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1.53 μm photoluminescence from ORMOSIL films doped with erbium complexes

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Abstract

Vinyltriethoxysilane (VTES)-derived ORMOSIL films directly doped with various erbium organic complexes were prepared through a multistep sol–gel process, among which VTES-derived film doped with erbium tris(hexafluoroacetylacetonate)bis(triphenylphosphine oxide) ($Er(HFA)_3(TPPO)_2$) exhibited the maximum photoluminescence intensity at 1.53 μm as the erbium doping concentration was 5 mol%. Moreover, the complex erbium tris(8-hydroxyquinolate) (ErQ_3) was in situ synthesized successfully in the VTES-derived film as expected and the film also exhibited comparatively intense 1.53 μm luminescence.

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1. Introduction

Trivalent erbium ion has attracted intense attention owing to its unique intra-4f transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ at 1.53 μm wavelength, which corresponds to the minimum-loss transmission window of silica fiber in the optical communication network [1]. Hereon, great effort is devoted to the realization of an erbium-activated planar optical waveguide amplifier in the photonic integrated circuit, namely an erbium-doped waveguide amplifier (EDWA) [2–16]. Additionally, through the sol–gel process erbium organic complexes are proposed to incorporate into inorgani-

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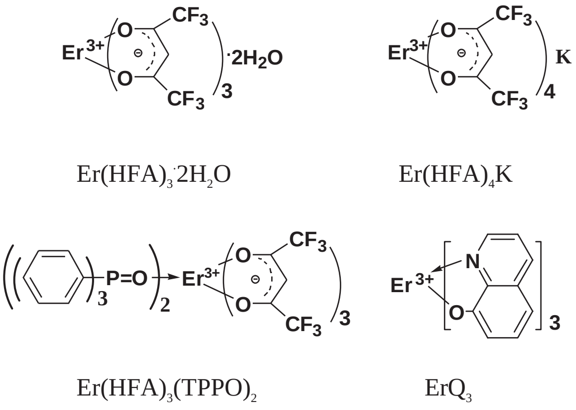
c–organic hybrid materials or organically modified silicates (ORMOSILs) for potential applications in planar optical amplifiers, since the soft chemistry process offers several advantages for the fabrication of planar optical waveguides that are flexible, inexpensive and easy to obtain over 1 μm thickness crack-free film via the single coating process [16–18]. Here, we present preliminary results about the luminescence properties of ORMOSIL films directly doped with various erbium organic complexes and in situ doped with erbium complex with 8-hydroxyquinoline, fabricated through the multistep sol–gel process.



$Er(HFA)_3 \cdot 2H_2O$ $Er(HFA)_4K$

$Er(HFA)_3(TPPO)_2$ ErQ_3

Fig. 1. Chemical structures of erbium organic complexes.

2. Experimental details

2.1. Synthesis of erbium complexes

All chemicals including hexafluoroacetylacetone (HFA), triphenylphosphine oxide (TPPO), 8-hydroxyquinoline (HQ), tetraethoxysilane (TEOS), vinyltriethoxysilane (VTES), methyltriethoxysilane (MTES) and erbium oxide (Er_2O_3) were reagent grade and used as received. $ErCl_3 \cdot 6H_2O$ was obtained from Er_2O_3 by dissolving Er_2O_3 in hydrochloric acid. Erbium organic complexes including dihydrate erbium tris (hexafluoroacetylacetonato) ($Er(HFA)_3 \cdot 2H_2O$), potassium tetrakis(hexafluoroacetylacetonato) erbate ($Er(HFA)_4K$), erbium tris(hexafluoroacetylacetonate)bis(triphenylphosphine oxide) ($Er(HFA)_3(TPPO)_2$) and erbium tris(8-hydroxyquinolate) (ErQ_3) were synthesized according to the method of Melby et al. [19]. Their chemical structures are depicted in Fig. 1, conformed by elemental analysis and FTIR in advance.

2.2. Preparation of undoped bulk matrix materials

TEOS-derived bulk silica gel glass was prepared by a simple one-step sol–gel process (pH$\approx$2). METS- and VTES-derived bulk ORMOSILs were prepared as follows. The initial sol was prepared by a multistep sol–gel route involving acid-catalyzed hydrolysis and base-catalyzed condensation of VTES or METS precursor at room temperature. The molar ratio of VTES or METS:ethanol:water was 1:3:3. After hydrolysis with HCl as acid catalyst (pH$\approx$2) for 1 h, a small amount of amine-modified silane *N*-(3-(triethoxysily)-propyl)-ethylenediamine was added as basic catalyst (pH = 5–6), followed by stirring for 30 min. The obtained sol was sealed in a Teflon beaker and kept in an oven at 40 °C for drying and aging for one month. MTES- and VTES-derived bulk ORMOSILs were double-facedly polished by hand.

