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Luminescent properties of neodymium organic complexes and as-doped organically modified silicate films

Huaishan Wang[a], Guodong Qian[a,*], Jiahua Zhang[b], Yongshi Luo[b],
Zhiyu Wang[a], Minquan Wang[a]

[a]Department of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University,
38 Zheda road, Hangzhou 310027, P.R. China
[b]Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, China Academy of Science,
Changchun 130021, P.R. China

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Abstract

Near-infrared (NIR) luminescent ternary and hydrated binary neodymium β-diketonates emitting at ca. 1330 nm are presented. The effects of ligand moieties on the photoluminescence properties of Nd^{3+} ions are discussed. Moreover, the neodymium organic complex neodymium tris(2-theonyltrifluoroacetonate)bis(triphenylphosphine oxide), $Nd(TTA)_3(TPPO)_2$, which has the best photoluminescence properties among all investigated neodymium complexes, is incorporated into vinyltriethoxysilane-derived ORMOSIL (organically modified silicate) film by a multistep sol–gel process. The Nd doping concentration was up to 5 mol% related to Si. The spectroscopic results about as-doped ORMOSIL films indicate that the ligands around Nd^{3+} ions indeed shield effectively Nd^{3+} ions from luminescence-quenching impurities in the host matrix, such as OH groups.

Keywords: Sol–gel; Luminescence; Neodymium; Optical properties

1. Introduction

The organic–inorganic hybrid materials from sol–gel-derived organically modified silicate (ORMOSIL) are of increasing interest in the integrated optical amplification, offering several advantages for fabrication of planar optical waveguides as follows [1–7]. The sol–gel technology is a flexible and inexpensive one to deposit films as an attractive alternative to conventional technologies such as the ion-exchange technology. It allows for fabricating waveguides at moderate processing temperatures, then possibly combining with the photolithographic technique available. The refractive index is easy to tune through introducing heavy metal ions such as Ti^{4+} and Zr^{4+}. Crack-free, over-1-μm-thick films can be obtained via a single coating process and the sol–gel method can accommodate a large amount of lanthanide organic complexes in the matrix. Neodymium trivalent ion has an intra-4f emission transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ at ca. 1.33 μm corresponding to the wavelength of the second standard telecommunication window. Recently, a lot of studies have been devoted to near-infrared (NIR) luminescent properties of Nd organic complexes in solutions [8–18]. Polymers doped with various Nd complexes have also been reported [19–29].

Here, we propose to incorporate Nd organic complexes with encapsulating ligands into ORMOSIL films for potential applications in planar optical waveguide amplifiers of photonic integrated circuit. The reasons for selecting Nd organic complexes as dopants are that (i) the encapsulating ligands should serve to shield Nd^{3+} ions from luminescence-quenching impurities like residual OH groups in the

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* Corresponding author. Tel.: +86 571 87952334; fax: +86 571 87951234.
E-mail address: gdqian@zju.edu.cn (G. Qian).

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ORMOSIL host matrix and allow minimal pathways for the nonradiative decay, (ii) the presence of bulky ligands around Nd^{3+} ions is expected to isolate Nd^{3+} ions sterically from each other in the matrix and consequently minimize deleterious ion–ion interactions which result from the heavily doping concentration that is required for compensating the short path length of planar optical waveguides, and (iii) the luminescent properties of Nd^{3+} ions could be tailored through designing the ligands. However, to our knowledge, only a small quantity of systemic studies on NIR luminescence properties of Nd complexes with β-diketones especially those of ternary Nd complexes are available [14–16].

As our preliminary work to approach the purpose of ORMOSIL derived planar optical waveguide amplifiers, we investigate a series of Nd organic complexes with various ligands (mainly β-diketones) in order to obtain the preferable dopant. Then the appropriate complex is incorporated into the ORMOSIL film. In this paper, we present some results about NIR luminescent properties of pure Nd organic complexes and ORMOSIL films doped with Nd complexes.

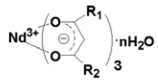
2. Experimental details

2.1. Reagents

All chemicals including AcAc (acetylacetone), TFAA (trifluoroacetylacetone), HFA (hexafluoroacetylacetone), TTA (2-theonyltrifluoroacetone), DBM (dibenzoylmethane), Phen (1,10-phenanthroline), TPPO (triphenylphosphine oxide), Py (pyridine), VTES (vinyltriethoxysilane), and Nd_2O_3 (neodymium oxide) were reagent grade and used as received. $NdCl_3 \cdot 6H_2O$ was obtained through dissolving Nd_2O_3 in the hydrochloric acid solution (1:1) and subsequently removing the solvent carefully.

