8 nm seems to be the optimal conditions for the up-conversion effect in the 550nm. The up-conversion mechanism was proposed. The Y_2O_3:Eu nanophosphors were prepared by combustion reaction between Glycine and Yttrium nitrate. The results of TEM images indicate that the size of particles is very small. The luminescent spectra were measured after excitation at a wavelength of 254 nm. The $^5D_0$-^7F_j transitions of Eu^{3+} were recorded. The excitation spectrum of the 610 nm line was measured for the Y_2O_3: Eu (5 % mol), which is obtained by the calcination at 600 $^\circ$C for 1hour with G:M^{3+}=1. The decay time of Y_2O_3: 5% mol Eu, heat treatment at 400 and 570 $^\circ$C, 1 hour were measured and compared. The optimal concentration of Eu is 7 % mol.

Acknowledgement. Our work was financially supported by the National Basic Research Program. We would like to thank Prof. Nguyen Van Hieu, Assoc. Prof. Vo Vong for their help.

REFERENCES

1. X. Jing, C. Ireland, D.J. Barber, J. Silver, A. Vecht, G. Fern, P. Trowga and D.C. Morton, *J. of the electrochemical society* **146** (1999) 4654-4658.
2. Konrad, T. Fries, A. Gahn, F. Kummer, U. Herr, R. Tidecks and K. Samwer, *J. Appl. Phys.* **86** (1999) 3129-3133.
3. K. L. Choy , J. P. Feist, A. L. Heyes and B. Su, *J. Mater. Res.* **14** (1999) 3111-3114.
4. B. R. Ratna, A. D. Dinsmore, Y. Tian, S. B. Qadri, D. S. Hsu and H. F. Gray, *The 5th Inter. Conf. on the Sci. and Tech. of Display Phosphor.* **295** November (1999) 8-10.
5. J. A. Capobianco, T. D'Alesio, F. Vetrone, G. Tessari H. R. Moon, B. T. Ahn, J. I. Han, A. Speghini and M. Bettinelli, *The 2nd International Symposium on LASER, Scintillator and Nonlinear Optical Materials*, Lyon, 2000.
6. Nguyen Vu, Pham Thu Ha, Tran Kim Anh, Nguyen Xuan Nghia, Le Quoc Minh. National Conference on Solid States, Nha Trang, 8-2001
7. P. N. Prasad, *Nanophotonics Wiley-Interscience*, New York, 2004
8. D. Matsuura, *Applied Physics Letters*, **8** (24) (2002) 4526-4528.

Received January 17, 2005.