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Preparation and spectral properties of ORMOSIL films doped with neodymium organic complex

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Abstract

Vinyltriethoxysilane-derived organically modified silicate (ORMOSIL) films doped with the organic complex neodymium tris(2-theonyltrifluoroacetonate)bis(triphenylphosphine oxide) by a multistep sol–gel process exhibit near-infrared luminescence at ca. 1330 nm ($^4F_{3/2}$ $^4I_{13/2}$). Spectral properties of as-doped films with a series of doping concentration from 1 to 10 mol.% (Nd related to Si) are investigated for the optimum doping concentration. The vinyltriethoxysilane-derived ORMOSIL host matrix is considered to have little effect on spectral properties of Nd^{3+} ions due to the ligands' protection. The effect of heat-treatment on photoluminescence properties is also revealed.

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Keywords: B. Photoelectron spectroscopy; C. Sol gel; D. Neodymium; X. ORMOSIL film

1. Introduction

Neodymium trivalent ion has a unique intra-4f transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at 1.33 μm, corresponding to the wavelength of the second standard telecommunication window. Polymers doped with various neodymium complexes have also been exploited with an attempt to fabricate planar-integrated optical amplifiers [1–7]. Recently, sol–gel-derived organically modified silicates (ORMOSILs) have attracted increasing attention for fabrication of planar-integrated optical amplification, since the sol–gel process involved with ORMOSILs offers several advantages for fabrication of planar optical waveguide such as flexible, inexpensive and easy to obtain over 1 · m thickness crack-free film via the single coating process [8–10]. Our purpose is to obtain neodymium (III)-doped ORMOSIL films for potential applications in planar optical amplifiers at 1.33 μm. Here, we present preliminary results about spectral properties of ORMOSIL films directly doped with a neodymium organic complex fabricated through a multistep sol–gel process.

2. Experimental details

2.1. Synthesis of neodymium complex and preparation of VTES-derived ORMOSIL films doped with neodymium complex

All reagents including 2-theonyltrifluoroacetone (TTA), triphenylphosphine oxide (TPPO), vinyltriethoxysilane (VTES) and neodymium oxide (Nd_2O_3) were reagent grade and used as received. $NdCl_3 \cdot 6H_2O$ was obtained from Nd_2O_3 by dissolving Nd_2O_3 into hydrochloric acid and

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subsequently removing the solvent carefully. Neodymium organic complex $Nd(TTA)_3(TPPO)_2$ [Nd tris(2-theonyltrifluoroacetonate)bis(triphenylphosphine oxide)] was synthesized according to the method of Melby et al. [11]. Its chemical structure is depicted in the inset of Fig. 1, conformed by elemental analysis and FTIR in advance.

The initial VTES-derived sol was prepared by multistep sol–gel route involving acid-catalyzed hydrolysis and basic-catalyzed condensation of VTES precursor at room temperature. The molar ratio of VTES/ethanol/water was 1:1.5:3. After hydrolysis with HCl as acid catalyzer (pH 2) for 1 h, a small amount of amine-modified silane *N*-(3-(triethoxysilyl)-propyl)-ethylenediamine was added as basic catalyst (pH 5–6), followed by stirring for 30 min. $Nd(TTA)_3(TPPO)_2$ was dissolved into another 1.5 part of ethanol with an appropriate amount of dimethylformamide (DMF) and subsequently added into the sol. The neodymium doping concentration was denoted as molar percentage relative to silicon. Thereafter, the mixed solution was kept in a sealed flask aging for 1 week at room temperature. Spin coating repetitiously on glass slides for ultraviolet-visible-near infrared (UV-Vis-NIR) absorption and photoluminescence (PL) measurements gave visually transparent films. Deposited films were allowed to dry at room temperature for 1 week before heat-treatment at various temperatures for 24 h. The multilayer films thicker than 10 · m were obtained on glass slides to ensure that PL measurement was done without an aid of the lock-in mode technique.