2.3. Preparation of VTES-derived ORMOSIL films doped with erbium complex

The initial sol was prepared as the above-mentioned method for bulk ORMOSILs. For the directly doping process, erbium organic complexes were dissolved into an appropriate amount of dimethylformamide (DMF) and subsequently added into the sol. As to the in situ doping process with the complex ErQ_3, $ErCl_3 \cdot 6H_2O$ and 8-hydroxyquinoline (1:3) were mixed in DMF for several minutes and added into the sol. Thereafter the mixed solution was kept in a sealed flask aging for one week at room temperature. Spin coating repetitiously on glass slides for ultraviolet–visible–near-infrared (UV–Vis–NIR) absorption and photoluminescence (PL) measurements or Si wafers for FTIR measurement gives visually transparent films. Deposited films were allowed to dry at room temperature for one week before being densified at 50 °C in vacuo further to remove the solvents. For PL measurement, multilayer films with more than 10 μm thickness were obtained on glass slides.

2.4. Spectroscopic measurements

UV–Vis–NIR absorption spectra were measured on a JASCO V570 spectrometer at a spectral resolution of 1 nm. FTIR measurements were performed on a Nicolet AVTAR360 FTIR. Near-infrared (NIR) PL 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), with a Model 171 Ar^+ laser (Spectra-Physics USA) as the excitation source and the integral time as 0.8 s.

3. Results and discussion

3.1. Selection of matrix for doping erbium complex

Fig. 2 shows Vis–NIR optical loss for three undoped bulk matrix materials including TEOS- MTES- and VTES-derived silicate materials without subtraction of the local background absorption. Assignment of these absorption bands is as follows [20,21]. The absorption band at ca. 1150 nm is attributed to the third C–H vibration. The absorption band around 1400 nm is the second C–H stretch vibration mode coupling with C–H deformation vibration. The absorption band in the range of 1600–1850 nm is the second vibration of C–H moieties in various terminal organic structure units. The absorption band due to the second OH vibration mode is located at around 1420 nm. The absorption band at 1900 nm is also caused by residual molecular water hydrogen-bonded to silanol. The tails of absorption bands 1420 nm of OH and 1620 nm of C–H comprise the absorption band at 1500 nm. In comparison with the 1500 nm band, optical loss of TEOS-derived material is much larger than others, which originates from the intense OH absorption band. This demonstrates that the multistep sol–gel process especially for additional base-catalyzed condensation effectively eliminates residual moieties Si–OH. Furthermore, VTES-derived ORMOSIL exhibits lower optical loss at ca. 1500 nm than MTES-derived ORMOSIL. Heat treatment on VTES-derived ORMOSIL does not seem to decrease the intensity of OH-related absorption bands, which indicates that it is not necessary for VTES-derived ORMOSIL to heat treat at elevated temperature to remove the residual moieties Si–OH.

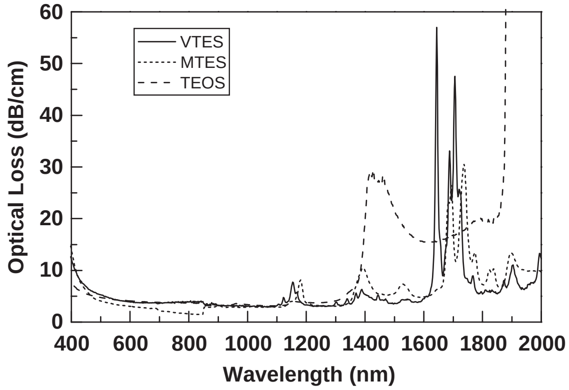


Fig. 2. Optical loss in Vis–NIR spectrum for three undoped bulk matrix materials including TEOS- MTES- and VTES-derived silicate materials.

According to the above-mentioned results, VTES-derived ORMOSIL has the minimum optical loss at ca. 1500 nm and is chosen as the host matrix for doping erbium complex in this work. The vinyl groups bonded to the SiO_2 backbone could increase the solubility of erbium complex in the host matrix.