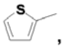
2.2. Synthesis of Nd organic complexes

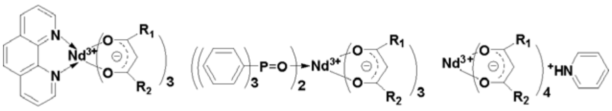
The investigated Nd organic complexes are subdivided into two categories (1) hydrated binary Nd complexes with β-diketone: $Nd(AcAc)_3 \cdot 2H_2O$, $Nd(TFAA)_3 \cdot 2H_2O$, $Nd(HFA)_3 \cdot 2H_2O$, and $Nd(DBM)_3 \cdot H_2O$, and (2) ternary Nd complexes including (i) tris(β-diketone) chelate with the adduct (Phen or TPPO): $Nd(AcAc)_3Phen$, $Nd(TFAA)_3Phen$, $Nd(HFA)_3Phen$, $Nd(DBM)_3Phen$, $Nd(HFA)_3(TPPO)_2$ and $Nd(TTA)_3(TPPO)_2$, and (ii) tetrakis(β-diketone) chelate with a pyridinium cation HPy^+ that does not act as a ligand but a counterpart of the ion pair: $Nd(AcAc)_4HPy$ and $Nd(TTA)_4HPy$. Their chemical structures are depicted in Fig. 1. They were synthesized by employing the methods of Melby and Bauer et al. with a slight modification, using $NdCl_3 \cdot 6H_2O$ as the reactant [30,31]. All of them were recrystallized in ethanol and dried in vacuo for a prolonged period of time at the temperature below their decomposition temperatures. The chemical structures of all investigated complexes have been identified from elemental analysis results and Fourier transform infrared spectra. Noticeably, $Nd(DBM)_3 \cdot H_2O$ bears only one water molecule due to steric effect of DBM's large substituent phenyl [32–34].



(a) Hydrated binary Nd complexes $Nd(\beta\text{-diketone})_3 \cdot nH_2O$ (n=1~2)

AcAc: $R_1=R_2=CH_3$; TFAA: $R_1=CH_3$, $R_2=CF_3$; HFA: $R_1=R_2=CF_3$;

DBM: $R_1=R_2=C_6H_5$; TTA: $R_1=$ , $R_2=CF_3$



$Nd(\beta\text{-diketone})_3Phen$ $Nd(\beta\text{-diketone})_3(TPPO)_2$ $Nd(\beta\text{-diketone})_4HPy$

(b) Ternary Nd complexes

Fig. 1. Chemical structures of Nd organic complexes.

2.3. Preparation of ORMOSIL films

The initial VTES-derived sol was prepared by a multistep sol–gel route involved with acid-catalyzed hydrolysis (pH~2) and basic-catalyzed condensation (pH~5–6) of VTES precursor at room temperature. The initial molar ratio of VTES/ethanol/water was 1:1.5:3. After VTES precursor was hydrolyzed with HCl as the acid catalyzer for 1 h, a small amount of amine-modified silane *N*-(3-(triethoxysily)-propyl)-ethylenediamine was added into the solution as the basic catalyzer, followed by stirring for 30 min. The Nd complex was dissolved into another equal amount of ethanol with an appropriate amount of DMF (dimethylformamide) to promote the dissolution and subsequently added into the sol. The Nd doping concentration was 5 mol% relative to Si. Thereafter, the mixed sol solution was kept in a sealed flask aging for one week at room temperature. Then spin coating on glass slides gave visually transparent VTES-derived ORMOSIL films. Deposited films were allowed to dry at room temperature for at least 1 week before densified further at 50 °C in vacuo to remove the residual water, ethanol, and DMF. Relatively thick multi-layer films (over 10 μm) were obtained for spectroscopic characterization to ensure that the intensity of the luminescence signal was strong enough to detect without an aid of the lock-in mode technique. It should be mentioned that VTES-derived ORMOSIL was chose as the host matrix because of its lower optical loss at *ca*. 1330 nm according to our preliminary study.

2.4. Spectroscopic measurements

NIR photoluminescence spectra were determined at room temperature by using a spectrometer equipped with a monochromatic (Spex 1269, SPEX industries inc. USA) and a liquid-nitrogen-cooled Ge detector (EO-817L, Yellow River systems inc. USA), together with a Model 171 Ar^+ laser (Spectra-Physics USA) as the excitation source. The integral time was aptly selected to be 0.8 s. The absorption spectra were measured on a Perkin Elmer Lambda 20 spectrometer at room temperature at a spectral resolution of 1 nm.