2.2. Spectroscopic measurements

UV-Vis-NIR absorption spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer at a spectral resolution of 1 nm. FTIR measurements were performed on a Nicolet AVTAR360 FTIR. Near infrared PL spectra were determined at room temperature by using a TRIAX 550 spectrometer equipped with a thermoelectric cooled DSS-IGA020T InGaAs detector (JOBIN YVON/SPEX), with an 800-nm semiconductor LD as the excitation source. The spectral resolution and the integral time were 2 nm and 1.5 s, respectively, for all PL measurements.

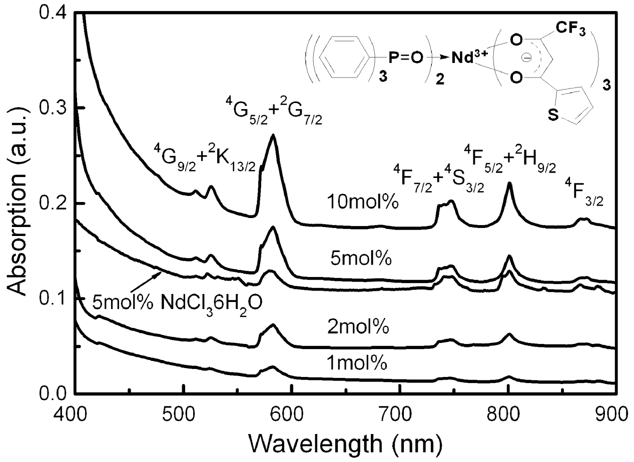

Fig. 1. Absorption spectra of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ of various doping concentrations and film doped with $NdCl_3\cdot 6H_2O$ (5 mol.%). The chemical structure of the complex $Nd(TTA)_3(TPPO)_2$ is shown in the inset.

3. Results and discussion

As the neodymium organic complexes are incorporated into VTES-derived ORMOSIL host, the pores that are residing in the SiO_2 network and are stuffed with vinyl groups can be rationally and qualitatively described as concentrated organic "solution" of neodymium organic complexes. The absorption spectra of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ of various doping concentrations and heat-treated at 50 °C for 24 h are shown in Fig. 1, which are corrected by film thickness and are presented together with the assignment of the absorption peaks according to Carnall et al. [12]. The absorption spectral features of samples with doping concentrations from 1 to 10 mol.% exhibit negligible differences, especially for the absorption band at 560–620 nm of $^4I_{9/2}\rightarrow{}^4G_{5/2}$ hypersensitive transition, which is known sensitive peculiarly to changes in the coordination structure around Nd^{3+} ion and hypersensitive to Nd^{3+} ion site symmetry of the ligand field, varies hardly with the Nd doping concentration (even up to 10 mol.%). This demonstrates that the effect of the host matrix is little pronounced on the chemical microenvironment around Nd^{3+} ions due to the presence of ligands, and correspondingly, the ligands shield Nd^{3+} ions from the environment effectively, which are known to strongly coordinate Nd^{3+} ions. In Fig. 1, the absorption spectrum of VTES-derived film doped with 5 mol.% $NdCl_3\cdot 6H_2O$ is also given for comparison, and large difference occurs upon comparison with that of VTES-derived film doped with 5 mol.% $Nd(TTA)_3(TPPO)_2$.

