

Sol-gel-derived hybrid materials multi-doped with rare-earth metal ions*

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Four different hybrid organic-inorganic materials based on TiO_2-SiO_2 matrices with organic additives and doped with rare-earth metal ions (III) from the group of europium, cerium, terbium, neodymium, dysprosium and samarium, were synthesized by sol-gel method. Tetraethyl orthosilicate, titanium (IV) isopropoxide and organic compounds, such as butyl acrylate, butyl methacrylate, ethyl acetoacetate, ethylene glycol dimethacrylate, ethyl acetate, propylene carbonate, organic solvents and certain inorganic salts were used in the synthesis. The inorganic part of the sols, which were used in the synthesis of all the hybrid materials, was prepared separately and then the organic parts were added. The materials obtained were aged for three weeks at room temperature and then heated in an electric oven for three hours at temperatures of 80 °C – 150 °C. Scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDX); X-ray diffraction (XRD); Fourier transform infrared spectroscopy (KBr technique); ²⁹Si magic-angle spinning nuclear magnetic resonance; and fluorescence spectroscopy were used for the examination of morphology, microstructure and luminescence properties, respectively. Photoluminescence properties with relatively intense narrow emission lines of Tb, Eu, Dy, Nd, Sm respectively to the RE-ions doping, were observed for all the hybrid materials.

Keywords: sol-gel, hybrid materials, lanthanide (III) ions, photoluminescence

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1. Introduction

The increasing interest in materials doped with rare-earth metals (RE) is observed due to their potential applications in the field of photonics and optoelectronics [1, 2]. Silica-based gels doped with RE³⁺ ions and organic-inorganic hybrid silicate gels have been revealed as a new class of luminescent materials, which can show a variety of luminescence properties [3–6]. During the last two decades, hybrid materials doped with rare-earth ions have gained extensive interest because of their potential applications in fluorescent and laser systems [7, 8]. Both TiO₂ and SiO₂ are commonly used in optical thin-film filters. The control of the refractive

index over a wide range of values can be obtained by mixing these materials. Sol-gel films of a SiO₂-TiO₂ system were investigated for the purposes of anti-reflecting and protective coating applications [9]. Recently, due to its excellent optical properties and good mechanical resistivity, titania-doped silica has been shown to play an important role in the development of optical fibres as well as of materials which can be applied in optoelectronics [10, 11]. Organic-inorganic hybrid materials produced by solgel method have many advantages, including the relatively easy modification of their chemical composition and tunable optical properties compatible with both organic and inorganic ingredients and dopants [12, 13]. The low-temperature synthesis and mild conditions of processing allow many organic moieties to be incorporated into an inorganic network. Various organic-inorganic hybrid materials with promising optical properties suitable for the

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design of optoelectronic devices, solid tunable laser devices, nonlinear optics, etc., have been prepared using sol-gel method [8, 14–18].

The important advantages of lanthanide ion activators of luminescence are the relatively long decay times and narrow-band emission spectra related to the fact that the emitting excited state and the ground state have the same f^n electronic configuration and that the f orbital is shielded from its environment by the fully or partially filled 5s and 5p outer shells. Unfortunately, the luminescence of RE (III) ions results from Laporte-forbidden ff transitions [7, 13]. Since they are forbidden, these transitions suffer from low extinction coefficients and thus the direct excitation only produces weak emission spectra. When the metal ions are compounded or chelated with organic moieties, which are capable of efficiently absorbing and transferring energy, a significant enhancement of emission can be obtained [8, 14, 15]. Therefore, the luminescence properties of nanostructured xerogels and sol-gelderived glasses and organic-inorganic hybrids doped with RE ions, transition-metal ions, RE-metal complexes, semiconductor nanocrystals and noble metal particles are widely investigated with regard to the excitation energy transfer processes in relation to the morphology and microstructure of thus obtained materials [14–18]. Thus, in common practice, organic ligands, with their good light absorption and strong coordination capability to lanthanide ions, are used as building units for lanthanide-doped hybrid materials. Carboxylic acids and their derivatives, especially poly(methyl methacrylate) (PMMA) are known for their capability to bind lanthanide ions by means of interaction with C=O oxygen atoms [8, 19–21]. However, so far, little work has been devoted to butyl derivatives of carboxylic acids.

In this work, four different materials were selected from a larger set of hybrid organicinorganic materials based on a TiO_2-SiO_2 inorganic part and doped with rare-earth metal ions (III) (europium, cerium, terbium, neodymium, dysprosium, samarium). The hybrid materials were produced by sol-gel method using tetraethyl orthosilicate, titanium(IV) isopropoxide and organic precursors, such as n-butyl methacrylate [H₂C=C(CH₃)COO(CH₂)₃CH₃, M = 142.20 g/mol], butyl acrylate [CH₂=CH $COO(CH_2)_3CH_3$, M = 128.17 g/mol], ethyl acetoacetate [CH₃COCH₂COOC₂H₅, Μ 130.14 g/mol], ethylene glycol dimethacrylate $(CH_2=C(CH_3)C(O)OCH_2CH_2OC(O)C(CH_3)=CH_2,$ M = 198.22 g/mol), ethyl acetate ($C_4H_8O_2$, M = 88.11 g/mol), and propylene carbonate ($C_4H_6O_3$, M = 102.09 g/mol). The obtained materials were characterized in terms of their morphology, structure and luminescence properties. The main objective was to investigate the potential application of the prepared hybrid gels as the hosts for rare-earth metal ion multidoping, with the aim to obtain photoluminescent materials that could act as emitters, in which the emission wavelength tuning can be obtained by changing the excitation wavelength.

