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Preparation and luminescence of terbium and cerium-doped silica xerogels

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Sol-gel chemistry offers a possibility for preparation of optical materials like xerogels, aerogels, or thin films doped with rare earth ions [1–5]. In the case of silica-based materials the physical properties of the produced xerogels depend on the physicochemical processes accompanying the hydrolysis and gelation of tetraethylorthosilicate (TEOS) at different temperatures and time durations. In our previous contributions we demonstrate a higly efficient germanium–terbium energy transfer in silica sol-gel derived glasses [4, 5], the synthesis of transparent holmium-doped silica xerogels [3], as well as the luminescence of silica gels doped with terbium benzoate complexes [4]. The aim of the present investigation is the study of the preparation and luminescence of Ce^{3+}/Tb^{3+} codoped silica xerogels. Optical materials containing Tb^{3+} and Ce^{3+} are important green emitting phosphors due to Ce^{3+} $(5d^1) \rightarrow Tb^{3+}$ $(4f^7 5d^1)$ energy transfer [6–8]. Despite the intense investigations of polycrystalline Ce^{3+}/Tb^{3+}-doped materials [8], the luminescence of amorphous xerogels remains unexplained so far.

The silica xerogels in the present contribution were prepared by acid-catalyzed hydrolyzation of TEOS dissolved in ethanol (EtOH), and then gelation and drying (Techne 3D dry block with 5.6 ml starting amount of TEOS for all samples). Both ethanol addition and doping, followed by hydrolysis with HCl at pH 2 were performed under stirring. The molar ratios were TEOS:EtOH:H_2O:HCl = 1:1:4:0.003. The pH of the 0.45 M Tb^{3+} nitrate solution is 4–5. For the cerium codoping a 1.8 M Ce^{3+} nitrate solution with pH 4–5 was added to the terbium containing sol. The duration and temperature conditions for all samples of the different sol-gel steps following the cerium codoping are: hydrolysis—1 hr at room temperature, gelation—48 hr at 50 °C and drying—120 hr at 50 °C. Samples containing 1 mol% Tb/Si and codoped with 0.5, 1, 2, 3, 4, 5, and 7.5 mol% Ce/Si as well as 1, 2, and 5 mol% Ce/Si were prepared. All dried samples are monolithic with a size of 1–2 cm.

All the prepared samples are X-Ray amorphous, proved by X-ray diffraction (standard powder Stoe-Stadip diffractometer). The xerogels were characterized by weight analysis and IR spectroscopy (standard Perkin-Elmer FT-NIR and FT-IR unit).

Luminescence spectra of the powdered monoliths have been acquired on a custom-made spectrometer with a 300 W Xenon lamp and two ARC Spectra Pro monochromators at room temperature with a resolution 1 nm between 200 and 700 nm . For the measurements a metal holder with a quartz-window has been used. The intensity error in the emission spectra in this study is about 2%. The intensity error in the excitation spectra is about 2% between 280 and 380 nm and 20% below 280 nm. The excitation spectra were corrected using the excitation spectrum of a commercial $LaPO_4$:Ce, Tb phosphor.

IR-analysis of dry gels shows the absence of any organic residues after re-drying the samples (absence of an absorption feature at 2800 cm^{-1}). IR absorption features at 1600, 3500, 5200, and 4400 cm^{-1}, however, show the presence both of OH groups and H_2O molecules in the monoliths [9]. The samples showed about 30% weight loss due to water content at heating between room temperature and 800 °C according to weight analysis. The water content (about 30%) of the samples investigated is similar to that in Ho-doped, Tb-doped, and Ge-Tb doped silica xerogels prepared under the same conditions [3–5] and is determined by the preparation conditions. All xerogels were transparent after drying, they display a green Tb^{3+} luminescence at UV-excitation.

In Fig. 1 typical excitation and emission spectra of samples doped with Tb and Ce/Tb are given. The excitation spectra contain significant maxima at 325 nm (splitted), 341, 355, and 370 nm (splitted) as well as a

