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Rare earth doped sol–gel materials as potential absorbance standards

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Abstract

Our studies are aimed towards the preparation of absorbance materials for use in the UV and combined UV–VIS regions using sol–gel derived silica as the matrix. Our current research is directed towards understanding the extent of molecular interactions between the dopant phase (in this case metal salts) and the gel matrix and the effect of these interactions on the spectroscopic signature of all components in the gel–glass composite. The addition of cerium(III) to the sol–gel reagents affected the rate of drying of the gel–silicas suggesting a direct interaction between the gel matrix and the metal ions themselves. Confirmatory evidence was provided by low temperature ^{29}Si solution NMR measurements during the early stages of gel formation where Q_0 and Q_1 species disappeared from the reaction medium more quickly in the presence of the dopant. The UV–VIS spectrum of dried sol–gel glasses containing Ce(III) showed that the as-prepared material contained principally the aqua-ion with nine-fold coordination. Evacuation of the cerium doped glass gave a spectrum commensurate with the metal ion having a lower coordination number and after heating the Ce(III) spectral response was no longer observed. It is suggested that oxidation of Ce(III) to Ce(IV) occurred during thermal treatment. When gel glasses were prepared with both cerium(III) and neodymium(III) the signal arising from the presence of the cerium ions was diminished. Moreover, after evacuation of the glasses and heat treatment (800°C), the Ce(III) spectrum could no longer be observed.

Keywords: Cerium(III); Neodymium(III); Sol–gel; ^{29}Si NMR; UV–VIS spectroscopy

1. Introduction

Glasses have been conventionally prepared by high temperature methods [2] but the use of the sol–gel process enables the preparation of porous or dense glasses with superior homogeneity, purity, and good optical qualities (high transmittance) at significantly lower temperature [3].

Sol–gel materials provide an excellent vehicle for the incorporation of secondary phases including metal ions, organic molecules or macromolecules. These species may be doped into the gel-matrix as it is being formed (pre-doping) [4] or incorporated after the glass has been prepared (post-doping). In this paper we present results obtained from gel–glass monoliths prepared using the pre-doping method. The effect of the dopant on the development of the sol–gel matrix was studied as well as the effect of the matrix on the dopant.

Our goal is to develop suitable materials for applications as optical standards. Ce^{3+} and Nd^{3+} ions were used for the preparation of standards as they have useful spectroscopic signatures in the UV and Visible regions, respectively. Cerium doped glasses also have potential application as phosphors, scintillators, detectors, UV absorbers, emitters and activators due to their luminescence behaviour [5]. Neodymium doped densified sol–gel materials are currently being investigated for high power laser systems and as fiber optic amplifiers [6].

2. Experimental

Solutions containing various dopants ($Nd(NO_3)_3\cdot 6H_2O$, $CeCl_3\cdot 7H_2O$, $Ce(NO_3)_3\cdot 6H_2O$ from Aldrich) were prepared in dry ethanol (distilled from 95% ethanol over magnesium) and distilled deionised water.

The solutions were analysed by UV–VIS spectroscopy using a Unicam UV2 UV–VIS spectrometer (scan speed 600 nm min^{-1}, data interval 0.5 nm).

Using the sol–gel process silica monoliths were prepared. Non-doped and doped silica gel glasses were made using tetraethylorthosilicate 98% (Aldrich) mixed with dry ethanol (distilled from 95% ethanol over magnesium) and stirred gently for few seconds to obtain an homogeneous solution. Then, if necessary, the dopant was added. Finally, 0.5 M HCl (prepared from 11.3 M HCl (Fisher)) was added at the following molar ratio: for normal sol–gels: 1

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TEOS:4 EtOH:4 H_2O:0.045 HCl; for doped sol–gels: the molar ratio was maintained with the dopant either in the aqueous or ethanolic phase at a range of concentrations ($1–10^{-6}$ M in the initial solutions) with $CeCl_3 \cdot 6H_2O$ (Aldrich) and $Nd(NO_3)_3 \cdot 6H_2O$ (Aldrich) used as dopants.

The solution was mixed at room temperature for 1 h before being put (4 ml) in Petri dishes (diameter 3.5 cm, depth 1 cm from Nunc) covered with Nesco film in which five holes (0.6 mm diameter) had been made before being placed in a fan-assisted oven at 40°C to dry. For every type of sol–gel, a batch of eight samples was prepared.