2. Experimental

2.1. Precursors and synthesis

Analytical grade reagents (Aldrich-Chemie, Fluka, Merck) were used for the preparation of organic-inorganic hybrid materials, which we called A, B, C and D. The inorganic part of hybrid gels was prepared using a two-step procedure in order to avoid the problems related to the difference in the rate of hydrolysis reaction between silica and titania precursors. The silica component of the organic-inorganic hybrids was first produced by mixing TEOS Si $(OC_2H_5)_4$ (M = 208.33 g/mol), ethanol and distilled water at the molar ratio of TEOS:ethanol: $H_2O = 2:5:1$. As a catalyst, 36.6 % HCl was added drop by drop up to pH = 2. TEOSsol was first hydrolyzed under magnetic stirring for 1 h. The solution of titanium(IV) isopropoxide $Ti(C_3H_7O)_4$, (M = 284.26 g/mol) in the mixture of methanol and isopropyl alcohol (v/v=1:1) with a small amount of acetic acid (85 %, about 2 vol.%) was prepared separately under continuous stirring and added to the partially hydrolyzed solution of TEOS. The mixtures of appropriate amounts of these solutions were heated at 50 °C for 20 min and left to cool to room temperature. Subsequently, the mixtures of organic precursors and RE^{3+} metal salts and zirconyl acetylacetonate for

Components	Sample/content of components [mol]				
components	А	В	С	D	
TEOS-solution (ml)	0.056	0.056	0.112	0.168	
PC (propylene carbonate, ml)	0.118	_	-	-	
Ethyl acetoacetate	_	0.078	-	-	
Butyl acrylate	0.14	0.14	0.14	-	
Butyl methacrylate	0.032				
Ethyl acetate	0.05	-	-	0.05	
Ethylene glycol dimethacrylate	_	-	-	0.037	
Titanium(IV) isopropoxide Ti(C ₃ H ₇ O) ₄	0.023	0.023	0.044	0.067	
$ZrO(C_5H_7O_2)_2 (Zr^{4+} - 0.12 g)$	_	-	0.0013	-	
LaCl ₃ · 7 H ₂ O, (La ³⁺ – 0.20 g/0.02 g)	-	0.0014	-	0.00014	
$Ce(NO_3)_3 \cdot 6 H_2O$, $(Ce^{3+} - 0.04 g)$	_	-	-	0.0003	
$Nd(NO_3)_3 \cdot 6 H_2O$, $(Nd^{3+} - 0.08 g/0.04 g)$	_	-	0.0006	0.0003	
Dy $Cl_3 \cdot 6 H_2O$, $(Dy^{3+} - 0.08 g/0.08 g)$	0.0005	_	0.0005	-	
Eu Cl ₃ · 6 H ₂ O, (Eu ³⁺ – 0.05/0.08 g)	_	_	0.0003	0.0005	
Sm Cl ₃ · 6 H ₂ O, (Sm ³⁺ – 0.35 /0.50/0.45 g)	0.002	0.0033	0.003	-	
Tb $Cl_3 \cdot 6 H_2O$, $(Tb^{3+} - 0.12 g)$	0.0008	_	-	-	

Table 1. Components of the starting solutions.

sample C (2 at.% of Zr⁴⁺ in methylene chloride and acetylacetone v/v = 1:1) were added under vigorous stirring. The volume ratio of Ti(C₃H₇O)₄:solvent mixture:CH₃COOH was 40:100:2 and the content of TEOS, Ti-(tetraisopropoxide) and other organic and inorganic additions of sols for each sample are given in Table 1. The luminescence-active rare-earth ions were added to the sols in the total amount (with respect to the mass of the gel precursors) of about 1 wt.% (0.9, 1.0, 1.1 wt.%) for materials A–C and of about 0.2 wt.% for material D. The hybrid materials were aged for at least three weeks, the gel samples were subsequently heated for three hours at a temperature of 80 °C and 150 °C, respectively.

2.2. Characterization of the sample

The hybrid materials characterized in this paper were chosen from among several sets of various sol-gel materials doped with RE and other metal ions based on a TiO₂–SiO₂ inorganic part and synthesized with organic compounds, which were selected mainly from derivatives of acrylic acid capable of providing hybrid gel systems with carboxylic groups. The morphology of the hybrid materials obtained in this work was investigated by X-ray diffraction (XRD 7, Seifert diffractometer) and scanning electron microscopy equipped with

energy dispersive X-ray spectroscopy SEM/EDX, (JEOL JSM 5400 with LINK An 10/5, NOVA NANOSEM-FEI). The microstructure of the obtained materials was examined using Fourier transform infrared spectroscopy (FT-IR, Bio-Rad FTS-60VM FTIR spectrometer, KBr technique) and magic-angle spinning nuclear magnetic resonance MAS NMR (NMR spectrometer working at the magnetic field of 7.05 T). ²⁹Si MAS NMR spectra of the samples were measured at room temperature, using tetramethylsilane, TMS as the external standard. The luminescence spectra of the hybrid materials were registered in the wavelength range of 200-800 nm for excitation and 200-900 nm for emission (with a red-sensitive photomultiplier) by means of a Perkin-Elmer LS-55 fluorescence spectrometer. The radiation source was a xenon discharge lamp equivalent to 20 kW for the duration of 8 µs. The pulse width at half height was $< 10 \,\mu s$, excitation slit width was 2.0 nm, and the emission slit width was 2.5 nm.

3. Results and discussion

3.1. XRD and SEM/EDX characterization

All the obtained gels revealed an amorphous structure under XRD examination. The absence of



Fig. 1. XRD pattern of hybrid A, typical of the investigated hybrids.

crystalline phases of lanthanide inorganic salts in the gels suggests that the RE dopants were probably well dispersed in the host materials. The XRD pattern of sample A, typical of the hybrids under investigation, is shown in Fig. 1.

SEM images (at magnification of $50\,000\times$) of the hybrids obtained in this work are shown in Fig. 2(a–d). EDX elemental analysis of the samples heated at 150 °C yielded the total amounts of RE (III) luminescence activators of about: 0.3 at.% (Sm – 0.09, Tb – 0.07, Dy – 0.12 at.%); about 0.9 at.% (Sm – 0.83 at.%); 2.0 at.% (Sm – 1.03, Nd – 0.49, Eu – 0.27, Dy – 0.21 at.%); and about 0.1 at.% (Eu – 0.03, Ce – 0.03, Nd – 0.02 at.%) in the hybrid materials A, B, C and D, respectively. The amounts obtained from EDX spectroscopy for other dopants (lanthanum and zirconium) were: La – 0.46 at.% and 0.07 at.% for materials B and D, respectively, and 0.03 at.% of Zr for material C.