3. Results and discussion

3.1. Luminescence of pure Nd organic complexes

Photoluminescence from bulky Nd organic complex powder was obtained at room temperature using 488 nm line light from an Ar^+ laser as the excitation light. The investigated samples did not adopt the solution but the bulky powder in order to avoid the partial dissociation of the complexes [15,35] and the additional coordination of the solvents, which might take place in the solution, and to exclude the quenching effect of the solvents. A sequence of photoluminescence spectra are presented in Fig. 2(a) and (b). Three infrared emission lines are assigned to Nd^{3+} ion's f–f transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (~900 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (~1060 nm), and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (~1330 nm), respectively. The relative intensities of the peaks at ~900 nm are relatively low in comparison to those that other references have reported [2,3], which may be attributed to the factors such as the solid form adopted for all investigated samples and the sensitivity at ~900 nm of the Ge detector used. The 488 nm excitation light is beyond the absorption band of ligands but just in the absorption tail of Nd^{3+} ion's absorption transition $^4I_{9/2} \rightarrow {}^2K_{13/2}$, $^2G_{9/2}$, and is absorbed intrinsically by Nd^{3+} ion. Consequently, the direct excitation is concerned to occur excluding that Nd^{3+} ions are indirectly excited via ligands. Nonradiative decay from the level $^2G_{9/2}$ or $^2K_{13/2}$ populated upon excitation at 488 nm to the level $^4F_{3/2}$ originates NIR characteristic luminescence (see the schematic energy-level diagram of Nd^{3+} ion in Fig. 2(c)). The photoluminescence properties such as the normalized integral intensity, the peak position and the effective line width for three transitions of all investigated complexes are summarized in Table 1, together with the intensity ratio η of the individual emission transition relative to the total intensity of three emission transitions $^4F_{3/2} \rightarrow {}^4I_J$ (J=13/2, 11/2 and 9/2, except for the transition $^4F_{3/2} \rightarrow {}^4I_{15/2}$). The complexes derived from TTA have better luminescent properties than their analogs from other β-diketones, with the complex $Nd(TTA)_3(TPPO)_2$ as the best one among all investigated complexes. The variation of the normalized integral intensity or the intensity ratio of a specified transition upon the change of organic ligands is impressively distinct, but not following a very regular pattern for all complexes. That is because the transition probabilities inside the 4f shell of Nd^{3+} ion are directly and significantly affected by the factors such as the symmetry and intensity of the ligand field around Nd^{3+} ion especially for the complex with mixed ligands [32].

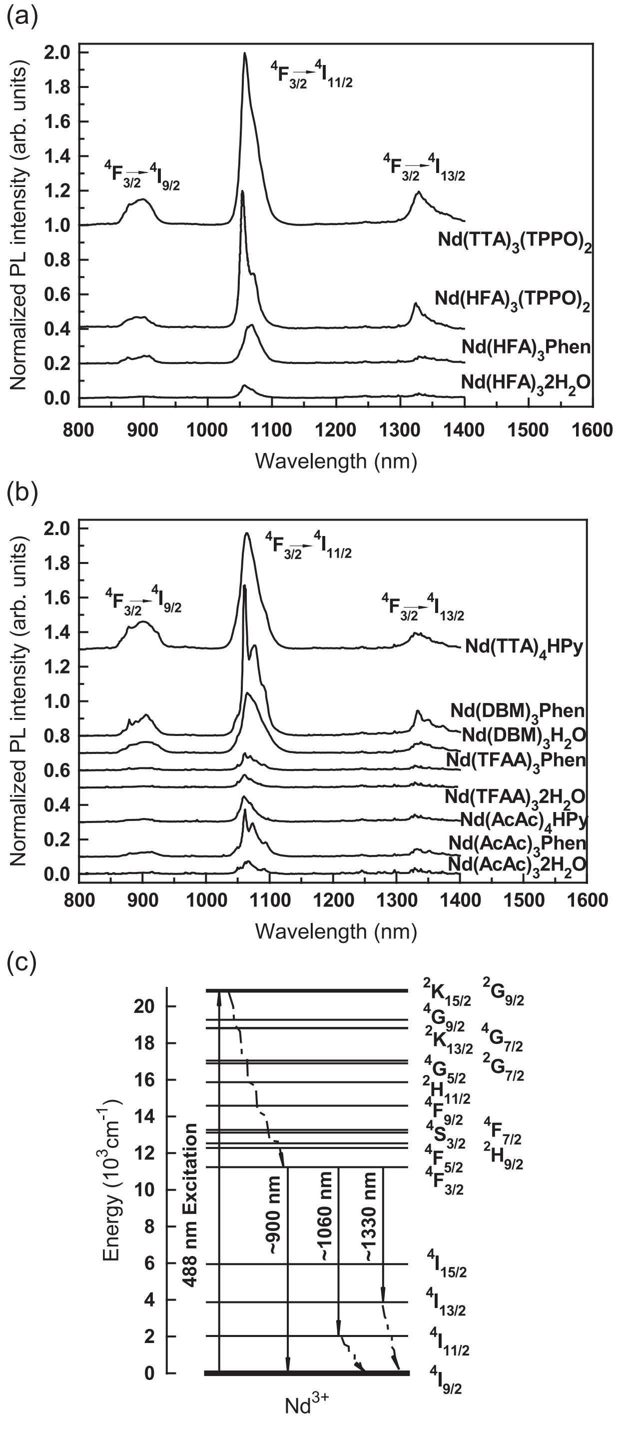


Fig. 2. Normalized photoluminescence spectra of Nd complexes in bulky powder excited at 488 nm (a) and (b), and the schematic energy level diagram for Nd^{3+} ion (c).