Samples were weighed daily (%weight loss versus time was plotted). Statistical analysis using the Student's *t*-test was performed in order to assess the significance of variations measured. When the samples showed no measurable weight loss, they were analysed by UV–VIS spectroscopy using a Unicam UV2 UV–VIS spectrometer (scan speed 600 nm min^{-1}, data interval 0.5 nm). The glasses (around 1.05 mm thickness) were analysed in the bulk supported by a metallic holder. Samples were also investigated as dried pieces of glass, immediately after dehydration by subjecting the samples to a vacuum pressure of 6 mbar (measured by an Edwards Pirani 10 pressure sensor) for 18 h, and after thermal treatment (with a ramp temperature of 0.1°C min^{-1}) for 4 h at 800°C. The samples were cooled down at a ramp temperature of 5°C min^{-1}, the whole process taking 36 h. A Carbolite programmable furnace was used.

^{29}Si NMR spectroscopy was performed on the reaction mixtures used to prepare doped and undoped sol–gels in order to identify the different silica species present in the system at certain times of hydrolysis and condensation. The samples were placed in liquid nitrogen at the required times to stop further reaction. The apparatus used was a Jeol EX 270-MHz NMR spectrometer operating at 11 013.3 Hz. In total, 1000 scans were collected between 0 and -130 ppm for every spectrum with an acquisition time of 1.488 s and a pulse delay of 6.5 s. The data were collected at -60.6°C in the NNE mode with the negative nuclear Overhauser effect suppressed by inverse-gated decoupling. The internal standard (in a 5-mm diameter tube coaxially suspended in the sample to prevent any possible interaction with the sample) was a mixture of d_6-acetone and 25% TMS as reference.

3. Results and discussion

3.1. Spectroscopy

The preparation of standards in the UV region requires the doping of sol–gel glasses with metal ions which possess characteristic bands in the UV region. Cerium(III) was chosen as it shows several characteristic broad bands between 200 and 350 nm. The electronic spectrum of Ce(III) consists of a single transition between $^2F_{5/2}$ (ground state) and $^2F_{7/2}$ [7]. This transition could in principal be observed in the infrared region (5000 nm), but is hidden by vibrational bands occurring in this region. The broad bands observed in the UV region are due to $4f^n \rightarrow 4f^{n-1}d^1$ transitions [8]. Five bands are expected corresponding to the five Kramers doublets of ^2D ($5d^1$) [9]. The positions and intensities of these bands are affected by the metal ion site symmetry and the chemical species coordinated to the metal ion which in turn affect the ligand field [10]. Spectral features from Ce(IV), including a charge transfer band at around 200 nm may also be expected as all solutions and the gel glasses were prepared and treated in air [11].

Fig. 1 shows spectra of $CeCl_3 \cdot 7H_2O$ solutions in either ethanol or water at various concentrations and also $Ce(NO_3)_3 \cdot 6H_2O$ in water. $CeCl_3 \cdot 7H_2O$ at a concentration of 0.01 M in ethanol shows bands at 201, 213, 230, 252, and at 309 nm. $CeCl_3 \cdot 7H_2O$ in water solution shows bands at 200, 208, and 223 nm. The band which was observed at 252 nm in ethanolic solution is observed as two bands at 239 and 253 nm. Moreover, the band observed at 309 nm in ethanol is shifted in water and observed at 298 nm but at a much lower intensity than in ethanol. Solutions of $Ce(NO_3)_3 \cdot 6H_2O$ only show one band at 250 nm. The broad and noisy band observed in the UV region between 205 and 240 nm corresponds to charge transfer between the metal ion and the ligands. The very close proximity of the charge transfer band and bands arising from electronic transitions prevents a clear assignment of the bands.

By comparison of our data with that collected by Keller et al. [11] for solutions of cerium(III) chloride in methanol and isopropanol, the spectra of Ce(III) chloride in water