The hybrid materials were synthesized using several organic precursors and solvents. Taking into account the weight losses related to the sol-gel transformation, the aging process and heat treatment, the results of EDX analysis, with reference to the content of silicon and carbon in the hybrid materials, were in a good agreement with respect to the relative contribution of dopants added to sols. The EDX spectrum for sample C, typical of the hybrids under investigation, is shown in Fig. 3.

The SEM images of hybrids A–C show nanosized morphology with agglomerations of smaller particles that are homogeneously distributed, but differ in size and porosity of the particles. In the case of gel D (Fig. 2(d)), which was synthesized without acrylate components, the morphology is particularly fine and smooth, similar to that of silica gels or glasses. Such results clearly correspond to different compositions due to the variety of organic additions and metal ions introduced as host matrix precursors and dopants as well as to the mild conditions of synthesis and the heat treatment of the hybrid materials.

3.2. FTIR and ²⁹Si MAS NMR measurements

3.2.1. FTIR spectra

FTIR spectra were registered for the samples of hybrid gels after heating for three hours at a temperature of 80 °C and 150 °C, respectively. The results of IR spectroscopy obtained for the hybrids heated at 150 °C are shown in Fig. 4. For comparison, the FTIR spectrum of sample D after heating at 80 °C is given in Fig. 5.

All the hybrid gels were synthesized using TEOS and titanium isopropoxide as inorganic precursors, which differ from each other with regard to the type and amount of organic components and rare-earth metal doping. Except for gel D, other gels (A–C) were prepared with the addition of butyl acrylate as the main organic precursor.

The absorption bands characteristic of Si–O–Si bonds, assigned to the Si–O–Si asymmetric stretching in the range of 1060–1072 cm⁻¹, Si-OH asymmetric stretching at around 950 cm⁻¹ (946–953 cm⁻¹), Si–O–Si symmetric stretching at around 800 cm⁻¹ (782–795 cm⁻¹) and the bending vibration of Si–O–Si groups at around 450 cm⁻¹ (434–451 cm⁻¹) were found in the FTIR spectra of all the hybrid gels under investigation (Fig. 5). The presence of these bands, and particularly of the bands at about 800 cm⁻¹ is an evidence of a considerable degree of polymerization of the silica fragments in the network [22–24].

The main band in the spectra of all silica gels occurring at about 1100 cm⁻¹, which corresponds to the asymmetric Si–O stretching vibrations, was shifted towards the lower wavenumber values of



Fig. 2. SEM images of hybrids: A (a), B (b), C (c) and D (d) at magnification of $50000 \times$.

about $1060-1070 \text{ cm}^{-1}$. This is indicative of a densification of the silicon-oxide skeleton [23, 25].

The bands derived from the vibration of water (OH– stretching at *ca.* $3341-3414 \text{ cm}^{-1}$, and H–O– H bending at *ca.* 1656 cm^{-1}) and those of organic matter (at *ca.* $1360-1577 \text{ cm}^{-1}$) were observed in the spectra of all the hybrid gels. These bands, indicating the presence of water and hydroxyl groups, as well as the bands originating from the organic part decreased in intensity with a higher temperature

of heat treatment (150 °C). This is characteristic of hybrid gels heated at relatively low temperatures. The peak corresponding to the symmetric stretching vibrations of $-CH_2-$, which was present at about 2980 cm⁻¹ in the spectra of the hybrids heated at 80 °C (Fig. 5) nearly vanished after heating at 150 °C and could be still observed as a very weak signal, but only in the spectrum of sample C. Such behavior can be attributed to densification taking place during the heat treatment [24, 25].



Fig. 3. Typical EDX spectrum obtained from the surface micro-area of sample C at magnification of $50\,000\times$.

The absorption band at *ca.* 2944 cm⁻¹, corresponding to the asymmetric vibration of C–H bonds in –CH₃ groups can be attributed to the traces of organic reagents. This absorption was weakly marked in all the gels heated at 80 °C and practically vanished after heating at 150 °C. The absorption at *ca.* 1575 cm⁻¹ (1577, 1571 and 1575 cm⁻¹, respectively) in the spectra of hybrid materials A, B and C was attributed to the carbonyl group (C=O) in the carboxylate moiety. Small peaks at *ca.* 1440 cm⁻¹ may have been triggered by the formation of coordinated bonds between the oxygen atoms of carboxylic groups (COO–) and the rare-earth ions [26, 27].

The absorption at about 1180 cm^{-1} was attributed to Si–O–C stretching vibrations. This absorption was greatly reduced in the spectrum of hybrid A and it was not marked in the spectra of hybrids B–D indicating that the majority of Si–O– C groups were eliminated during the condensation process between the Si–OH and Si–OCH₃ species.

In silica gels, the absorption band at about 950 cm^{-1} was attributed to the stretching vibrations of Si–OH and SiO⁻ groups [22, 23]. For the materials which additionally contained titanium oxide, this band can be superimposed onto the overlapped absorption caused by Si–O–Ti stretching modes [28, 29]. At low concentration, titanium introduced a new adsorption band on the low energy side of the principal silica absorption in the IR range of the spectrum, which was attributed to per-



Fig. 4. FTIR spectra of hybrid gels A–D heated at a temperature of 150 °C.



Fig. 5. FTIR spectrum of sample D typical of gels heated at 80 °C.

turbed vibrational modes involving Ti-O-Si bonds resulting from the substitution of Ti^{4+} for Si^{4+} [30]. In glasses, gels, hybrid materials and catalysts of the TiO_2 -SiO₂ system, the peaks at about 930- 960 cm^{-1} are commonly attributed to the absorption due to Si-O-Ti bonds, in which Ti ions have been introduced into four-coordinated sites [29-32]. In the case of the investigated hybrid gels, an intense absorption band, centered in the spectra of hybrid gels at about 946–953 cm⁻¹, can be assigned to Si– O-Ti vibrations, although, their being overlapped by those of Si-O-C bending modes of Si-bonded functional groups is also possible. The signals from metal-oxygen bonding vibrations (in this case, Ti-O-Ti and probably oxygen-bonded rare-earth metal ions) can appear in the range of 547-674 cm⁻¹. This was confirmed by the presence of other titanium-(and possibly, another metal-ion-) associated absorptions reported at about $650-730 \text{ cm}^{-1}$ [30, 32]. However, the absorption at about 670 cm^{-1} could be attributed to the out-of-plane deformation vibrations of C-H due to the organic groups introduced into the silica network, which indicate the hybrid organic-inorganic structure of the obtained gels [28]. The bands on the low wavenumber side at about 434- 451 cm^{-1} can be attributed to the bending vibrations of Si–O–Si, whereas the bands at 562–576 cm^{-1} – to O-M-O and/or Si-O ring (4).