3.2. NIR PL properties of VTES-derived ORMOSIL films directly doped with various erbium complexes

In order to design erbium complexes with optimal properties as dopants, a good understanding of the basic properties of erbium complexes is necessary. Fig. 3 displays PL spectra of various erbium complexes in bulky powder excited at 488 nm by an Ar^+ laser at room temperature. Direct excitation is considered to occur, decay from the level $^4F_{7/2}$ populated upon excitation at

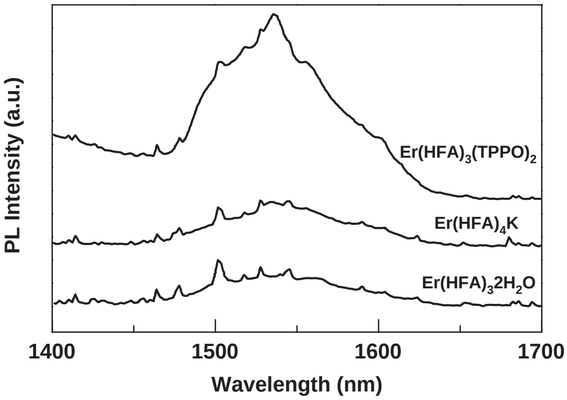


Fig. 3. NIR PL spectra of various erbium complexes in bulky powder excited at 488 nm by an Ar$^+$ laser at room temperature.

488 nm to the level $^4I_{13/2}$ originate luminescence at ca. 1530 nm corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. The full-width at half-maximum (FWHM) values for all investigated erbium complexes are estimated over 78 nm, which is potential for wide bandwidth gain of optical amplification. Water molecules are efficient quenchers for NIR luminescence of the erbium ion as the second overtone of OH vibration bridges well the energy gap between $^4I_{13/2}$ and $^4I_{15/2}$. As a result, the complex $Er(HFA)_3 \cdot 2H_2O$, which has two water molecules, exhibits relatively low luminescence intensity. The introduction of the fourth HFA ligand for $Er(HFA)_4K$ does not apparently favor the increase of the luminescence intensity as shown in Fig. 3, since small water molecules still compete to penetrate into the inner coordination shell of the erbium ion due to the weak coordination ability of HFA during the hydrous synthesis process and there is still a trace of coordinating water according to a slight deviation for the elemental analysis result (not shown here). Meanwhile, the synergistic coordination of an adduct TPPO for $Er(HFA)_3(TPPO)_2$ can remarkably enhance the luminescence intensity in that TPPO saturates the coordination of erbium ion simultaneously avoiding the inner coordination of water molecules by virtue of its large and steric structure.

When erbium organic complexes are directly incorporated into the VTES-derived ORMOSIL matrix, the organic ligands are expected to shield erbium ions from luminescence-quenching impurities in matrix and isolate erbium ions sterically from each other in the SiO_2 backbone. Moreover, as is well known it is considered that they are entrapped in the pores stuffed with vinyl groups since ORMOSIL is an amorphous porous solid. PL spectra of VTES-derived films doped with various erbium organic complexes are present in Fig. 4 as the doping concentration of the erbium complex for all samples is 5 mol% relative to silicon. The appearance of luminescence spectra is distorted by background noise and matrix absorption due to a relatively low luminescence signal. A similar PL trend with pure solid complexes is observed. The VTES-derived film doped with $Er(HFA)_3(TPPO)_2$ exhibits the largest luminescence intensity, and luminescence from the VTES-derived film doped with $Er(HFA)_4K$ is larger than that from corresponding film doped with $Er(HFA)_3 \cdot 2H_2O$. It should be noted that no luminescence from the VTES-derived film doped with equal amounts of $ErCl_3 \cdot 6H_2O$ has been observed, which indicates that luminescence from erbium ions is completely quenched by the surroundings in the absence of ligands. These results may demonstrate that the coordination ability of ligands is strong enough and ligands shield erbium ions from the environment effectively.

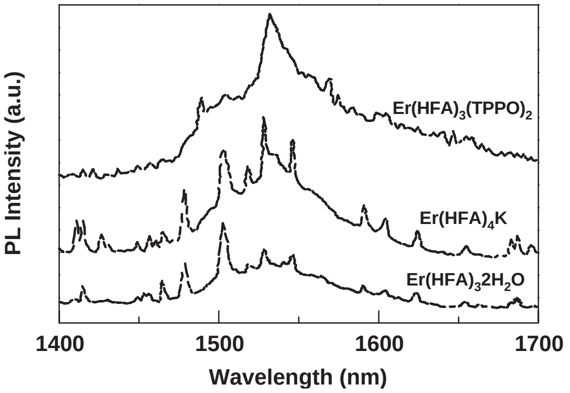


Fig. 4. NIR PL spectra of VTES-derived ORMOSIL films doped with various erbium complexes (Er/Si = 5 mol%) excited at 488 nm by an Ar$^+$ laser at room temperature.