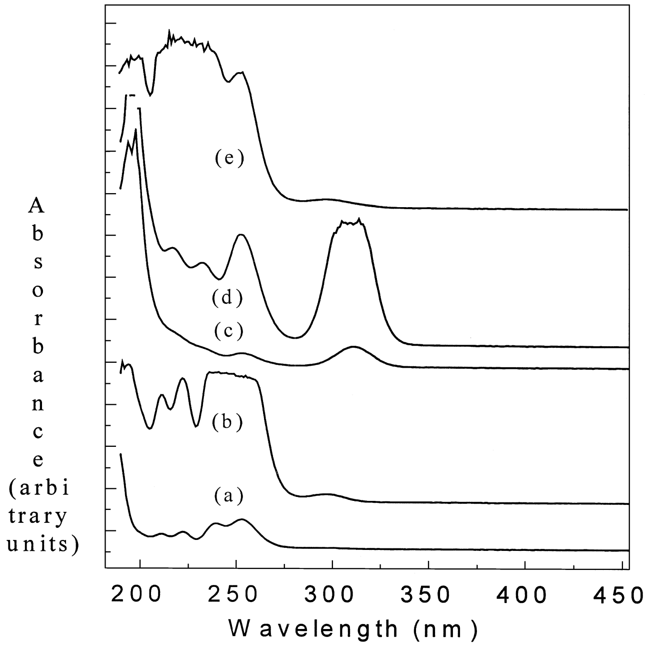

Fig. 1. UV–VIS spectra of $CeCl_3 \cdot 7H_2O$ solutions: (a) 0.01 M and (b) 0.001 M in water, (c) 0.01 M and (d) 0.001 M in ethanol, (e) $Ce(NO_3)_3 \cdot 6H_2O$ 0.01 M in water.

corresponded to the aqua-cation Ce(III) in nine-fold coordination and the spectra of Ce(III) in ethanol corresponded to Ce(III) with fewer ligands surrounding the metal ion. In all spectra, the significant intensity at around 200 nm corresponds to the presence of some Ce(IV).

Doped sol–gels were prepared with Ce(III). The samples prepared with $Ce(NO_3)_3 \cdot 6H_2O$ did not show a band in the UV region and hence were studied no further.

When the sol–gel had been dried, the presence of Ce(III) was detected by its UV–VIS spectrum. The characteristic bands of Ce(III) (from $CeCl_3 \cdot 7H_2O$) (at 200, 208, 222, 245, 298 nm) in the UV region were observed (Fig. 2a). The spectrum corresponds to the spectrum of Ce(III) in water regardless of the solvent in which the metal ion had originally been added to the sol–gel mixture, suggesting the presence of water in the first coordination sphere around the metal ion in the sol–gel glass. A coordination number of 9 for the metal ion is also proposed.

After evacuation, a change in the bands characteristic of Ce(III) were observed (Fig. 2b). A very low intensity band was detected at 242 nm with further bands at 269 nm and ≈316 nm. A shift of the bands toward higher wavelength had occurred indicating a weaker ligand field around the metal ion. During evacuation, the remaining water and the solvent contained in the pores of the sol–gel were removed. Once again the environment around the metal ion changes. The spectrum observed for the cerium(III) ion became more like that expected for cerium(III) in an environment with fewer ligands akin to the situation observed for anhydrous cerium(III) chloride in isopropanol [11]. In this instance the ligands around the cerium(III) metal ions could be residual solvent/water, silanol groups and/or chloride ions trapped within the sol–gel as has been observed previously for our studies on cobalt(II) chloride doped sol–gel glasses [12].

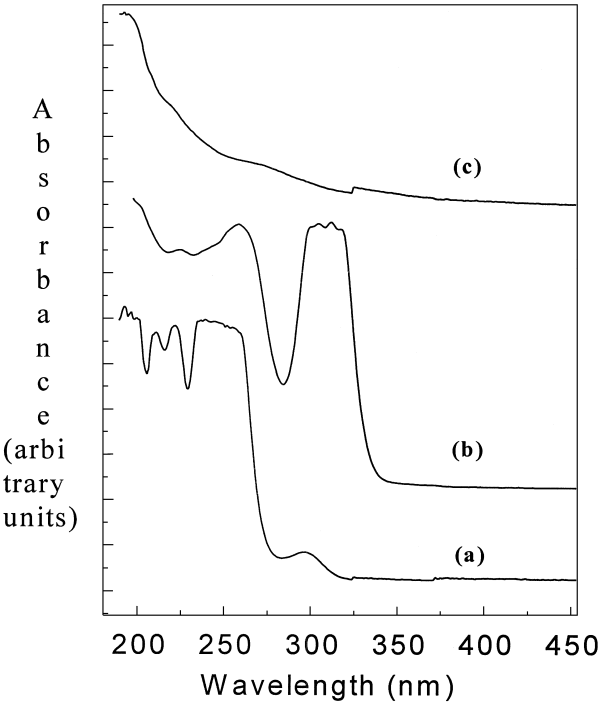

Fig. 2. Ce(III) sol–gel prepared using 0.7 M solution of $CeCl_3 \cdot 7H_2O$: (a) dried, (b) after evacuation, (d) after heating to 800°C.