The results of FTIR analysis indicate that in the case of sample D with a relatively small amount of the organic part, the inorganic network modified with titanium dominated. In the remaining samples, the organic-inorganic structure is possible owing to the incorporation of acrylate-derived groups into the silica network without phase separation. This was visible in the FTIR spectra of gels after the treatment at 150 °C. The FTIR spectrum of gel D was similar to the spectra of inorganic silica gels, where three main absorption bands derived from the vibration of Si-O- groups occur at about 1100, 800 and 450 cm^{-1} . In the case of samples A–C containing significant amounts of organic additions, FTIR analysis indicated that the polymerization of the silica network was less developed than in the case of gel D, and the bands derived from organic groups were marked more strongly in their spectra. However, in the spectra of all the gels, the main absorption



Fig. 6. ²⁹Si MAS NMR spectra of hybrid materials A– D heated at a temperature of 150 °C. The main peaks in the spectra correspond to Q², Q³ and Q⁴ structural units, corresponding to Si species in coordination 2, 3 or 4 with respect to the bridging oxygen atoms.

band corresponding to asymmetric Si–O stretching vibrations was shifted towards the lower wavenumber values of about 1060–1070 cm⁻¹, which confirmed the considerable degree of densification of the silicon-oxide skeleton.

3.2.2. ²⁹Si MAS NMR measurements

The results of ²⁹Si MAS NMR measurements and the spectra for the hybrid gels after heat treatment at 150 °C, are shown in Table 2 and Fig. 6, respectively. ²⁹Si MAS NMR spectra (Fig. 6) of the hybrid organic-inorganic gels exhibited peak profiles with different amounts of the Q⁴, Q³ and Q² structural units, corresponding to Si species in coordination 2, 3 and 4 with respect to the bridging oxygen atoms. The mean values of the peak posi-

	Q^2	Q ³	Q^4	A1 =	A2 =
G 1	$-\delta$, hwhm (ppm);	$-\delta$, hwhm (ppm);	$-\delta$, hwhm (ppm);	Q^4/Q^3	Q^4/Q^2
Sample	relative contribution	relative contribution	relative contribution		
	(%)	(%)	(%)		
А	-89.8 (4.0) 6	-99.8 (8.9) 45	-109.0 (9.4) 49	1.09	8.17
В	-92.1 (10.2) 17	-104.4 (5.9) 29	-109.0 (9.4) 49	1.86	3.18
С	-89.2 (8.1) 9	-100.5 (6.5) 38	-109.0 (10.2) 54	0.78	4.44
D	-92.8 (6.5) 8	-100.7 (5.5) 52	109.5 (8.6) 54	1.42	6.75

Table 2. Isotropic chemical shifts (δ , ppm), line widths (half width at half maximum: hwhm, ppm) and the relative contribution (%) of Qⁿ units in hybrid gels A–D.

tion corresponding to chemical shifts (δ) for Q², Q³ and Q⁴ species occurred at -91.3, -100.4 and -109.3 ppm, respectively. The positions of the peaks were nearly constant across the samples, but the relative intensities varied.

The analysis of the NMR results was based on the numerical values of the parameter A1 which was the ratio of Q^4/Q^3 and parameter A2 – the ratio of Q^4/Q^2 , calculated from the relative fractions of the peak area corresponding to the appropriate Qⁿ species (Table 2). The higher the values of A1 and A2, the higher the degree of poly-condensation of the silicon-oxygen network. The good agreement between NMR measurements and the results of FTIR spectroscopy indicates less developed polycondensation of the inorganic network in samples A and C. The main organic compound used as a precursor in hybrids A-C was butyl acrylate. Gel A was synthesized using a relatively large content of additional organic compounds (propylene carbonate, butyl methacrylate, ethyl acetate). Gel B additionally contained ethyl acetoacetate, while gel C was without additional organic additives. In the spectrum of gel D, the peaks from Q^3 and Q^4 species dominated and were clearly distinguished, indicating that this gel had the most advanced polymerization process. This is in good agreement with FTIR data. The relatively lower development of the inorganic network can be expected for hybrid gels with a significant amount of organic additives. Apart from the different amounts and different organic species, the derivatives of acrylic and acetic acid, (acrylates, and ethyl acetoacetate, which is acetoacetic acid ethyl ester) can also affect the polycondensation process due to the presence of carboxylic groups. Moreover, carboxylic groups were reported to reveal the cross-linking effect [33, 34]. Among other things, such an effect on the surface polymerization of the particles in silica gel has been observed by Boonstra et al. [35]. The presence of bonding with carboxylic groups was revealed in FTIR spectra of the obtained gels and in this case, the polycondensation process most likely overlapped with cross-linking polymerization. Another possible effect in the case of ²⁹Si NMR results, observed particularly for hybrid A, can be related to the slow relaxation due to the content of paramagnetic metal ions, which can complicate the interpretation of the data. Such an effect has been often observed in SiO2 and alkali silicate glasses, systems in which the magnetization recovery after the saturation initially follows a power law rather than being characterized by exponential behavior. This can make it difficult to obtain "fully relaxed" ²⁹Si spectra of silicates with slow relaxation, especially when it is caused by very low contents of paramagnetic impurities [36, 37].

3.3. Luminescence properties

The hybrid organic-inorganic materials obtained in this work were based on the TiO_2 – SiO_2 inorganic part of the hybrid matrices, while their organic parts differed in the content of such compounds as butyl acrylate, n-butyl methacrylate, ethyl acetoacetate, ethylene glycol dimethacrylate, ethyl acetate and propylene carbonate, which were used as precursors of the hybrid materials.

Rare-earth metal ions (RE^{3+}) introduced as dopants were: (Dy, Sm, Tb), (Sm, La), (Nd, Dy, Eu, Sm) and (Nd, Eu, Ce, La) for hybrid materials



Fig. 7. Luminescence spectra of hybrid material A doped with Dy^{3+} , Sm^{3+} and Tb^{3+} ions, obtained for the sample heated at a temperature of 150 °C.