Fig. 2(a) shows PL spectra under 800 nm LD excitation of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ and $NdCl_3\cdot$6H2O, both with the doping concentration 5 mol.% and the heat-treatment temperature 50 °C, together with that for pure complex $Nd(TTA)_3(TPPO)_2$ in bulky powder. Two NIR characteristic emission bands are assigned to f–f transitions of Nd^{3+} ion $^4F_{3/2}\rightarrow{}^4I_{11/2}$ (~1060 nm) and $^4F_{3/2}\rightarrow{}^4I_{13/2}$ (~1330 nm), respectively, which arise from the decay of the level $^4F_{5/2}$ or $^2H_{9/2}$ populated upon direct excitation at 800 nm to the $^4F_{3/2}$ level. By comparing the PL spectra between the films doped with $Nd(TTA)_3(TPPO)_2$ and $NdCl_3\cdot 6H_2O$, respectively, the luminescence intensity is increased over fivefold at the presence of ligands, preliminarily indicating efficient protection of bulky ligands from the environment. It is speculated that, for $Nd(TTA)_3(TPPO)_2$-doped film, the quencher moieties, like O–H groups, are removed from inner coordination shell of Nd^{3+} ion, and the encapsulating ligands provide minimal pathways for nonradiative decay. The energy gap between the level $^4F_{3/2}$ of Nd^{3+} ion and its next level $^4I_{15/2}$ is about 5100–5600 cm^{-1}, matching well the second vibration modes of oscillating groups O–H (6900 cm^{-1}) and C–H (smaller, 5900 cm^{-1}), which may contribute to efficient nonradiative deactivation of $^4F_{3/2}$ level. Additionally, for $NdCl_3 \cdot 6H_2O$-doped film, the small water molecules can occupy directly the inner coordination shell of Nd^{3+} ion. It is deduced that C–H of ligands (TTA and TPPO) for $Nd(TTA)_3(TPPO)_2$ is relatively far away from Nd^{3+} ion in comparison to O–H of coordinating H_2O for $NdCl_3 \cdot 6H_2O$. Thus, O–H groups from coordinating H_2O are principally detrimental to the luminescence from Nd^{3+}-doped films. The full width at half maximum (FWHM) values of 1060 and 1330 nm bands for $Nd(TTA)_3(TPPO)_2$-doped films are 24.8 and 25.6 nm, respectively, whereas larger values 32.7 and 32.2 nm, respectively, are for $NdCl_3 \cdot 6H_2O$-doped films. This can be understood as follows. In the case of $NdCl_3 \cdot 6H_2O$ doping into VTES-derived gel glass, Nd^{3+} ions are considered to be simultaneously coordinated to bridging or nonbridging oxygen atoms of SiO_2 tetrahedron network as well as inherent water molecules in various disorder ways. The local electric fields at the Nd^{3+} sites vary considerably, and subsequently large stark splitting of the energy levels of Nd^{3+} ions, i.e., inhomogeneous broadening of linewidth, occurs due to site-to-site variations originated from complicated surroundings. For $Nd(TTA)_3(TPPO)_2$ in film, Nd^{3+} ions are still restricted in the ligands encapsulating unit with Nd^{3+}, occupying sites relatively changeless.

Moreover, upon comparing the shape and relative intensity of luminescence spectra, we note that, in this case, there is no significant difference between the emission feature of $Nd(TTA)_3(TPPO)_2$ in pure solid state and in VTES-derived films, further demonstrating that the ORMOSIL host does not modify the local microenvironment of Nd^{3+} ions. The intensity ratio of $^4F_{3/2} \rightarrow {}^4I_{13/2}$ emission transition to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission transition is 19.9% for $Nd(TTA)_3(TPPO)_2$-doped film, 20.2% for pure $Nd(TTA)_3(TPPO)_2$ complex powder and 24.6% for $NdCl_3 \cdot 6H_2O$-doped film. It is noticeable that the intensity ratio of the transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ for $NdCl_3 \cdot 6H_2O$-doped film possesses larger value, which is also speculated on the presence of inner-shell coordinating water for $NdCl_3 \cdot 6H_2O$ doped in film. Since the lower level $^4I_{13/2}$ for the transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ lies about 4000 cm^{-1} higher than the ground level $^4I_{9/2}$ [12], $^4I_{13/2}$ deactivates relatively easily to $^4I_{9/2}$ through vibronic coupling with the vibrational state of O–H groups (3450 cm^{-1}). Then, the transition possibility of $^4F_{3/2} \rightarrow {}^4I_{13/2}$ is favored for $NdCl_3 \cdot 6H_2O$-doped film since the $^4I_{13/2}$ level can be depopulated quickly. On the contrast, $Nd(TTA)_3(TPPO)_2$-doped film as well as pure complex powder possesses relatively smaller intensity ratio, and this can be attributed to strong coordinate ability of TTA or TPPO, which gives no possibility of water directly coordinating Nd^{3+} ion.