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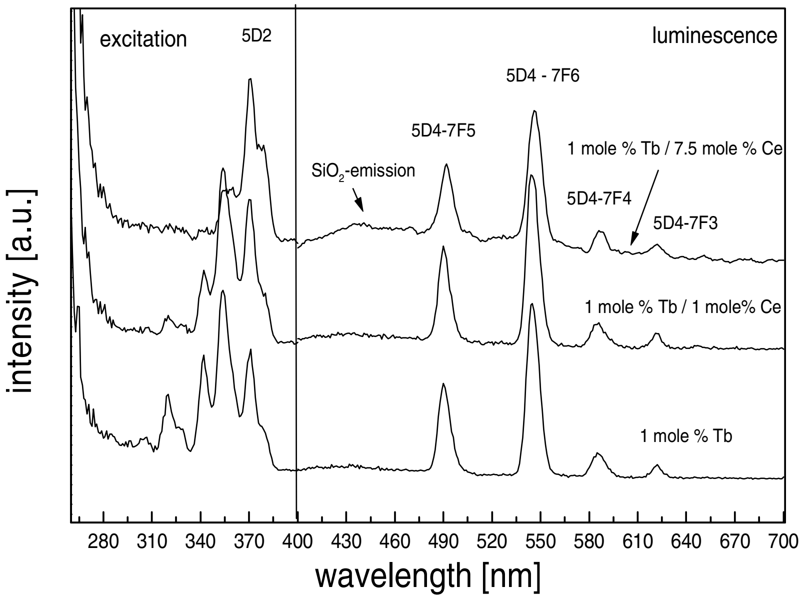

Figure 1 Typical luminescence (355 nm excitation) and excitation spectra (monitoring the $^5D_4$–$^7F_6$ terbium transition) of terbium and cerium-doped xerogels. The Tb^{3+} electronic transitions are given. The lines are guidelines for eye.

maximum below 300 nm, which could not be measured due to experimental limitations. The Ce^{3+} codoping increases dramatically the relative intensity of the 370 nm feature in the excitation spectrum, especially the shoulder at 378 nm. The relative intensity of the 325 and 341 nm excitation band decreases with the Ce-content resulting in a red-shifting of the excitation maximum. Due to the large experimental error below 300 nm, the contribution of 254 nm excitation could not be determined quantitatively. Note that the 254 nm excitation is a very weak process in water containing xerogels which are essential with their long-wavelength excitation luminescence, coinciding with the 365 nm Hg-excitation [3, 4].

Besides the typical Tb^{3+} luminescence the samples exhibit an additional weak emission, coming from defects in the SiO_2 gels (nonbridging oxygen, Si–Si bonds, peroxobridges) with an emission maximum at 433 nm and excitation maximum at 350 nm. The luminescence from defects in the SiO_2-network improves the emission of SiO_2:Tb^{3+} at 350 nm excitation through energy transfer [5, 10]. A similar emission in sol-gel hybrid silica gels obtained through carboxylic acid solvolysis has been discussed in [2]. Fig. 1 shows that the intensity of the SiO_2 luminescence increases with the Ce-content. The SiO_2:Ce^{3+} xerogels display a very weak, broad luminescence with maximum at about 370 nm (excitation maximum 315 nm) due to the well known Ce^{3+} $f \rightarrow d$ excitation [10].

It is known that electronic transitions in rare earth ions occuring with $\Delta J = 1$ (J is the total angular momentum quantum number) are magnetic-dipole, transitions with $\Delta J = 2$, 3, 4, and 6 are electric-dipole where transitions with $\Delta J = 2$ are strong (hypersensitive electric-dipole transition). The situation in the case of Tb^{3+}-transitions is generally complicated because of the existence of electronic terms with high J-values and J-mixing by the crystal field [6, 7].

The intensity ratio $R_{\text{int, Tb}}$ between the intensities of the $^5D_4$–$^7F_5$ magnetic dipole electronic transition and the $^5D_4$–$^7F_6$ electric dipole transition in Tb^{3+} is qualitative sensitive to the site symmetry of the Tb^{3+} ion [6].

For characterization of the Tb^{3+} site symmetry the $R_{\text{int, Tb}}$ intensity ratio for the Tb and Tb-Ce doped samples was defined as:

$$R_{\text{int,Tb}} = \frac{I_{\text{5D4}-\text{7F5}}}{I_{\text{5D4}-\text{7F6}}} \tag{1}$$

$I_{\text{5D4}-\text{7F5}}$ and $I_{\text{5D4}-\text{7F6}}$ are the integral luminescence intensities from the luminescence spectra obtained with Gaussian deconvolution. $R_{\text{int,Tb}}$ is varying between 0.45 ± 0.03 and 0.50 ± 0.03 for samples containing 1 mole% Tb and up to 7.5 mole% Ce suggesting a narrow distribution of Tb^{3+}-sites with a noncentrosymmetrical environment. It seems, that the site-symmetry of Tb^{3+} is not affected by the Ce-codoping. The $R_{\text{int,Tb}}$ values for SiO_2:0.01Tb,Ge and SiO_2:0.01Tb xerogels are 0.42 ± 0.02 and 0.48 ± 0.03, respectively [5]. Similar spectra–structure correlations exist for other rare earth ions like Eu^{3+} and Ho^{3+} and can be used as a spectroscopic probe for their local environment in xerogels, hydroxides, and powders [3, 8, 9]. In doped xerogels an increase in the rare earth ion concentration leads to the formation of sites with a centrosymmetrical environment detected by luminescence and absorption spectroscopy [3, 5].