A, B, C and D, respectively. The samples of these materials were heated at 150 °C in order to minimize the water (O-H oscillators) quenching effect [38, 39]. Based on the expected luminescence enhancement effect of the active rare-earth ions (Eu^{3+} , Tb^{3+} , Dy^{3+} , Ce^{3+} and Sm^{3+}) triggered by inert rare-earth ions, hybrid materials B and D were codoped with La^{3+} ions [40, 41]. Additionally, a small amount of zirconium ions in the form of zirconyl acetylacetonate was introduced into hybrid material C. The possible influence of Zr ion co-doping on photoluminescence properties was mainly attributed to the large ionic radius of Zr^{4+} (0.8 Å) compared with that of Si⁴⁺ (0.41 Å). Zr^{4+} can therefore be incorporated interstitially and can serve as an electron trap [42, 43].

Figs. 7–14 show the luminescence spectra of hybrid materials A, B, C and D obtained at room temperature for the samples previously heated for 3 hours at a temperature of 150 °C. The emission lines shown in Figs. 7–10 were obtained under excitation at wavelengths established as the maxima in the excitation spectra. The excitation and emission wavelengths were monitored at the positions of the main emission transitions and excitation lines. All the hybrid materials revealed relatively broad excitation bands in the UV and visible parts of the spectrum with the strongest peaking at *ca.* 200 nm.

The emission peaks observed for hybrid material A (Fig. 7) were obtained under excitation at wavelengths of about 256 nm, 330 nm, 530 nm and 715 nm and they corresponded to the tran-



Fig. 8. Luminescence spectra of hybrid material B doped with Sm³⁺ ions, obtained at $\lambda_{exc.} \sim 294-303$ nm for the sample heated at a temperature of 150 °C.



Fig. 9. Luminescence spectra of hybrid material C doped with Dy³⁺, Eu³⁺, Nd³⁺ and Sm³⁺ ions for the sample heated at a temperature of 150 °C.

sitions of Tb, Dy and Sm ions. The terbium ion transitions ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$ (J = 6.5) were observed in the green region of the spectrum at ca. 502 nm (electric dipole transition) and 552 nm (magnetic dipole transition), respectively. The emission line attributed to the ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ transition (at about 502 nm) seems to be overlapped with another band situated at wavelengths higher than the commonly reported terbium emission corresponding to this transition at about 480 nm to 505 nm [44]. This band in the emission spectrum probably originated from the upconversion in the presence of Sm^{3+} and Dy^{3+} ions or was triggered by the dopant metal ions situated interstitially in the host matrix. The emission lines centered at ca. 662 nm and 758 nm were attributed to ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{9/2} + {}^{6}F_{11/2}$ transitions of dysprosium ions, respectively [38]. The emission peak cen-



Fig. 10. Luminescence spectra of hybrid material D doped with Ce³⁺, Eu³⁺ and Nd³⁺ ions for the sample heated at a temperature of 150 °C.



Fig. 11. Luminescence spectrum of hybrid material A doped with Dy^{3+} , Sm^{3+} and Tb^{3+} ions, registered at $\lambda_{exc} \sim 205$ nm for the sample heated at a temperature of 150 °C.

tered at *ca.* 758 nm consisted of five components at 750.99 nm, 754.08 nm, 755.99 nm, 757.96 nm and 762.48 nm and it was very weak, probably due to strong self-absorption and energy transfer to the other emission centers. In the case of emission attributed to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$ transition of samarium ions with the peak centered at *ca.* 712 nm, we observed a strong overlap (almost without Stokes shift) between the excitation and emission spectra. The presence of two emission lines from terbium and dysprosium suggests that these ions can occupy two different places in the hybrid matrix [41]. The photoluminescence lines of hybrid material B doped with Sm³⁺ ions are shown in Fig. 8.

The emissions observed in Fig. 8 were registered at maximum wavelengths of the excitation spectrum, centered at about 298 nm, 322 nm, 358 nm, and 444.5 nm. The relatively broad and strong emission lines at about 599.75 nm, 644.50 nm, 714.25 nm and 884.98 nm corresponded to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}, \, {}^{4}G_{5/2} \rightarrow {}^{6}H^{9/2}, \, {}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$ and ${}^4G_{5/2} \rightarrow \, {}^6F_{1/2}$ transitions of the Sm^{3+} ion, respectively. The excitation line in Fig. 12(b) was monitored for ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ emission of Sm³⁺ ion at 560 nm. The broadening of the luminescence bands can be attributed to structural disorder. It indicates the presence of an amorphous phase, mainly in the hybrid material. Such a result is in a good agreement with the results of SEM/EDX and XRD examinations. Fig. 9 presents certain luminescence signals of hybrid material C doped with Dy^{3+} , Eu^{3+} , Nd^{3+} and Sm^{3+} ions. The excitation bands of hybrid material C were centered at ca. 219-222 nm, 337.75nm, 439.50-440.5 nm, 446.00 nm and 465 nm. The ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ emission of Dy^{3+} centered at *ca*. 668.23 nm split into several components peaking at about 666.83 nm and 671.35 nm, indicating the lowering of the local site symmetry of Dy^{3+} ions. The emission lines centered at 696.91 nm, 716.25 nm and 879.98 nm were attributed to ${}^5D_0 \rightarrow {}^7F_4$, ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transitions of Eu³⁺, Sm³⁺ and Nd³⁺ ions, respectively. The emission that dominated in the luminescence spectra of hybrid material C was a relatively strong red signal of the Sm^{3+} ions.

The luminescence emissions of hybrid material D doped with Eu³⁺, Ce³⁺ and Nd³⁺ ions under excitation with resonant wavelengths are shown in Fig. 10. The emission lines obtained under excitation at about 223 nm, 337.8 nm, and 440.50 nm are characteristic of ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transitions of Eu³⁺ and Nd³⁺ ions, respectively [38, 45]. Fig. 14(b) shows the excitation band of material D, monitored at $\lambda_{em} \sim 612$ nm, corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electric dipole hypersensitive transition of Eu³⁺ ions.