When the sample had been thermally treated to 800°C, the signal arising from the presence of cerium(III) was no longer observable suggesting a transformation of Ce(III) into Ce(IV) which, under the conditions of measurement did not exhibit a detectable transition in the UV region [13,14]. As the sample had been heated up in air, oxidation of the metal ion could have occurred.

The spectral results obtained indicate that cerium(III) doped porous gel glasses could be used as UV standards. They cannot, however, be used in the densified form.

3.2. Matrix-dopant interaction studies

The rate of weight stabilisation of the glass was affected by the presence of Ce(III) as the sol–gel glass took longer to dry. Two stages were observed for the drying process of normal sol–gels (Fig. 3). A linear decrease was observed for around 20 days followed by a period of time with a slower weight loss. After 25 days, the samples were dry. In the presence of Ce(III) as the dopant, the sol–gel showed a three stage drying process (Fig. 3). A slow weight loss was observed for a few days at the beginning of the drying process, followed by a linear weight loss and finally a stabilisation of the weight after 38–40 days. The effect of the dopant was concentration dependant and at 10^{-4} M, the drying process of the doped sol–gel became similar to that of normal sol–gels. The effect on rate of drying of the gel–silicas suggested a direct interaction between the gel matrix and the metal ions themselves. In a similar way an effect of the dopant on the development of the silica matrix was noticed when sol–gels were doped with Nd(III) [1]. Other studies by Ganguli et al. [15] on the effect of a variety of other metal ions on gelation have shown that the hydrolysis state of the metal ion is important in its ability to speed up or slow down the gelation process.

In order to further investigate the nature of the interaction between the dopant and matrix the early stages in the formation of the gel matrix were studied by ^{29}Si NMR. Qualitative analysis of the silica speciation were carried out with identification of the peaks being performed with reference to previous work [16–20]. By monitoring the proportion of Q_0, Q_1, Q_2 and Q_3 silica species, an effect of the dopant on the formation of the different silica species as a function of reaction time was observed (Fig. 4). In the presence of cerium(III) a shift (0.8 ppm for the highest concentration of the metal ion) for all peaks towards lower field was observed. This shift arises due to the electronegative effect of Ce(III) which reduces the local diamagnetic shielding in the vicinity of the attached protons [21]. In the

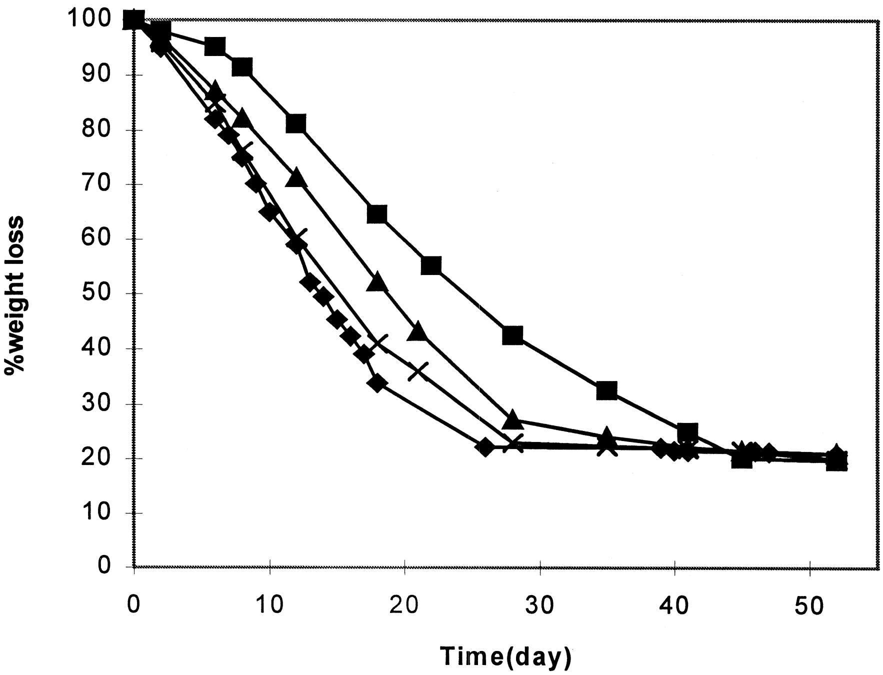

Fig. 3. The effect of dopant on time taken for weight stabilisation for undoped and Ce(III)-doped sol–gel glasses (average of eight samples per type of sol–gel). Legend: (♦) normal sol–gel, (■) Ce sol–gel 0.7 M, (▲) Ce sol–gel 0.1 M, (×) Ce sol–gel 0.01 M.

