Nanophotonic materials containing rare earth ions Er and Eu

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The nanomaterials containing rare earth Eu, Er such as Y\textsubscript{2}O\textsubscript{3}:Eu Y\textsubscript{2}O\textsubscript{3}:Er nanophosphors that are good used for two dimensional displays and infrared detector cards, Silica Titania or Silica Zirconia doped Er for planar wave guide in telecommunication application. Silica hybrid PMMA:Er with different concentration of Er 1, 3, 5, 7 mol % for photonic materials in near infrared. The hybrid Sol-Gel Materials doped with Europium III were presented. The concentrations of the Eu\textsuperscript{3+} change from 1-10\% (g Eu/g SiO\textsubscript{2}). The results indicated that change the ratio of solvents/TEOS, the solvents, PH, the concentration of modified polymer (PMMA) greatly improving the quality of syntheses materials doped with Eu\textsuperscript{3+} as the mechanical and spectroscopy properties. We have been investigating the optical properties of these materials. Particular emphasis is given to discussion the role of active center concentration of erbium and europium, the promising optical properties of Y\textsubscript{2}O\textsubscript{3} codoped Er- Yb which up-conversion effect. The influence of the synthesis conditions to the molecular structure of Sol-gel hybrid material were studied by the methods of differential thermoanalyse (DTA), infrared absorption(IR). The spectroscopy properties of the Eu\textsuperscript{3+} and ability of application in visible range of Y\textsubscript{2}O\textsubscript{3}:Eu and silica hybrid PMMA:Eu will be disscused.

Key words: photonic materials, rare earth ions Er, Eu, hybride silica

Introduction

Nanophosphors is one of the most interesting subject of nanotechnology. Today people need devices able to store information at high densities and high speeds using little energy. Nanotechnology for new industry creation and life style innovation. It has promising application efficiency, high - luminosity device as well as on drug injection . 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\textsubscript{2}O\textsubscript{3}:Eu nano particles and thin films. We present the results of Y\textsubscript{2}O\textsubscript{3}:RE(Eu, Er, Yb) nanophosphors prepared by new method of combustion reaction between Glycine and Yttrium nitrate in oder to find the best agent for combustion reaction [6]. The role of active center concentration and the decay time of new samples nanophosphors doped with Europium will be presented in detail.

The sol-gel process has been successful in producing silica glass with higher dopant concentrations than conventional melt glass. The process is a convenient method for the preparation bulk materials via hydrolysis and condensation [7-10]. The technology has great advances in ceramic which produce homogeneous materials with lower syntheses temperature. Sol-gel is not only a producing process for the homogeneous inorganic glasses but also a technique for the synthesis of organic- inorganic hybrid materials [7,8].

The hybrid systems polymethacrylate/ silica [7] with hydrogen bonds as the main interaction at the organic- inorganic interface formed materials. The hydrogen bonding binds the organic phase to the inorganic matrix that limited macro-phase separation. Nowadays, sol-gel process has been been used investigated in industrials and laboratories developed for various applications of optical, electrical purposes [11,12]. It has been found

that homogeneity and phase behavior of hybrid materials is related to the organic-inorganic interfacial interaction [10]. Heat effect may cause further condensation or structure deformation for sol-gel synthesized hybrid system. The optical properties of rare earth ion doped silica glass have been studied extensively as optical materials [7,9,12].

The PMMA was added to silicate glasses as modified organic component and influence of its addition on optical properties of rare earth ion doped glass was investigated. Ion Eu³⁺ is used to determine local structure, one feature is that the ⁵D⁰→⁷F⁰ luminescence band is completely nondegenerate. This transition can not be split by a crystal field. The splitting or inhomogeneous broadening of this transition are due to dissimilar Eu³⁺ ion bonding environments. The transition ⁵D⁰→⁷F₂ of Eu³⁺ is hypersensitive. The deviation of the Eu³⁺ site from inversion symmetry linked to an increase in relative intensity of ⁵D⁰→⁷F₂ luminescence band. Furthermore ion Er³⁺ was doped in PMMA present transitions of Er³⁺ in the infrared region 1535 nm have received attention.