All the hybrid materials revealed relatively strong UV excitation bands in the wavelength range of 200–225 nm as well as the emission signals from ff electron transitions of all the luminescence-active RE^{3+} ions used as dopants, however, the intensi-



Fig. 12. Luminescence spectra of hybrid material B doped with Eu³⁺ and Nd³⁺ ions for the sample heated at a temperature of 150 °C: a) emission at $\lambda_{exc} \sim 215$ nm; b) excitation monitored at $\lambda_{em} \sim 560$ nm.

ties of emission lines varied. Figs. 11– 14 show the luminescence emission spectra of the hybrid materials excited at $\lambda_{exc} \sim 208$ nm, 205 nm, 220 nm and 215 nm for materials A, B, C and D, respectively. The luminescence abilities of the hybrid materials under excitation in the UV range of wavelengths were similar for all the materials.

Fig. 11 shows the emission spectrum of hybrid material A doped with RE^{3+} ions (Dy, Sm, Tb) under excitation at *ca.* 208 nm. As expected, the dominant emissions of the spectrum corresponded to ${}^{5}D_{3}$ and ${}^{5}D_{4}$ emitting levels of the terbium ions (${}^{5}D_{3} \rightarrow {}^{7}F_{J=5-1}$ band at *ca.* 400–432 nm and ${}^{5}D_{4} \rightarrow {}^{7}F_{3,2}$ at *ca.* 623 nm and 643.2 nm, respectively). The emission lines of significant intensity, corresponding to Dy^{3+} and Sm^{3+} ions can be seen in the visible and NIR range of the spectrum

 $({}^{4}G_{5/2} \rightarrow {}^{6}H_{13/2} \text{ and } {}^{4}G_{5/2} \rightarrow {}^{6}H_{15/2} \text{ transitions}$ in Sm³⁺ ions at *ca.* 787 nm and 880.5 nm, respectively, and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{5/2}$ transition of Dy³⁺ ions at *ca.* 840 nm). The presence of emission lines of samarium and dysprosium in the NIR spectral region together with far more intense visible emissions of terbium can be attributed to the effective energy transfer to the Tb³⁺ ions.

The emission spectrum of hybrid material B is shown in Fig. 12(a). Under UV excitation (excitation band peaked at about 205 nm), the intense emission line originated from the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ transition of Sm³⁺ ions and its splitting indicates the disordered structure of this material.

In the luminescence emission spectrum of hybrid material C doped with Dy^{3+} , Eu^{3+} , Sm^{3+} and Nd^{3+} ions, obtained under excitation at about 220 nm (Fig. 13), we can observe two prominent, broad emission bands of high intensity peaking at about 434–441 nm and 660–664.5 nm, respectively. The first band seems to be dominated by the emission bands originating from exciting the levels of Nd^{3+} ions lying in the UV range emitting at *ca*. 400 nm (${}^{2}F_{5/2} \rightarrow {}^{4}F_{5/2}, {}^{2}H_{9/2}$), 435 nm (${}^{2}F_{5/2} \rightarrow {}^{4}F_{9/2}$), 450–464 nm (${}^{2}F_{5/2} \rightarrow {}^{2}H_{11/2}$), and 480 nm (${}^{2}F_{5/2} \rightarrow {}^{4}G_{5/2}$) [38]. The second peak of this band situated at 455.93 nm can be attributed to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition of Dy^{3+} ions.

The peak of the upconversion emission of Nd^{3+} at 540.06 nm can be attributed to ${}^{2}\text{G}_{7/2} \rightarrow {}^{4}\text{I}_{9/2}$, while another upconversion emission peak at about 675 nm (${}^{4}G_{7/2} \rightarrow {}^{4}I_{13/2}, {}^{4}G_{5/2} \rightarrow {}^{4}I_{11/2}$) is likely to be overlapped with the emission band of Dy^{3+} ions (${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$, peak at 661.5 nm) [45, 46]. The line centered at 891.54 nm was attributed to the ${}^{4}F_{3} \rightarrow {}^{4}I_{9/2}$ emission of Nd³⁺ ions [43, 47]. The emission lines of Eu^{3+} and Sm^{3+} were weaker than those of Dy^{3+} ions. The lines in the spectrum at 618.54 nm and 650.16 nm can be attributed to a ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ hypersensitive electricdipole transition and to ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transitions of Eu^{3+} ions, respectively. The emission at 650.16 nm could be attributed to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition of Sm³⁺ ions, while the ${}^5D_0 \rightarrow {}^7F_3$ emission of Eu^{3+} ions overlap with the emission line of the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ transition of dysprosium (peaked at 661.51 nm in the second prominent band). The



Fig. 13. Luminescence spectrum of hybrid material C doped with Dy^{3+} , Sm^{3+} and Tb^{3+} ions, registered at $\lambda_{exc} \sim 205$ nm for the sample heated at a temperature of 150 °C.

energy transfer between samarium and europium influences the intensities of their emission bands [46]. The peak at 674.44 nm in the second prominent emission band can be attributed to the $^4F_{9/2} \rightarrow$ ${}^{6}\text{H}_{11/2}$ transition in Dy $^{3+}$ ions [44]. Due to the conditions of synthesis and poly-condensation process of the hybrid materials, particularly in the presence of a large amount of organics, partial reduction of europium and samarium ions is possible and must be taken into account. In such a case, the first prominent band can also overlap with the $4f^65d^1 \rightarrow 4f^7$ emission line of Eu^{2+} ions. The potential emission peaks of Eu²⁺ ions would be situated at 420 nm, 435 nm and 480 nm, and the peaks situated at these wavelengths would be visible in the spectrum of hybrid material C (Fig. 13) [48-50]. The emission line of Sm²⁺ was expected at about 686 nm, in which case it would overlap with other emission lines of the second prominent band. Under Hg lamp radiation, the color of this material changed to deep purple, which was in a good agreement with the emission lines in the luminescence spectrum recorded under excitation at wavelengths from the range of UV radiation.