Furthermore, the presence of different species, stereoisomers and monomer-dimer mixtures, for lanthanide organic complexes makes the luminescent characteristics complicated. Because of the presence of isomers, the local electric fields around the Nd^{3+} sites vary considerably and subsequently large Stark splitting of the energy levels of Nd^{3+} ions occurs due to the site-to-site variation [36]. That

Table 1
Photoluminescence properties of all investigated Nd complexes in bulky powder

Transitions	N.I.I	*P*	$\Delta\lambda$	η	N.I.I	*P*	$\Delta\lambda$	η	N.I.I	*P*	$\Delta\lambda$	η
	$Nd(AcAc)_3 \cdot 2H_2O$				$Nd(AcAc)_3Phen$				$Nd(AcAc)_4HPy$			
$^4F_{3/2}\rightarrow^4I_{9/2}$	1.5	915.4	33.3		4.2	915.4	44.2		2.3	901.5	40.6	
$^4F_{3/2}\rightarrow^4I_{11/2}$	7.5	1065.6	29.0	0.63	24.6	1061.4	25.5	0.73	13.8	1059.8	26.4	0.71
$^4F_{3/2}\rightarrow^4I_{13/2}$	2.9	1328.6	24.1	0.24	4.9	1332.1	35.4	0.15	3.4	1328.6	27.8	0.17
	$Nd(TFAA)_3 \cdot 2H_2O$				$Nd(TFAA)_3Phen$							
$^4F_{3/2}\rightarrow^4I_{9/2}$	1.1	915.6	33.3		2.1	915.2	45.1					
$^4F_{3/2}\rightarrow^4I_{11/2}$	6.4	1060.7	25.1	0.67	10.1	1061.5	28.6	0.69				
$^4F_{3/2}\rightarrow^4I_{13/2}$	2.1	1328.7	23.4	0.22	2.4	1328.6	29.2	0.16				
	$Nd(HFA)_3 \cdot 2H_2O$				$Nd(HFA)_3Phen$							
$^4F_{3/2}\rightarrow^4I_{9/2}$	0.9	901.1	38.1		6.3	900.8	40.7					
$^4F_{3/2}\rightarrow^4I_{11/2}$	6.5	1057.2	25.1	0.69	24.4	1069.4	31.0	0.68				
$^4F_{3/2}\rightarrow^4I_{13/2}$	2.0	1328.4	24.9	0.21	5.3	1338.1	41.3	0.15				
					$Nd(HFA)_3(TPPO)_2$							
$^4F_{3/2}\rightarrow^4I_{9/2}$					8.4	901.0	40.1					
$^4F_{3/2}\rightarrow^4I_{11/2}$					55.0	1053.6	19.4	0.71				
$^4F_{3/2}\rightarrow^4I_{13/2}$					14.4	1324.1	28.0	0.18				
					$Nd(TTA)_3(TPPO)_2$				$Nd(TTA)_4HPy$			
$^4F_{3/2}\rightarrow^4I_{9/2}$					22.1	899.6	43.4		26.5	900.6	49.3	
$^4F_{3/2}\rightarrow^4I_{11/2}$					100	1057.6	28.2	0.69	83.9	1064.4	35.2	0.68
$^4F_{3/2}\rightarrow^4I_{13/2}$					23.0	1328.7	37.4	0.16	13.2	1328.3	42.2	0.11
	$Nd(DBM)_3 \cdot H_2O$				$Nd(DBM)_3Phen$							
$^4F_{3/2}\rightarrow^4I_{9/2}$	11.7	905.0	51.9		16.2	905.0	38.1					
$^4F_{3/2}\rightarrow^4I_{11/2}$	47.1	1065.1	38.1	0.70	77.6	1061.2	25.0	0.72				
$^4F_{3/2}\rightarrow^4I_{13/2}$	8.1	1338.5	39.2	0.12	13.6	1334	29.6	0.126				

N.I.I., normalized integral intensity; *P, peak (nm); The effective width* $\Delta\lambda$ *(nm) is defined as* $\Delta\lambda=\int I(\lambda)d\lambda/I_P$*, where* I_P *is the intensity of the peak;* η*, relative intensity.*

is, the larger is the number of isomers and the larger is the number of Stark components for the energy levels. This is the origin of the inhomogeneous broadening and consequently the variation of the effective line width. As shown in Table 1, the effective line widths for all complexes except $Nd(HFA)_3(TPPO)_2$ exceed 25 nm for the peak at ~1060 and 24 nm for the peak at ~1330 nm. Such a wide spectrum provides the possibility to obtain an optical amplifier with a large gain-bandwidth when the complexes are incorporated into a suitable matrix.

3.1.1. *Effect of synergetic coordination agents on the luminescent properties of Nd organic complexes*

As we know, NIR luminescence of Nd^{3+} ions is to occur from the $^4F_{3/2}$ level to the ^4I_J multiplet levels. The energy gap between the $^4F_{3/2}$ level and its next level $^4I_{15/2}$ is about 5100~5600 cm^{-1} [37], matching well the second vibration modes of oscillating groups OH (6900 cm^{-1}) and CH (smaller, 5900 cm^{-1}) which can contribute the efficient nonradiative deactivation of $^4F_{3/2}$ level. In addition, the quenching process is strongly distance R-dependent ($1/R^6$). The small molecular H_2O can penetrate into the inner coordination shell of Nd^{3+} ion to satisfy the large coordination number of Nd^{3+} ion during the hydrous synthesis process especially for binary Nd complexes. It is deduced clearly from the molecular structures of hydrated binary Nd complexes and ternary Nd complexes that carbonic hydrogens of the β-diketone moieties and other ligands (Phen and TPPO) are relatively far away from Nd^{3+} ion in comparison to those hydrogens of the penetratingly coordinating H_2O [38–42]. Thus, CH groups will not significantly contribute the luminescence quenching due to two factors, their smaller vibration energy and the larger distance from Nd^{3+} ion [16]. Comparatively, OH groups from the coordinating H_2O are principal contributors to depress the luminescence of the complexes.