PL spectra of VTES-derived films with various Nd doping concentrations and heat-treated at 50 °C are

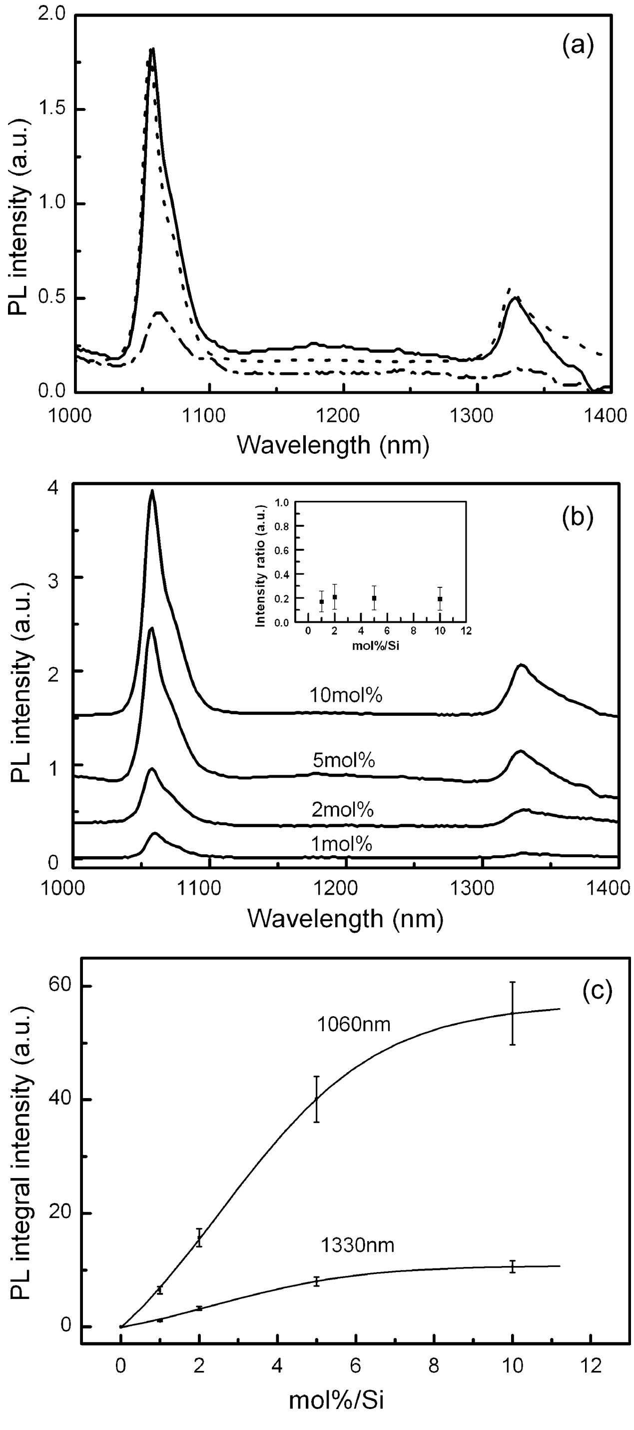

Fig. 2. (a) PL spectra of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ (solid line) and $NdCl_3 \cdot 6H_2O$ (dash-dot line) with the doping concentration 5 mol.% and the heat-treatment temperature 50 °C as well as the spectrum of pure complex $Nd(TTA)_3(TPPO)_2$ in bulky powder (dot line) which has artificially been accommodated identically with that for film doped with $Nd(TTA)_3(TPPO)_2$ only for visually comparison of the spectral appearance between them. (b) PL spectra of VTES-derived films with various Nd doping concentrations heat-treated at 50 °C. The inset shows the intensity ratio of $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (~1330 nm) to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (~1060 nm) vs. the Nd concentration. (c) Dependence of PL integral intensities at around 1060 and 1330 nm on the Nd concentration, the fitting curve being drawn for eyes guide. The excitation source is an 800-nm LD.