To demonstrate the improving of the Tb^{3+} luminescence at 370 nm excitation we calculated the ratio between the luminescence intensity of the Tb^{3+} $^5D_4$–$^7F_6$ transition at 370 nm excitation and 355 nm excitation. This ratio is

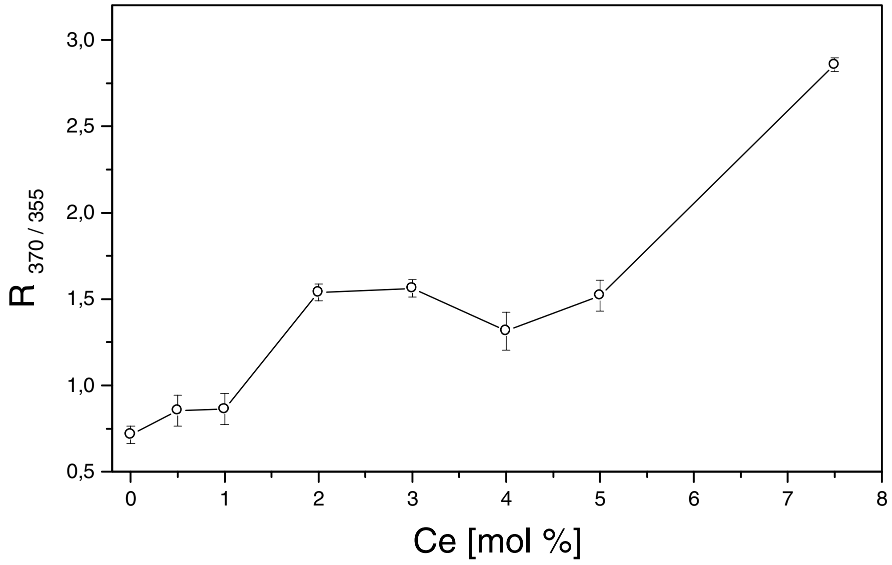

Figure 2 Increase of Tb^{3+} luminescence intensity at 370 nm excitation expressed with the ratio $R_{370/355}$ between the luminescence intensity of the $^5D_4$–$^7F_6$ transition at 370 nm excitation and 355 nm excitation. The $R_{370/355}$ ratio is independent from differences in the conditions of the luminescence measurements.

defined as:

$$R_{370/355} = \frac{I^{370\,\text{nm}}_{5D4-7F6}}{I^{355\,\text{nm}}_{5D4-7F6}} \qquad (2)$$

In Fig. 2. the increase of $R_{370/350}$ with the Ce content in the xerogels is shown. Fig. 2 points either to an energy transfer or to relaxation of the selection rules due to Ce-doping (heavy atom effect). A similar heavy atom effect has been demonstrated for Y^{3+} codoped ZrO_2:Cr^{3+} [11]. In cerium-doped silicate systems a long-wavelength absorption appearing at 320–360 nm due to Ce^{3+} $f^1 \rightarrow d^1$ transitions or $O^{2-} \rightarrow Ce^{4+}$ has been discussed [12]. We therefore conclude that the 370 nm excitation channels of Tb^{3+} gain intensity by the heavy atom effect from the neighboring cerium ions. The result is a red-shifting of the maximum of the terbium excitation spectra from 355 to 370 nm. Direct Tb^{3+} excitation is a very weak process, at the same time the blue SiO_2 emission intensity also increases with the Ce content.

In other words, the $SiO_2 \rightarrow Tb^{3+}$ energy transfer [5, 10], which generally is responsible for the high intensity of the Tb luminescence at long-wavelength excitation could be assisted by the Ce^{3+} ions. Further, lifetime measurements would clarify in detail the relations between the three optical components—SiO_2 defects, Tb^{3+} activator ions, and Ce^{3+} sensitizer ions as well as quenching due to H_2O or OH groups [8].

In summary, an effective one-pot sol-gel preparation from green emitting SiO_2:$0.01Tb^{3+}$ xerogels containing up to 7.5 mol% Ce^{3+}/Tb is demonstrated. The Tb^{3+} ions incorporated into the silica network possess a narrow non-centrosymmetrical site distribution. The Ce^{3+} codoping increases the relative intensity of the green Tb^{3+} luminescence at 370 nm excitation. The xerogels prepared in this way can be a useful precursor for green emitting luminescent materials. The analysis of the Tb^{3+} luminescence spectra may be a short-environment indicator similar to the Eu^{3+} or Ho^{3+} spectra–structure correlation.

Acknowledgments

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