Hence, the introduction of the adduct Phen or TPPO or the fourth β-diketone can enhance the luminescence intensity of the complexes in that Phen or TPPO or the fourth β-diketone in the ternary complexes saturates the coordination of Nd^{3+} ions avoiding simultaneously the coordination of water molecules. As shown in Table 1 and Fig. 2, the ternary Nd complex with Phen/TPPO or with the fourth β-diketone has much larger luminescence intensity than the corresponding hydrated binary Nd complex, e.g., the overall luminescence integral intensity for $Nd(HFA)_3$-Phen is about three times larger than that for $Nd(HFA)_3 \cdot 2H_2O$.

As shown in Table 1, the intensity ratios of the emission transition $^4F_{3/2}\rightarrow^4I_{11/2}$ for most complexes $(Nd(AcAc)_3 \cdot$

$2H_2O$ as an exception) are nearly invariable. Nevertheless, it is noticeable that the intensity ratio of the transition $^4F_{3/2}\rightarrow{}^4I_{13/2}$ for the hydrated binary Nd complex with AcAc, TFAA, or HFA is larger than that for the ternary Nd complex accordingly, as the luminescence at ~1330 nm is favored preferentially in this case. This phenomenon can also be speculated on the presence of water for hydrated binary complexes. Since the lower level $^4I_{13/2}$ for the transition $^4F_{3/2}\rightarrow{}^4I_{13/2}$ lies only about 4000 cm^{-1} higher than the ground level $^4I_{9/2}$ (see Fig. 2(c)), $^4I_{13/2}$ deactivates to $^4I_{9/2}$ through coupling with the vibrational state of OH oscillators relatively easily upon comparison to CH oscillators. Then, the transition possibility for $^4F_{3/2}\rightarrow{}^4I_{13/2}$ is enhanced since the $^4I_{13/2}$ level can be depopulated quickly for hydrated binary complexes. The less difference of the intensity ratio of the transition $^4F_{3/2}\rightarrow{}^4I_{13/2}$ between both of the complexes from DBM should support this explanation since $Nd(DBM)_3\cdot H_2O$ bears only one water molecule.

The ternary complexes with TPPO seem to perform better than their analogs with Phen. This may tentatively be attributed to the stronger coordinating ability of oxygen atom and the three-dimensionally steric structure for TPPO (when TPPO is compared correspondingly to Phen that has the modest coordinating ability of nitrogen atom and the planar structure), both of which can make TPPO prevent water molecules from coordinating Nd^{3+} ion more efficiently.

3.1.2. Effect of different substitution groups for β-diketones on the luminescent properties of Nd organic complexes

Since the first overtone of CF vibration (~1200 cm^{-1}) is less than that of CH vibration, which renders the deactivation of the excited level $^4F_{3/2}$ less efficient, one of the possible strategies to improve the luminescent properties of Nd β-diketonates is involved with the fluorination of β-diketones, namely CF_3 group substituting CH_3 group here. Unfortunately, it seems to be not effective to enhance the luminescent properties for the investigated complexes, whilst a slight descend in the luminescence intensity for some complexes from fluorinated ligands happens unexpectedly in contrast to those from unfluorinated ligands. This can be explained below.

As to the hydrated binary complexes Nd–AcAc/TFAA/HFA–H_2O, the fluorination of β-diketones can hardly improve the luminescence intensity due to the effective quenching of the coordinating H_2O (see Table 1). Thus, an attempt to enhance the luminescent properties for the hydrated binary complexes via fluorinating the β-diketone seems useless.

As to the ternary complexes Nd–AcAc/TFAA/HFA–Phen, similar results can be explained as that the weaker coordinating ability of fluorinated β-diketones (TFAA and HFA) due to their strong electron-withdrawing trifluoromethyl substituent results in a competition of the coordination sites between fluorinated β-diketones and water molecules [15]. There may be still a trace of the coordinating water molecules in the ternary complexes with fluorinated β-diketones. According to element analysis results, a larger deviation for the ternary complexes with fluorinated β-diketones may demonstrate this (e.g., Anal. Calcd. for $Nd(TFAA)_3Phen$: C 41.38; H 2.58; N 3.58; Nd 18.4. Found: C 39.94; H 2.97; N 3.82; Nd 17.8.). The trace of the coordinating water molecules may be the cause of the eliminating differences in luminescence intensities between the complex with fluorinated β-diketone and the complex with unfluorinated one owing to OH's strong quenching ability (see Table 1). Therefore, as the OH group is attached to Nd complexes, the substitution of CH by CF has no active effect on the luminescence intensity of the complex.

Interestingly, all Nd complexes with TTA or DBM have better performance than the analogs with other β-diketones, which is presumably correlated with the substituent thienyl or phenyl. An increase in the length of the conjugated system by attaching heterocyclic or aromatic substituents results in the enhancement of the enolate ring resonance and thereby the increase of the ligand's coordinating ability and the complex's stabilization.