presence of the dopant, Q_0 and Q_1 species disappear more quickly than when the dopant is absent. Q_0 and Q_1 species are used during hydrolysis and condensation reactions to form Q_2 and Q_3 species. The proportion of polymerised species is higher earlier on in the presence of dopant. This behaviour is concentration dependent. The presence of the dopant in the sol–gel acts as a catalyst to both hydrolysis and condensation reactions involving TEOS and its hydrolysis and condensation products.

3.3. Towards the preparation of a combined UV–VIS standard

Following our success in the preparation of Ce(III) doped sol–gel materials having a spectroscopic signature in the UV region we attempted to prepare rare earth doped sol–gels with spectroscopic signatures in both the UV and Visible regions. From our previous studies we know that neodymium ions are suitable for use as a dopant in the preparation of optical standards in the visible region [1]. For this reason solutions and sol–gel glasses containing both Ce(III) and Nd(III) were prepared. Several solutions were prepared containing $CeCl_3 \cdot 7H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$ at various concentrations in both water and ethanol. Similar behaviour was observed in both solvents. In the UV region, the bands characteristic of Ce(III) were masked by the signal from Nd(III) (Fig. 5a). The only band observed for Ce(III) was at 290 nm where changes in intensity and shape were noticed as the concentration of the Ce(III) ion was varied. The spectra were always very noisy, possibly due to the presence of the nitrate ion associated with the Nd(III) component.

In the glass, the presence of Ce(III) was also masked (Fig. 5b–d) regardless of the treatment to which the glass had been subjected. When the Nd(III) spectrum was compared with the spectrum of Nd(III) only sol–gel [1], no difference in the band positions but differences in the shape of the hypersensitive bands at 740 and 800 nm was noticed. The coordination number for Nd(III) in the materials prepared with Ce(III) and Nd(III) was the same as for the materials prepared with Nd(III) alone but the local environment around the Nd(III) ions was subtly different, perhaps suggesting a slightly different interaction between the metal ion and the matrix in the presence of Ce(III). Other workers have also found that the coordination chemistry of neodymium(III) changes with glass treatment, the effects being attributed to changes in coordination number and nearest neighbours [6,22].

It was not possible to prepare a combined rare earth doped standard for use in the Visible and UV region via sol–gel technology using the precursors chosen in this study. It is possible that another system with different metal ions might have the necessary characteristics for such an optical standard.