presented in Fig. 2(b). The intensity ratio of $^4F_{3/2} \rightarrow {}^4I_{13/2}$ emission transition to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission transition changes inconsiderably with the Nd content, as indicated in the inset. This behavior is similar with the above observed for absorption spectra shown in Fig. 1. It should be noted that the largest doping concentration is limited to 10 mol.% due to finite solubility of $Nd(TTA)_3(TPPO)_2$ in ethanol.

As illustrated in Fig. 2(c), the dependence of PL integral intensities at around 1060 nm and around 1330 nm on the Nd content is depicted as that the PL integral intensity increase nearly linearly with the Nd doping concentration in the range of 0–5 mol.%. However, a little saturation for PL intensity has been observed when the doping concentration reaches near to 10 mol.%, which may be due to concentration quenching (vide infra). Nevertheless, there is no maximum in the investigated range 0–10 mol.%, and from Fig. 2(c), the doping concentration of 7 mol.% is reckoned to be the optimum one without significant concentration quenching. As the Nd content increases in the host matrix, deactivation of excited states should occur via nonradiative dipole–dipole energy transfer between neighboring Nd^{3+} ions which mainly involves with cross relaxation process and excitation migration process [13]. In the cross relaxation process, one excited ion deexcites from $^4F_{3/2}$ level to $^4I_{15/2}$ level while another one is excited from the ground state $^4I_{9/2}$ to $^4I_{15/2}$ level as followed by rapid nonradiative decay back to the ground state; that is $(^4F_{3/2} \rightarrow {}^4I_{15/2})=(^4I_{9/2} \rightarrow {}^4I_{15/2})$. In the excitation migration process, similarly, it is described as $(^4F_{3/2} \rightarrow {}^4I_{9/2})=(^4I_{9/2} \rightarrow {}^4F_{3/2})$, which does not quench luminescence directly by itself but provide more possibility of rapid luminescence quenching. Meanwhile, the dipole–dipole energy transfer rate is strongly distance-dependent ($1/r^6$) according to Förster–Dexter theory [14,15].

The least distance between two emitting Nd^{3+} ion centers upon the presence of ligands is deduced from chemical structure of the simple $Nd(TTA)_3(TPPO)_2$ dimer on the basis of the van der Waals radii [16–18], which is over 8.0 Å and is still larger than the critical distance 4.07 Å for the cross relaxation process $[(^4F_{3/2} \rightarrow {}^4I_{15/2})=(^4I_{9/2} \rightarrow {}^4I_{15/2})]$ in Nd^{3+}-doped phosphate glass [13]. This fact demonstrates that the ligands isolate Nd^{3+} ions effectively even for the pure complex in multicrystalline solid, as the efficiency of energy transfer at 8.0 Å is only 1.7% of that at 4.07 Å. Therefore, it is suggested that, in $Nd(TTA)_3(TPPO)_2$-doped film, the cross relaxation process will play a minor role in deactivating the Nd^{3+} excited state $^4F_{3/2}$.