As to the effective line width which is mainly dependent on the nature of the chelating ligands, the comparison can carry through only between $Nd(AcAc)_4HPy$ and $Nd(TTA)_4HPy$ because only they have eight coordinating oxygen atoms from four uniform β-diketones around Nd^{3+} ion while others have different types of chelating atoms together (e.g., oxygen atoms and nitrogen atoms) or have same chelating atoms from different ligand sources (e.g., oxygen atoms from β-diketone or H_2O or TPPO). In addition, in the structure of $Nd(AcAc)_4HPy$ or $Nd(TTA)_4HPy$, the Nd^{3+} ion is dodecahedrally coordinated by eight oxygen atoms. The spectroscopic results show that the effective line widths of three transitions of Nd^{3+} ion for $Nd(TTA)_4HPy$ are larger than those of the corresponding transitions for $Nd(AcAc)_4HPy$ (Table 1). The reason is ascribed to asymmetric substituents thienyl group and trifluoromethyl group for TTA. The asymmetric substitution leads to the difference in the electron density distribution of two oxygen atoms in per TTA moiety of $Nd(TTA)_4HPy$ and simultaneity the difference in the length of two Nd–O bonds, which results in the enhancement of the ligand field's asymmetry and consequently the increase of the possibility for Stark splitting of Nd^{3+} ion's energy levels [14]. Meanwhile, the relatively large number of different isomers due to the asymmetric β-diketone is another factor because they diversify Nd^{3+} ions' sites in the complexes [32,37,43–47].

3.2. Spectroscopic properties of VTES-derived ORMOSIL film doped with Nd complexes

On basis of the above results, the complex $Nd(TTA)_3(TPPO)_2$ was chose as the active dopant to be incorporated into VTES-derived ORMOSIL film. Fig. 3 shows the normalized absorption spectra of VTES-derived ORMOSIL films doped with $Nd(TTA)_3(TPPO)_2$ (5 mol% related to Si) and $NdCl_3\cdot 6H_2O$ (5 mol% related to Si), respectively. The normalized absorption spectra of the two pure complexes dissolved in DMF (0.01 M) are also shown in Fig. 3 for comparison. The continuously decreasing background in the range up to 650 nm for VTES-derived films is attributed to the scattering from the glass substrate–film interface and the absorption tail of the VTES-derived matrix jointly. As is well known, when Nd organic complexes are incorporated into VTES-derived ORMOSIL, it is considered that they are entrapped into the pores stuffed with vinyl groups since ORMOSIL is an amorphous and porous solid.

Fig. 3(a) shows negligible differences in the feature of absorption spectra for $Nd(TTA)_3(TPPO)_2$ in VTES-derived film with respect to that in DMF solution. The absorption band at 560~620 nm corresponding to ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ transitions is known as the hypersensitive transitions of Nd^{3+} ion. This band is peculiarly sensitive to the change of the coordination structure around Nd^{3+} ion and its absorption oscillator strength will be enhanced as the symmetry of the ligand field reduces with the complicated surroundings [48,49]. Nevertheless, in Fig. 3(a), the feature of this band exhibits little variation, indicating that the ligands indeed shield effectively Nd^{3+} ions from the chemical microenvironment and giving an evidence of the lack of strong chemical interaction between the host matrix and the complexes when they are embedded into the matrix.

When it comes to the comparison of the absorption spectra for $NdCl_3 \cdot 6H_2O$ in VTES-derived film and in DMF solution (see Fig. 3(b)), a slight variation in the feature of the absorption spectra especially in that of the hypersensitive absorption band is ascribed to the different local environment around Nd^{3+} ions for different host matrices. However, it should be noted that the absorption intensity of the so-called hypersensitive transitions for $Nd(TTA)_3(TPPO)_2$ is much larger than that for $NdCl_3 \cdot 6H_2O$ accordingly, which also correlates with the ligands.

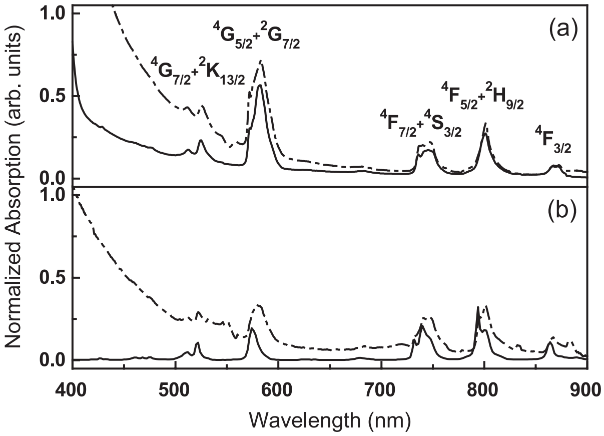


Fig. 3. (a) Normalized absorption spectra of VTES-derived films doped with $Nd(TTA)_3(TPPO)_2$ (- · -) and the complex dissolved in DMF (—); (b) normalized absorption spectra of VTES-derived films doped with $NdCl_3 \cdot 6H_2O$ (- · -) and the complex in DMF (—). The absorption bands are attributed to the transitions from the ground level ${}^4I_{9/2}$ to the corresponding levels ${}^{2s+1}L_J$.