Fig. 14(a) shows the luminescence emission spectra of europium-, neodymium- and cerium-doped hybrid material D under excitation at *ca*. $\lambda_{exc} \sim 215$ nm. Ce³⁺ is an efficient UV absorber and it also emits in the UV and blue region (5d(²D) \rightarrow ²F_{7/2,5/2}), depending on its concentration and the type of matrix [38, 51–54]. This is due to the fact



Fig. 14. Luminescence spectrum of hybrid material D doped with Eu³⁺ and Nd³⁺ ions for the sample heated at a temperature of 150 °C: a) emission at $\lambda_{exc} \sim 215$ nm; b) excitation at $\lambda_{em} \sim 612$ nm.

that the $5d^1 \rightarrow 4f^1$ transitions in Ce^{3+} ions are not orbitally forbidden (spin and parity allowed) [38, 41]. In the case of hybrid material D, the relatively wide emission band situated at about 370 nm with a shoulder extending to about 400 nm and another intense band at about 430 nm originated from Ce³⁺ ions (5d(²D) \rightarrow ²F_{7/2.5/2} transition) [51, 53]. Because of the low concentration of the Ce^{3+} ions (0.2 wt.%, 0.03 at.%) the reduction of emission intensity due to the cross-relaxation between neighboring Ce^{3+} ions was not observed. The $5d \rightarrow 4f$ transition of Ce³⁺ ions is known as very sensitive to the presence of other RE^{3+} ions in the host and the energy transfer from Ce³⁺ to other lanthanide ions is also depended on the structure of the host and its synthesis conditions [53, 55]. In the case of hybrid material D, apart from the complex main emission lines, we observed many weaker narrow lines originating from levels of Nd³⁺ ions lying in the UV range. The yellow to violet upconversion emission transition at about 401 nm from ${}^{4}D_{3/2} \rightarrow {}^{4}I_{13/2}$ or $^{2}P_{3/2} \rightarrow \,^{6}I_{11/2}$, blue emission transition at about 463 (${}^{4}D_{3/2} \rightarrow {}^{4}I_{15/2}$ or ${}^{2}P_{3/2} \rightarrow {}^{6}I_{13/2}$), and the ultraviolet emission transition at about 372 nm $({}^{4}D_{3/2} \rightarrow {}^{4}I_{11/2}, {}^{2}P_{3/2} \rightarrow {}^{6}I_{9/2})$ probably originated from the transitions in Nd^{3+} ions [55]. Additionally, the emissions in the visible spectrum range at about 538 nm, 606 nm and 675 nm can be attributed to ${}^4\text{G}_{7/2}
ightarrow {}^4\text{H}_{9/2}$ (green), ${}^4\text{G}_{7/2}
ightarrow {}^4\text{I}_{11/2}, \, {}^4\text{G}_{5/2}
ightarrow$ ${}^{6}I_{9/2}$ (orange) and ${}^{4}G_{7/2} \rightarrow {}^{4}I_{13/2} \; {}^{4}G_{5/2} \rightarrow {}^{4}I_{11/2}$ (red) upconversion emission transitions of Nd³⁺

ions [43, 57]. The emission lines in the range of 860-890 nm (split peaks in the wavelength range of about 860-880, the dominant at 869.48 nm) corresponded to ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ transitions in Nd³⁺ ions. These emission lines can be excited either by Nd^{3+} excitation signals or by the Ce^{3+} excitation band, because the excitation spectra of Ce^{3+} and Nd^{3+} emissions are almost identical in the range of 425-460 nm, with only minor exception in the range of 430–440 nm [54]. Since the energy transfer from Ce^{3+} to Nd^{3+} ions is always a typical resonant transfer, the sensitization of Nd³⁺ luminescence by Ce^{3+} ions depends on the overlapping of Ce^{3+} emission band with the absorption bands of Nd^{3+} ions [43, 54]. The emissions from 4f-4f transitions in Eu³⁺ ions arising from ⁵D₁ level \rightarrow ⁷F₀ and ⁵D₀ level \rightarrow ⁷F_I (J = 1 - 4) can be observed in the luminescence spectrum of hybrid material D at about 534 nm, 595 nm, 622 nm, 650 nm (overlapped in the emission band centered at 656.9 nm), and 694 nm, respectively [38, 43, 56]. The emission lines from the majority of transitions in Eu³⁺ ions are relatively weak under this excitation, with respect to the intensity of the prominent emission bands in the spectrum of material D. The decrease in luminescence intensity of Eu³⁺ in a compound containing both Ce^{3+} and Eu^{3+} ions can occur via a low energy transfer state (Eu^{2+}, Ce^{4+}) [58]. The lines at 410– 425 nm in the blue spectral region (with an overlapped shoulder in the green region at about 446 nm) could have originated from the transitions of Eu^{2+} ions. They can be attributed to the redox reaction of certain Ce and Eu ions during poly-condensation [48, 59]. However, the emission from the transitions of Ce^{3+} ions are not distinctly quenched and the strong emission band centered at ca. 656.9 nm could be attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transition in Eu^{3+} ions [38]. In hybrid material D co-doped with Eu^{3+} , La^{3+} , Nd^{3+} , and Ce^{3+} , the energy transfer could have more complicated character as a number of possible effects probably influenced the intensity of emission transitions.

Since the luminescence emission spectra of multi-doped hybrid materials consist of lines corresponding to numerous transitions, including those with low intensities, we omitted those lines in the emission spectra which were too weak or insignificant for the luminescence properties of hybrid materials. Additionally, in the multi-doped materials, certain parts of the emission bands can mix or overlap with other RE lines, making them undetectable by steady-state spectroscopy. For the pairs of such important adjacent elements as Sm–Eu, Tb–Dy, the analytical lines in the emission spectra are separated by no more than 30 nm. This makes it difficult to determine one of these elements in the presence of the other [60].

Due to the mild conditions of sol-gel processing, except for simple metal and silicon alkoxides which lead to the formation of an inorganic oxide network after hydrolysis, also (organo-alkoxy) silanes can be used to incorporate polymerizable organic substituents (epoxy, vinyl, and methacryloxy groups) into the final materials. This is due to the fact that Si–C bonds in these molecules are stable under lowtemperature synthesis [61–63].