A rough estimation for Nd^{3+} ion concentration in VTES-derived film doped with 10 mol.% of $Nd(TTA)_3(TPPO)_2$ is approximately 8.6×10^{20} ions/cm^3, which is based on an analogue bulk sample doped with 10 mol.% of $Nd(TTA)_3(TPPO)_2$ since it is difficult to survey the actual ion concentration in the VTES-derived films directly. Accordingly, the average distance between two Nd^{3+} ions is about 11.47 Å, only a little longer than the critical distance 11.14 Å for the excitation migration process $[(^4F_{3/2} \rightarrow {}^4I_{9/2})=(^4I_{9/2} \rightarrow {}^4F_{3/2})]$ in Nd^{3+}-doped phosphate glass [13]. Moreover, aggregation of the complexes is unavoidable in such a high doping concentration, which possibly makes some Nd^{3+} ions separated at the above-mentioned least distance 8.0 Å that is less than 11.14 Å. Hence, the effect of the excitation migration process is expected to hold back the elevation of PL intensity. It can be concluded that, on one hand, the ligands TTA and TPPO shield from the quencher moieties in the matrix, on the other hand, the ligands isolate Nd^{3+} ions.

Fig. 3 presents PL spectra of VTES-derived ORMOSIL films doped with 10 mol.% $Nd(TTA)_3(TPPO)_2$ and heat-treated at various temperatures for 24 h. According to our preliminary results about the different thermal analysis for $Nd(TTA)_3(TPPO)_2$-doped VTES-derived ORMOSIL, the partial combustion of organic moieties has been observed at over 190 °C, and the broad and flat endothermic band below 190 °C is ascribed to the evaporation of the residual solvents, which can serve as a guide to what will approximately happen to the film. Based on this, the heat-treatments for films are merely performed below 150 °C since it is not easy to obtain crack-free film over 150 °C due to apparent film shrinkage resulted from high Nd complex moiety content. The films darken a little as the heat-treatment temperature is elevated from 50 to 150 °C. In Fig. 3, the PL spectra features were kept unchanged for all samples, confirming that the heat-treatment does not significantly alter the microenvironment around Nd^{3+} ions. Furthermore, PL intensity increases slowly below 120 °C because the solvents such as ethanol, DMF and water are not drove off effectively, while it is enhanced remarkably at 150 °C. It is reasonable to concern that the heat-treatment at 150 °C densifies the film and removes the comparative quantity of the solvents, especially water molecules in the film, attenuating nonradiative deexcitation of the excited state from O–H groups which are

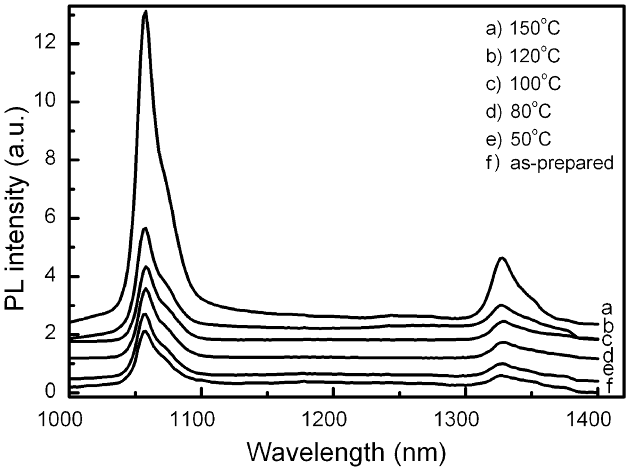

Fig. 3. PL spectra of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ (10 mol.%) and heat-treated at various temperatures for 24 h.

spaced at a rather long distance from Nd^{3+} ions by ligands.

4. Conclusion

We present VTES-derived ORMOSIL film doped with the complex $Nd(TTA)_3(TPPO)_2$ of 5 mol.%, which exhibit similar NIR PL properties with the complex in bulky powder and markedly better PL properties than that doped with only Nd^{3+} ions. The host matrix has feeble effect on the spectroscopic properties of doped neodymium organic complex as a result of the organic ligands effectively shielding Nd^{3+} ions from the surroundings, since VTES-derived films with various Nd contents and heat-treatment temperatures possess very similar absorption and PL properties.

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