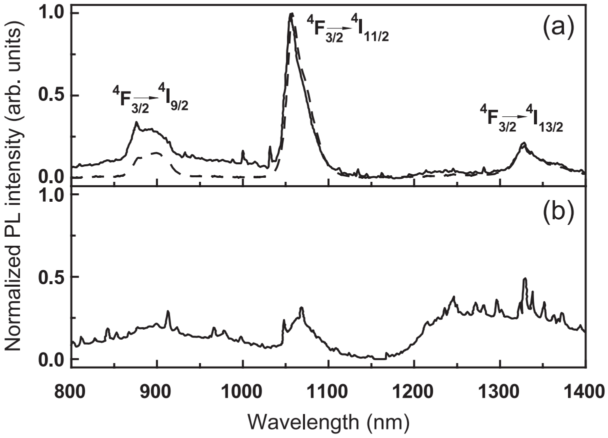


Fig. 4. Normalized photoluminescence spectra of VTES-derived film doped with $Nd(TTA)_3(TPPO)_2$ (—) (a) and doped with $NdCl_3 \cdot 6H_2O$ (b) excited at 488 nm. The photoluminescence spectrum of $Nd(TTA)_3(TPPO)_2$ bulky powder is also shown in panel (a) (- - -) for comparison.

Fig. 4 gives the normalized luminescence spectra of VTES-derived films doped with $Nd(TTA)_3(TPPO)_2$ and $NdCl_3 \cdot 6H_2O$, respectively, with that of bulky $Nd(TTA)_3(TPPO)_2$ powder for comparison. The integral luminescence intensity of 1060 nm band is increased by a factor of over 5 upon the presence of organic ligands, indicating the efficient protection of Nd^{3+} ions from the environment by bulky ligands. It is suggested that the quencher moieties like OH groups are removed from first coordination shell and the encapsulating ligands provide no or minimal pathways for nonradiative decay as mentioned above.

On comparing the shape and relative intensity of luminescence spectra in Fig. 4(a), we note that less variation in them occurs, further demonstrating that the ORMOSIL matrix does not modify the local environment of Nd^{3+} ions.

As a result, the encapsulation of Nd^{3+} ions by organic ligands and their shielding Nd^{3+} ions from the host environment improve not only the compatibility of Nd^{3+} ions with the organically modified matrix but also their spectroscopic properties. Since it is difficult to estimate the actual ion concentration in the as-doped VTES-derived film directly, the ion concentration in an analogue bulk sample is estimated to be approximately 4.3×10^{20} ions/cm^3.

4. Conclusions

The introduction of synergetic coordination agents into Nd complexes improves NIR photoluminescence intensity of Nd^{3+} ion since the agents can exclude water molecules from the inner coordination shell of Nd^{3+} ions. The intensity ratio of the transition ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ at ca. 1330 nm for the hydrated binary Nd complex is larger than that for the corresponding ternary Nd complex due to the presence of water molecules, although the overall photoluminescence intensity of the former is much smaller than that of the latter. VTES-derived film doped with the complex $Nd(TTA)_3(TPPO)_2$ exhibits similar NIR luminescent properties with the complex in bulky powder and better luminescent properties than the film doped with Nd^{3+} ion only. The host matrix has feeble effect on the spectroscopic properties of the doped Nd organic complex as a result of organic ligands shielding Nd^{3+} ions effectively from the environment.