Various experiments demonstrated that incorporating lanthanide complexes into sol-gel-derived materials can improve the luminescence properties of the corresponding lanthanide complexes and a variety of RE³⁺ complexes were successfully synthesized and incorporated into sol-gel-derived host matrices [8, 14, 15, 64–67]. The "antenna effect" due to intramolecular transfer of the absorbed energy to the active RE^{3+} ions can also be an effective mechanism of the luminescence enhancement [8–14]. Reisfeld et al. obtained a significant intensification of luminescence by incorporating europium ions into a cryptate cage, thus allowing energy transfer to Eu. This was achieved by the exchange interaction [14] and by doping sol-gel materials with luminescence dyes and sol-gel complexes with silver nanoparticles [15]. However, certain problems including possible water quenching, inhomogeneous dispersion of the components and the leaching of dopants in sol-gel hybrid materials, could not be avoided due to weak interactions between the dopants and silica gel [8].

In the case of this work, the organic additives were chosen so as to obtain a good dispersion of the dopants and to allow them to hydrolyze and polymerize with organic moieties and alkoxide precursors of the inorganic network originating from TEOS and titanium tetraisopropoxide. Additionally, a new synthesis procedure was successfully utilized, in which organic compounds of low molecular weight were used both as co-solvents for RE^{3+} inorganic salts and as organic precursors. The organic environment of the inorganic salts of metals could result in the formation of a hybrid structure at the molecular level, since molecular species are immediately capable of chemical bonding with oxygen atoms of the TiO₂–SiO₂ network through organic groups. We carried out multi-doping with active RE^{3+} , co-doping with La^{3+} (as inert lanthanide ion) and doping with Zr^{4+} ions (chelated in acetylacetonate compound).

The introduction of inert RE^{3+} ions (in this work, La^{3+}) together with RE^{3+} active luminescence centers is known for its luminescence enhancement effect, which takes place due to the intramolecular energy transfer and possible decreasing influence on the non-radiative transitions [8, 41, 68]. The organic surroundings of the rare-earth ions can prevent their energy loss due to collision with hydroxyl groups of water molecules, which lead to the quenching of luminescence [8, 68]. Acetylacetone (acac) used in sol-gel-derived systems doped with metal ions can improve the synthesis conditions and reduce the negative effect of hydroxyl groups [69]. The advantageous effect of acac groups on obtaining the longer distances between rare earth ions and residual OH groups has been reported in the sol-gel cordierite system [70]. In the case of synthesis of the hybrid materials, the addition of acetylacetone resulted in easier dissolving of both organic and inorganic species.

Apart from titanium and silicon alkoxides which led to the formation of an inorganic oxide network after hydrolysis, organic moieties were introduced into the hybrid materials in order to incorporate functional groups and acryloxy groups as polymerizable organic substituents, which in turn introduce Si–C [61].

The investigated hybrid materials proved to have remarkable luminescence properties owing to RE³⁺ luminescence active and inert ions introduced as dopants and co-dopants and despite the fact that the O–H oscillators from water molecules were revealed in the FTIR spectra. This can also be related to the preparation procedure of rare-earth salt solutions, which depend on using low-molecular-weight organic species both as solvents and as organic precursors of the hybrids, which is the novelty of this work. The emission lines from the active luminescence centers were narrow and of relatively significant intensity. The examination of the luminescence properties indicated the hybrid matrices obtained by sol-gel method using the inorganic part of the TiO₂-SiO₂ system as efficient hosts for the lanthanide ion doping, including simultaneous co-doping with a combination of different RE³⁺ ions. The examination of excitation and emission spectra revealed a significant possibility of controlling the photoluminescence emission of all the materials by varying the excitation wavelengths in the range of about 200 nm to over 400 nm. Additionally, the emission spectra of the hybrid materials were in a good correlation with the excitation bands lying in the range of 200 nm to over 500 nm. This means that the energy transfer to RE³⁺ centers through a host material is also possible [38, 46, 47]. The matrix hosts of the hybrid materials proved to be transparent and mechanically stable, which indicates that they can be applied to the designed luminescent materials, e.g. as up/down-converting light sources, electroluminescent films and luminescent concentrators [13, 18].

However, in the case of multi-doping with active and luminescence inert metal ions, an interaction between the metal ions can be expected. The results obtained in this work suggest that this interaction is rather complex and that the optical properties can be strongly influenced by a range of excitation wavelengths and possible energy transfers. The materials presented in this paper are still under investigation, therefore, a more detailed study of possible interactions is in progress and its results will be published in the near future.

4. Conclusions

Four hybrid organic-inorganic materials codoped with rare-earth ions (RE^{3+}) (where RE = Nd, Dy, Eu, Sm, Ce, La) were synthesized by sol-gel method and were examined with respect to morphology, structure and luminescence properties. All the materials characterized in this paper were based on hybrid organic-inorganic matrices with an inorganic oxide part of the TiO₂-SiO₂ system. Different metal-ion dopants and different organic compounds (such as butyl acrylate, n-butyl methacrylate, ethyl acetoacetate, ethylene glycol dimethacrylate, ethyl acetate or propylene carbonate) were used as organic precursors and solvents. The hybrid sol-gel materials were heat-treated at 150 °C in order to reduce the quenching influence of O-H oscillators and show their good luminescence properties in the visible and near-infrared region, which depend on the doping with active rare-earth metal ions. Different compositions of organic-inorganic hybrid hosts influenced the structure and thus the luminescence properties of the hybrid materials. The novel procedure consisting in the use of using organic compounds of low molecular weight both as solvents for dopants and as organic precursors was utilized to the preparation of the hybrid gels. Owing to this procedure, the dopants can homogeneously disperse in the TiO₂-SiO₂/organic matrix, and such negative effects as the clustering of RE³⁺ ions and water quenching of luminescence can be significantly reduced. Therefore, the hybrid materials exhibited relatively high intensities of luminescence emission despite the presence of hydroxyl groups revealed by FTIR spectroscopy. The examination of luminescence properties indicated that the hybrid matrices obtained by sol-gel method using an inorganic part of TiO₂-SiO₂ are efficient hosts for the doping of the lanthanide ions and the simultaneous codoping with a combination of different RE^{3+} ions. Moreover, the hybrid materials are transparent and have rigid structures, which can be applied in the designed luminescent materials, e.g. such as the up/down-converting light sources, electroluminescence films, and luminescent concentrators.

Furthermore, the hybrid materials co-doped with a combination of different RE^{3+} ions can be used as multicolor emitters, in which emission wavelength tuning can be obtained by varying the excitation wavelength.

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