Experimental

The combustion method was used for preparation of Y₂O₃:RE nanophosphors [6]. For Y₂O₃:Eu samples, the Eu concentration is 1, 3, 5, 7 mol %. Reaction of an aqueous solution containing NH₂CH₂COOH, Eu(NO₃)₃ or Er(NO₃)₃ and Y(NO₃)₃.

Gel sample were prepared via the hydrolysis and condensation of trathoxysilane TEOS with distilled water. Methyl methacrylate (Merck) and TEOS (Merck) were used as received. Nitric acid was applied as the catalyst. The solvents: ethanol, methanol, formamide were all of reagent grade. TEOS solution was prepared with reagent ratio H₂O: alcohol:TEOS = 4:4:1. Small amount of acid HNO₃ was added alter the sol PH. Subsequently, the TEOS solution was added into MMA with initiator peroxide Benzoil (BP), various organic-inorganic ratios: 20/80; 40/60; 60/40; 80/20 and 100/0 (w/w) for TEOS/ MMA and mixed, then rare earth solution with alcohol was added. The sol-gel process was carried out at 40°C. After 1 hour homogeneous solution can be obtained. It was poured into a plastic box kept covered and aged at 50°C for 20 days.

The precursor was solidified and wet gel was formed. After that the holes were made in the cover to allow the organic solvates to evaporate. After a week, a monolithic, transparent SiO₂/PMMA hybrid material was obtained. The scheme of the preparation procedure is demonstrated in Fig.1. In order to elucidate the influence of the polarity of solvent to the luminescent characteristics for doped hybrid materials. We have used two alcohol as ethanol and methanol to prepare hybrid materials doped with difference concentration of Europium (III). The results show that the hybrid systems prepared with methanol what dried easy and luminescence better than ethanol systems. It may be caused by low evaporate temperature and similar radical as methyl methacrylate (MMA) of methanol. This technological conditions seem to be a good for producing hybrid sol-gel materials doped with RE³⁺ salt.

Infrared spectra (IR) of the hybrid materials were obtained from infrared spectrophotometer (Nicolet Impact 4100 (USA)) in spectra range of 2000- 400 cm⁻¹. The
emission spectra were obtained on spectrometer (FL3-22) with double monochromater, the excitation source is Xenon lamp XBO 450w. The decay times were measured with monochromator HDR1, Oscilloscope Lecroy 9362, Nitrogen laser 1ns, 20 Hz, 11µ. The morphology and particle sizes of Y$_2$O$_3$:Eu were observed by using high resolution transmission electron microscopy (CM 200, 160KV). The Y$_2$O$_3$:Eu powder was analyzed by X-ray diffraction D5000 (Siemens).

**Results and discussion**

The transmission electron microscopic (TEM) and X-ray diffraction was measured for Y$_2$O$_3$: Eu powder. Figure 1 shows the image of high resolution TEM of Y$_2$O$_3$: Eu 5 mol %. We can see that the particles size is smaller than 50 nm. The luminescent spectra of the nanophosphors in the visible region was studied. The luminescent spectra are described by the well known $^5$D$_0$ – $^7$F$_J$ line emissions (J=0, 1, 2…) of the Eu$^{3+}$ ion with the strongest for J=2 at 612 nm. Emission intensity at 612 nm with the concentration of Eu, 1, 3, 5, 7 mol % were presented in the Figure 2.

![Image of TEM images](image1)

**Fig.1** The TEM images of Y$_2$O$_3$:5%mol Eu (600°C, 60 min)

![Image of Emission intensity](image2)

**Fig.2:** Emission intensity at 612 nm with the concentration of Eu, 1, 3, 5, 7 mol %

Figure 3 shows the decay times of Y$_2$O$_3$: Eu (2 and 3 mol %), with different annealing temperature of 600 and 700°C.