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References

[1] Y. Sorek, R. Reisfeld, Appl. Phys. Lett. 63 (1993) 3256.
[2] Y. Sorek, R. Reisfeld, Appl. Phys. Lett. 66 (1995) 1169.
[3] X. Orignac, D. Barbier, X.M. Du, R.M. Almeida, Appl. Phys. Lett. 69 (1996) 895.
[4] P. Innocenzi, G. Brusatin, M. Guglielmi, A. Martucci, G. Battaglin, S. Pelli, G. Righini, J. Non-Cryst. Solids 220 (1997) 202.
[5] G.R. Atkins, R.M. Krolikowska, A. Samoc, J. Non-Cryst. Solids 256 (2000) 210.
[6] A.L. Douglas, MRS Bull. (2001) 364.
[7] M. Casalboni, F. Belli, M. Cirillo, F. De Matteis, P. Prosposito, R. Russo, R. Pizzoferrato, J. Sol-Gel Sci. Technol. 26 (2003) 937.
[8] A. Heller, J. Am. Chem. Soc. 88 (1966) 106.
[9] Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.H. Kim, N. Nakashima, T. Yamanaka, S. Yanagida, Chem. Phys. Lett. 260 (1996) 173.
[10] Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, S. Yanagida, J.H. Kim, N. Nakashima, T. Yamanaka, J. Phys. Chem. 100 (1996) 10201.
[11] Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J.H. Kim, N. Nakashima, T. Yamanaka, Chem. Phys. Lett. 248 (1996) 8.
[12] M.H.V. Werts, J.W. Hofstraat, F.A.J. Geurts, J.W. Verhoeven, Chem. Phys. Lett. 276 (1997) 196.
[13] F.J. Steemers, W. Verboom, J.W. Hofstraat, F.A.J. Geurts, D.N. Reinhoudt, Tetrahedron Lett. 39 (1998) 7583.
[14] M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, N. Nakashima, T. Yamanaka, S. Yanagida, J. Lumin. 79 (1998) 29.
[15] Y. Hasegawa, M. Iwamuro, K. Murakoshi, Y. Wada, R. Arakawa, T. Yamanaka, N. Nakashima, S. Yanagida, Bull. Chem. Soc. Jpn. 71 (1998) 2573.
[16] S. Yanagida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yamanaka, Coord. Chem. Rev. 171 (1998) 461.
[17] M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura, S. Yanagida, Chem. Lett. 35 (1999) 539.
[18] M. Iwamuro, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, Phys. Chem. Chem. Phys. 2 (2000) 2291.
[19] R.T. Chen, M. Lee, S. Natarajan, C. Lin, Z.Z. Ho, D. Robinson, IEEE Photonics Technol. Lett. 5 (1993) 1328.
[20] S. Lin, R.J. Feuerstein, R. Micklson, J. Appl. Phys. 79 (1996) 2868.
[21] D. An, Z. Yue, R.T. Chen, Appl. Phys. Lett. 72 (1998) 2806.
[22] G.V. Karve, B. Bihari, R.T. Chen, Proc. SPIE 3950 (2000) 186.
[23] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, S. Yanagida, Appl. Phys. Lett. 74 (1999) 3245.
[24] Y. Hasegawa, K. Sogabe, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, Chem. Lett. 35 (1999) 35.
[25] L.H. Slooff, A. Polman, S.I. Klink, G.A. Hebbink, L. Grave, F.C.J.M. van Veggel, D.N. Reinhoudt, J.W. Hofstraat, Opt. Mater. 14 (2000) 101.
[26] S.I. Klink, G.A. Hebbink, L. Grave, F.C.J.M. van Veggel, D.N. Reinhoudt, L.H. Slooff, A. Polman, J.W. Hofstraat, J. Appl. Phys. 86 (1999) 1181.
[27] K. Kuriki, S. Nishihara, Y. Nishizawa, A. Tagaya, Y. Okamoto, Y. Koike, Electron. Lett. 37 (2001) 415.
[28] K. Kuriki, T. Kobayashi, N. Imai, T. Tamura, S. Nishihara, A. Tagaya, Y. Koike, Y. Okamoto, IEEE Photonics Technol. Lett. 12 (2000) 989.
[29] L.H. Slooff, A. van Blaaderen, A. Polman, G.A. Hebbink, S.I. Klink, F.C.J.M. van Veggl, D.N. Reinhoudt, J.W. Hofstraat, J. Appl. Phys. 91 (2002) 3955.
[30] L.R. Mebly, N.J. Rose, E. Abramson, J.C. Caris, J. Am. Chem. Soc. 86 (1964) 5117.
[31] H. Bauer, J. Blanc, L. Ross, J. Am. Chem. Soc. 86 (1964) 5125.
[32] C.K. Jørgensen, in: K.A. Gschneidner Jr., L.R. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 3, North-Holland Publishing Company, Amsterdam, 1979, p. 266.
[33] F.A. Cotton, P. Legzdins, Inorg. Chem. 7 (1968) 1777.
[34] K.J. Eisentraut, R.E. Sievers, J. Am. Chem. Soc. 87 (1965) 5254.
[35] M.L. Bhaumik, P.C. Fletcher, L.J. Nugent, S.M. Lee, S. Higa, C.L. Telk, M. Weinberg, J. Phys.Chem. 68 (1964) 1490.
[36] N. Filipescu, K. Moorjani, N. Mcavoy, S. Bjorklund, C.R. Hurt, J. Zumoff, Appl. Spectrosc. 22 (1968) 513.
[37] R. Reisfeld, C.K. Jørgensen, Laser and Excited state of Rare Earths, Springer-Verlag, Berlin, 1977.
[38] W.H. Watson, R.J. Williams, N.R. Stemple, J. Inorg. Nucl. Chem. 34 (1972) 501.
[39] T. Phillips II, D.E. Sands, W.F. Wanger, Inorg. Chem. 7 (1968) 2295.
[40] J.G. White, Inorg. Chim. Acta 16 (1976) 159.
[41] J.A. Cunningham, D.E. Sands, W.F. Wanger, M.F. Richardson, Inorg. Chem. 8 (1969) 22.
[42] M. Nakamura, R. Nakamura, K. Nagai, M. Shimui, S. Tomoda, Y. Takeuchi, A. Ouchi, Bull. Chem. Soc. Jpn. 59 (1986) 332.
[43] R.A. Lalancette, M. Cefola, W.C. Hamilton, S.J. La Placa, Inorg. Chem. 6 (1967) 2127.
[44] M.J. Beskett, F.A. Cotton, P. Legzdins, S.J. Lippard, Inorg. Chem. 7 (1968) 1770.
[45] J.H. Bcrxs, M.D. Daxford, Inorg. Chem. 8 (1969) 1780.
[46] S.J. Lippard, J. Am. Chem. Soc. 88 (1966) 4300.
[47] S.J. Lippard, F.A. Cotton, P. Legzdins, J. Am. Chem. Soc. 88 (1966) 5930.
[48] C.K. Jørgensen, B.R. Judd, Mol. Phys. 8 (1964) 281.
[49] B.R. Judd, J. Chem. Phys. 44 (1966) 839.