Acknowledgements

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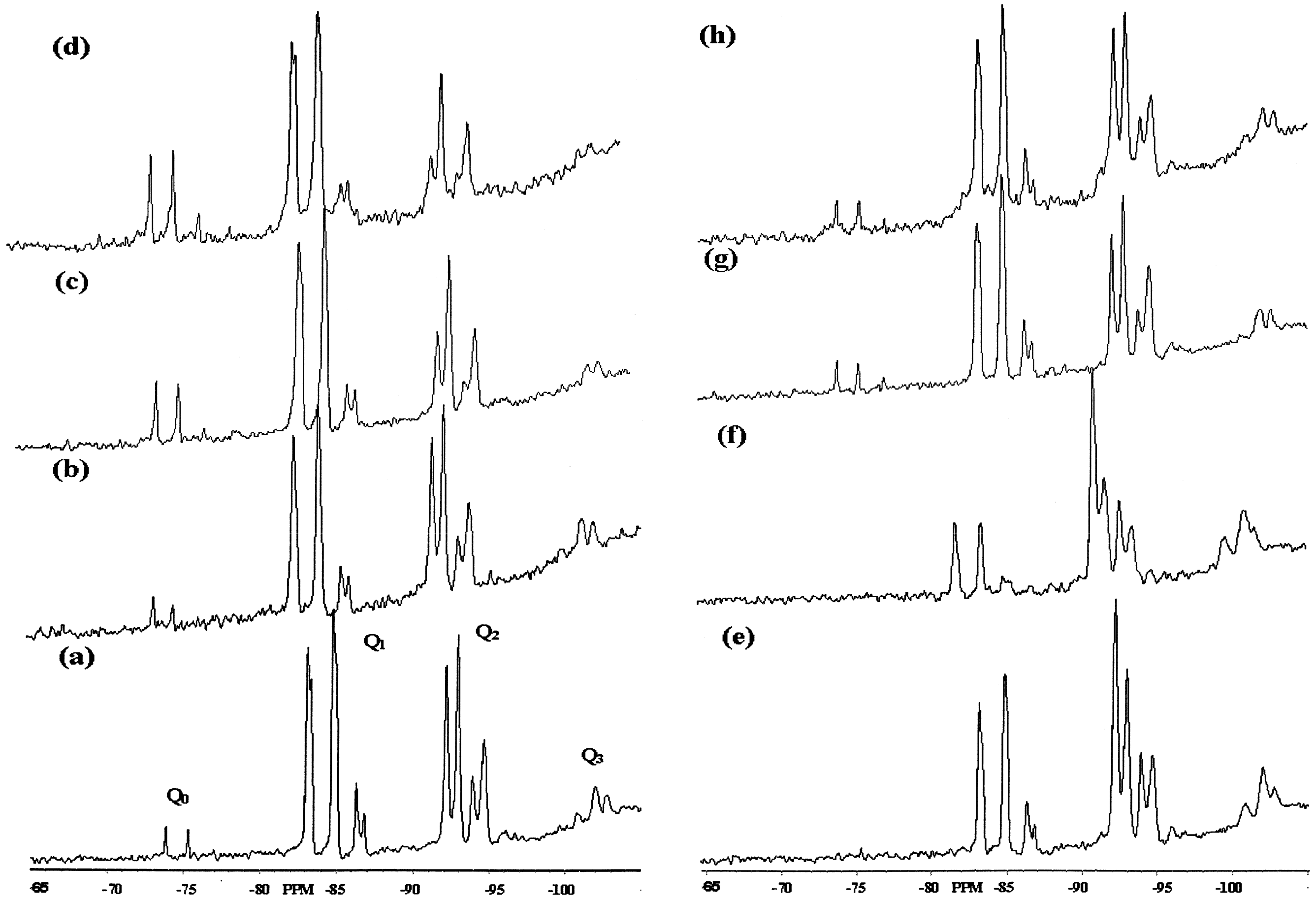

Fig. 4. ^{29}Si NMR of doped and undoped sol–gels during hydrolysis and condensation. (a–d) 10 s of reaction: (a) normal sol–gel, (b) Ce(III) 0.7 M sol–gel, (c) Ce(III) 0.1 M sol–gel, (d) Ce(III) 0.01 M sol–gel; (e–h) 1 min of reaction: (e) normal sol–gel, (f) Ce(III) 0.7 M sol–gel, (g) Ce(III) 0.1 M sol–gel, (h) Ce(III) 0.01 M sol–gel. Legend: Q_0 corresponds to $\underline{Si}(OR)_4$, Q_1 corresponds to $\underline{Si}(OR)_3(OSi{\equiv})$, Q_2 corresponds to $\underline{Si}(OR)_2(OSi{\equiv})_2$, Q_3 corresponds to $\underline{Si}(OR)(OSi{\equiv})_3$.

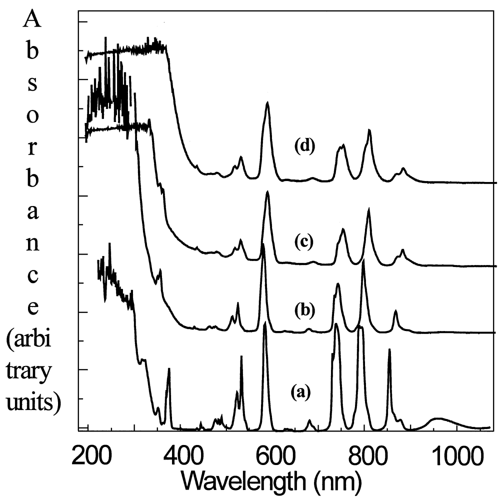

Fig. 5. UV–VIS spectra of Ce(III) and Nd(III) ions (a) in solution with Ce^{3+} 0.1 M+Nd(III) 1 M; (b–d) sol–gel prepared using 1 M Nd(III) and 1 M Ce(III), (b) dried, (c) after evacuation, (d) after heating to 800°C.

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