3.3. NIR PL properties of VTES-derived ORMOSIL films in situ doped with ErQ_3

Since the Q moiety gives the possibility for indirect excitation on erbium ion [18,22–27], it possibly gives rise to luminescence upon excitation at long wavelengths extending well into the visible region to above 450 nm. Nevertheless, the complex ErQ_3 is poorly soluble in solvents for the sol–gel process such as ethanol and DMF. Hence, an alternative strategy is proposed, that is the in situ doping sol–gel process. Recently, complexes of rare earth ion (Eu^{3+}, Tb^{3+}) with β-diketone, aromatic carboxylic acid and heterocyclic ligands containing nitrogen, which may be decomposed or hardly dissolved in sol–gel precursor solutions and thus cannot be doped in gel glasses by a traditional sol–gel process, were successfully doped in sol–gel glasses at molecular level and high concentration by using the in-situ synthesis technique [28–30].

The in situ synthesis of ErQ_3 in VTES-derived ORMOSIL film was confirmed by FTIR and UV–Vis–NIR absorption spectra. Fig. 5 presents FTIR spectra of HQ, VTES-derived ORMOSIL, ErQ_3 KBr pellets as well as in situ ErQ_3-doped VTES-derived film on Si wafer. The C=N stretching vibration and C–H in-plane bending of the Q moiety in ErQ_3 as well as the in situ ErQ_3-doped film are shifted to lower frequencies, from 1506 cm^{-1} of free HQ to 1498 cm^{-1} of coordinated Q and from 1471 to 1465 cm^{-1}, respectively, indicating the formation of the complex through nitrogen coordination. Phenolic OH stretching vibration at ~3180 cm^{-1} for free HQ in zwitter ionic form is absent on coordination in the spectra of ErQ_3 and in situ ErQ_3-doped film [31]. The new band at 1317 cm^{-1} in the spectra of ErQ_3 and in situ ErQ_3-doped film was connected with erbium ion and ligand, being attributed to the in-plane ring deformation vibration of C–N coupling with N–Er stretching. Moreover, the peak at 1106 cm^{-1} for ErQ_3 was superimposed on the band around 1100 cm^{-1} related with Si–O–Si for the in situ ErQ_3-doped film, so that the appearance of the band around 1100 cm^{-1} exhibits remarkable difference upon comparing the spectrum of the undoped film with that of the doped one. Out-of-plane C–H bending mode for ErQ_3 (823 cm^{-1}) and in situ ErQ_3-doped film (825 cm^{-1}) have shifted to higher frequency upon coordination due to steric effect when compared with that for free HQ (817 cm^{-1}) [32–34]. Fig. 6 gives the UV–Vis–NIR absorption spectrum of in situ ErQ_3-doped VTES-derived film on glass slide (Er/Si = 5 mol%). The main absorption peak for in situ ErQ_3-doped VTES-derived film at 366 nm corresponds to the $\pi-\pi*$ transition of the Q moiety, which is red shifted from 315 nm for free HQ in DMF as that for ErQ_3 in DMF at 367 nm [35]. Also, two weak erbium-related absorption bands are seen

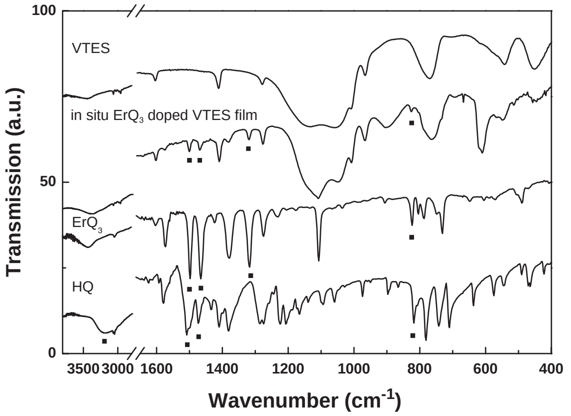


Fig. 5. FTIR spectra of HQ, VTES-derived ORMOSIL, ErQ_3 KBr pellets as well as in situ ErQ_3-doped VTES-derived film on Si wafer.