![Image of Decay times](image3)

**Fig 3:** The decay times of Y$_2$O$_3$: Eu (2 and 3 mol %), with different annealing temperature of 600 and 700°C

![Image of IR spectra](image4)

**Fig. 4:** The IR spectra of the hybrid materials, neat-PMMA (1), hybrid materials TEOS/MMA: 20/80(2), 40/60(3), 60/40(4), 80/20(5), 100/0(6)
The IR spectra of the hybrid materials in various organic-inorganic ratio of the organic compose 20/80, 40/60, 60/40, 80/20 and 100/0 (w/w) for TEOS/PMMA are show in Figure 4. The main absorption and characteristic vibration modes of groups are summarized in Table 1. These infrared absorption peaks were all well resolved and can be used in order to investigate the development of material structure with increasing silica content.

**Table 1** Main IR absorption bands and characteristic groups of SiO2 xerogel

<table>
<thead>
<tr>
<th>Absorption frequency(cm⁻¹)</th>
<th>Assignment</th>
<th>Absorption frequency(cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1690</td>
<td>νc=0</td>
<td>1098</td>
<td>νas Si-O-Si</td>
</tr>
<tr>
<td>1392</td>
<td>νas CH3</td>
<td>973</td>
<td>νas Si-OH</td>
</tr>
<tr>
<td>1205</td>
<td>νas Si-O-Si</td>
<td>796</td>
<td>δ Si-O-Si</td>
</tr>
<tr>
<td>457</td>
<td>δSi,Si</td>
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Fig.5. Representative room temperature Eu³⁺ luminescence spectra with various 1÷7 wt.% of the dopant. $\lambda_{ex}=467$ nm.

Fig.6. Representative room temperature Eu³⁺ luminescence spectra with various 1÷7 wt.% of the doping. $\lambda_{ex}=254$ nm.

The absorption peak at 973 cm⁻¹ seem to be the peak of silanol group (Si-OH). However, with the TEOS content increased to 60 vol.% in which two absorption peaks located at 1205 and 796 cm⁻¹ were detected. The peaks would be a result from the existence of unreacted silica network. In the spectral range of 1780 – 1680 cm⁻¹, all the organic-inorganic hybrid material with more 60 vol.% PMMA display small shoulder at 1730 cm⁻¹, which was due to the formation of hydrogen bonds between carbonyl group (organic phase) and silanol group (inorganic phase). The formation of hydrogen bonds may induce organic-inorganic interfacial
interaction. Increasing of hydrogen bonds content may result from the increasing of carbonyl group or silanol group content.

Fig.5 illustrate representative room temperature Eu$^{3+}$ luminescence spectra of samples prepared with Europium nitrate. Spectra are provided for the gel point of the sol-gel process. The increasing of intensities with various concentration of dopant (Eu$^{3+}$) under $\lambda_{ex}=467$nm. The spectra in Fig.5 and Fig.6 have been normalized to the peak intensity for comparison purposes. We observed the decreasing in relative intensities of Eu$^{3+}$ under high energy excitation $\lambda_{ex}=254$ nm. This phenomena may due to quenching effect of high concentration of dopant (Eu$^{3+}$) in hybrid sol-gel organic-inorganic. All samples are good luminousness.

Luminescent spectra of Silica/PMMA doped with various concentration of the Er complex under 972 nm excitation wavelength were presented in figure 7. Doping hybrid silica matrices of Er(BA)$_2$(MMA)phen with Si-O-C bonds, which leads to appear of fluorescence picks at 1475 to 1525 nm. Er$^{3+}$ complex grafted to the silica/PMMA, which causes to decrease of -OH groups of matrices.

Conclusions

The Y$_2$O$_3$:RE 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 $^7D_0-^5F_j$ transitions of Eu$^{3+}$ were recorded. The optimal concentration of Eu is 7 mol%.

PMMA/ silica hybrid system, hydrogen bonds can be formed from carbonyl group and silanol group between organic-inorganic phase. Hence TEOS/ PMMA (20/80) and TEOS/ PMMA (40/60) hybrid materials exhibit two closer glass transition temperatures.

We obtained high Eu$^{3+}$-doped TEOS/ PMMA by sol-gel method using aqueous europium nitrate sol. Specific emission bands in these doped samples are useful optical probes of the local environment around ions in the hybrid matrix. The luminescent spectra of Europium (III) in sol-gel hybrid material (TEOS/ PMMA) observed an increasing of relative intensities of hypersensitive transition with various Eu$^{3+}$ concentration.

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References