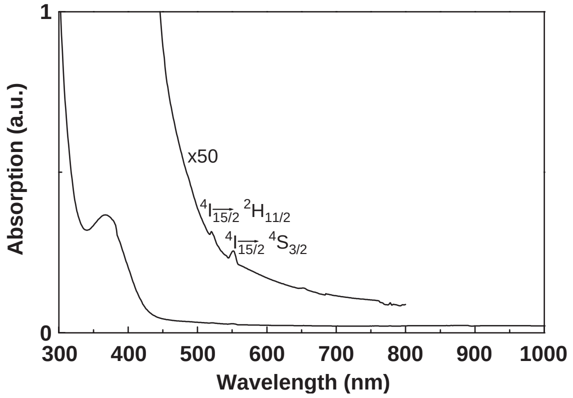


Fig. 6. UV–Vis–NIR absorption spectrum of in situ ErQ_3-doped VTES-derived film on glass slide (Er/Si = 5 mol%). The top line is magnified from the bottom one for visualization of erbium-related absorption bands.

corresponding to the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4I_{15/2} \rightarrow {}^4S_{3/2}$ transitions, respectively. On the basis of results of FTIR and UV–Vis–NIR absorption spectra, the complex ErQ_3 is suggested to be in situ synthesized in the host.

Fig. 7 shows normalized NIR PL spectra of bulk ErQ_3 powder, VTES-derived film doped in situ with 5 mol% ErQ_3 and VTES-derived film doped in situ with 2.5 mol% ErQ_3 excited at 488 nm by an Ar^+ laser at room temperature. The feature of emission spectra exhibits little variation when comparing ErQ_3 bulky powder with in situ doped VTES-derived film especially with the 5 mol% sample, also demonstrating that ErQ_3 has been in situ synthesized in the matrix and the matrix seem to have little effect on the microenvironment around the erbium ion due to effective protection of Q moieties.

Pure complex ErQ_3 powder and VTES-derived film doped in situ with ErQ_3 have better luminescence properties than other erbium complexes and the films doped with other erbium complexes, respectively, though no direct comparison among them has been performed (see Figs. 3,4,7). Nevertheless, as shown in Fig. 6 the absorption band tail of the Q moiety brushes 488 nm and indirect excitation via Q moieties contributes partially to the luminescence, except for direct excitation via Er^{3+} ion's intrinsic absorption of the level $^4F_{7/2}$, when excited at 488 nm. This should provide the explanation for the apparently higher luminescence intensity for samples related with the Q moiety [18,26-27].

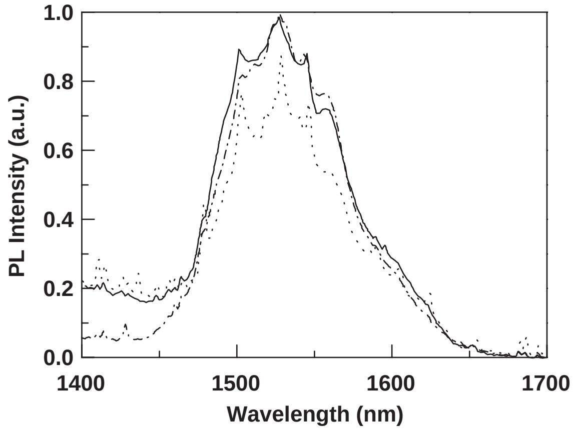


Fig. 7. Normalized NIR PL spectra of bulk ErQ_3 powder (dash-dot line), VTES-derived film doped in situ with 5 mol% ErQ_3 (solid line) and VTES-derived film doped in situ with 2.5 mol% ErQ_3 (dotted line) excited at 488 nm by an Ar^+ laser at room temperature.

4. Conclusion

Among the investigated matrix materials, VTES-derived ORMOSIL has the minimum optical loss at around 1500 nm. The 1.53 μm PL intensity for the erbium organic complexes in bulky powder increases in the order $Er(HFA)_3 \cdot 2H_2O <$ $Er(HFA)_4K <$ $Er(HFA)_3(TPPO)_2$. VTES-derived ORMOSIL films directly doped with various erbium organic complexes are prepared through a multistep sol–gel process, among which VTES-derived film doped with $Er(HFA)_3(TPPO)_2$ exhibits the maximum PL intensity at 1.53 μm as the erbium doping concentration is 5 mol%. Furthermore, VTES-derived films in situ doped with erbium complex with 8-hydroxyquinoline are realized successfully and also exhibit comparatively intense luminescence due to the contribution of indirect excitation via Q moieties. The complex ErQ_3 is in situ synthesized in the host matrix as expected.

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