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Investigation of Er, Er:Yb and Er:Tm systems in silica sol–gels

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Abstract

Complexes of the type $[Ln_2(Ala, Ile)_4(H_2O)_8](Cl)_6$ (Ala: alanine, Ile: isoleucine, Ln=Er^{3+}, Er^{3+}:Tm^{3+}, Er^{3+}:Yb^{3+}) were incorporated into silica sol–gels. The samples were transferred into glasses by heating in an N_2/CCl_4 and air atmospheres. Emission and absorption spectra for gels and glasses were measured and compared to those of the lanthanide precursor salt single crystals. Positions of broadened f–f bands of lanthanide ions make the resonance energy transfer between Er^{3+}, Yb^{3+} and Tm^{3+} much more probable. Intensity analysis was performed, values of oscillator strengths were determined and τ_λ parameters were calculated from the Judd–Ofelt relation. Intensity of erbium hypersensitive transition were used as a test of metal clustering.

Keywords: Er^{3+}; Er^{3+}:Tm^{3+}; Er^{3+}:Yb^{3+}; Sol–gel; Spectroscopy

1. Introduction

Sol–gel silica glasses doped with lanthanide ions are of current technological interest for a variety of applications including solid state lasers, optical waveguides and fiber amplifiers [1–3]. In particular, Er^{3+}-doped glasses are being considered for use as laser materials [4–6] and as amplifiers for optical communications [7]. Besides, Er^{3+}-silica glasses co-doped with Yb^{3+} [8] and Tm^{3+} [9] ions are being investigated as up-conversion laser materials because of the need for a solid state short-wavelength laser.

The sol–gel process offers an attractive way for preparing these materials at relatively low temperature without melting, and gives a possibility of control over the microstructure and composition of host matrix [10]. High concentration of hydroxyl groups that remain in sol–gel glasses is a disadvantage of the sol–gel method [10] because it limits the fluorescence efficiencies and shortens lifetimes of rare-earth dopant ions. Techniques leading to hydroxyl-free matrices include high temperature treatment in the presence of carbon tetrachloride [11] the or introduction of hydrofluoric acid to the initial solution [12]. Another problem encountered with the sol–gel process is rare-earth ion clustering [13], leading to concentration quenching of luminescence through cross-relaxation or energy transfer processes. Rare-earth clustering can be reduced by co-doping with Al^{3+} [14], encapsulation by organic ligands or by using organic salts instead of mineral acid salts as lanthanide precursors [15–19].

In this paper, we investigate optical properties of Er^{3+}, Er^{3+}:Yb^{3+} and Er^{3+}:Tm^{3+} co-doped silica gels and glasses obtained through sol–gel route. The mixed Er^{3+}:Yb^{3+} and Er^{3+}:Tm^{3+} single crystals with alanine and isoleucine were used as lanthanide precursors to study the up-conversion luminescence from separated pairs of lanthanide ions. The effect of Er^{3+}:Yb^{3+} and Er^{3+}:Tm^{3+} mutual contents on luminescence properties of silicate glasses is also discussed.

2. Experimental

Silica sol–gel samples were prepared using $Si(OC_2H_5)_4$ (TEOS), deionized water and methanol as a solvent. The molar ratio TEOS/water/methanol in the initial solution was 1:4:4. Small amounts of hydrochloric acid were added as a catalyst. Mixed Er^{3+}:Yb^{3+} and Er^{3+}:Tm^{3+} single crystals with alanine and isoleucine were used as a lanthanide precursors. The molar Er^{3+}:Yb^{3+} and Er^{3+}:Tm^{3+} ratios in the crystals were: 0.5, 0.2, 0.1, and 1, 2, 4, respectively. The crystals were grown from water solutions in which lanthanide chlorides and ligands were dissolved with molar ratios of 1. The initial solutions were mixed until homogeneous, cast in polypropylene vials, and left for gelation at room temperature. The gels were dried at 80°C over 24 h and the glasses were obtained by further heating in an oven up to 900°C, in an air or N_2/CCl_4 atmosphere.

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Concentration of erbium in the glass samples is expressed in terms of weight percent of Er_2O_3 that would be present in a fully densified SiO_2 glass in which water and organics are absent.

3. Results and discussion

Lanthanide ions form, in complexes with alanine and isoleucine, the dimeric units of the type Ln–O–C–O–Ln, in which M–M distances are 4.120 and 4.478 Å, respectively. The aim of this work was to investigate the effect of the dimeric structure on lanthanide ions distribution in glass and eventually up-conversion probability. Fig. 1 shows the single crystal spectra of $[Er_2(Ala)_4(H_2O)_8](Cl)_6$ and the same complex incorporated into silica sol–gel.

Both the spectra show similarities in the range of the hypersensitive transition of Er^{3+} ion. According to the earlier reported up-conversion of Er^{3+} systems, in which the dimeric units were formed, two metal centers are linked together by a ligand bridge. If so, when the dimeric units remain undisturbed in the gel, it can be a good way to promote up-conversion excitation. Recently, very important results were reported by Güdel [20]. Moreover, Peterson et al. [21] recorded the Er^{3+} up-conversion emission in the gels with relatively high concentration of water molecules. It leads to the conclusion that in some conditions the water molecules remaining in the gel do not effectively eliminate up-conversion excitation. Comparison of the hypersensitive transition intensities in both systems (the ratio $P^4G_{11/2}/P^4F_{7/2}$ is 3.09 and 2.69 for crystal and gel, respectively) confirms the similarities in the direct environment of two metal centers coupled in the dimer.

In our earlier investigations, we used intensity analysis to control the metal ion centers in gels and glasses. We showed that cluster formation at high concentrations leads to nonlinear changes of intensities of active ions transitions with their contents [19].

Figs. 2 and 3 show the typical absorption spectra of Er^{3+} doped silica gels and glasses also co-doped with Tm^{3+} and Yb^{3+}, at room temperature. In the wavelength range of 300–850 nm the spectrum of erbium consist of 11 absorption manifolds corresponding to transitions from the Er^{3+} ion ground state, $^4I_{15/2}$, to its excited states $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $(^2G, ^4F, ^2H)_{9/2}$, $^4G_{11/2}$, $^4G_{9/2}$, and $^2K_{15/2}$ levels. It is worth to notice that

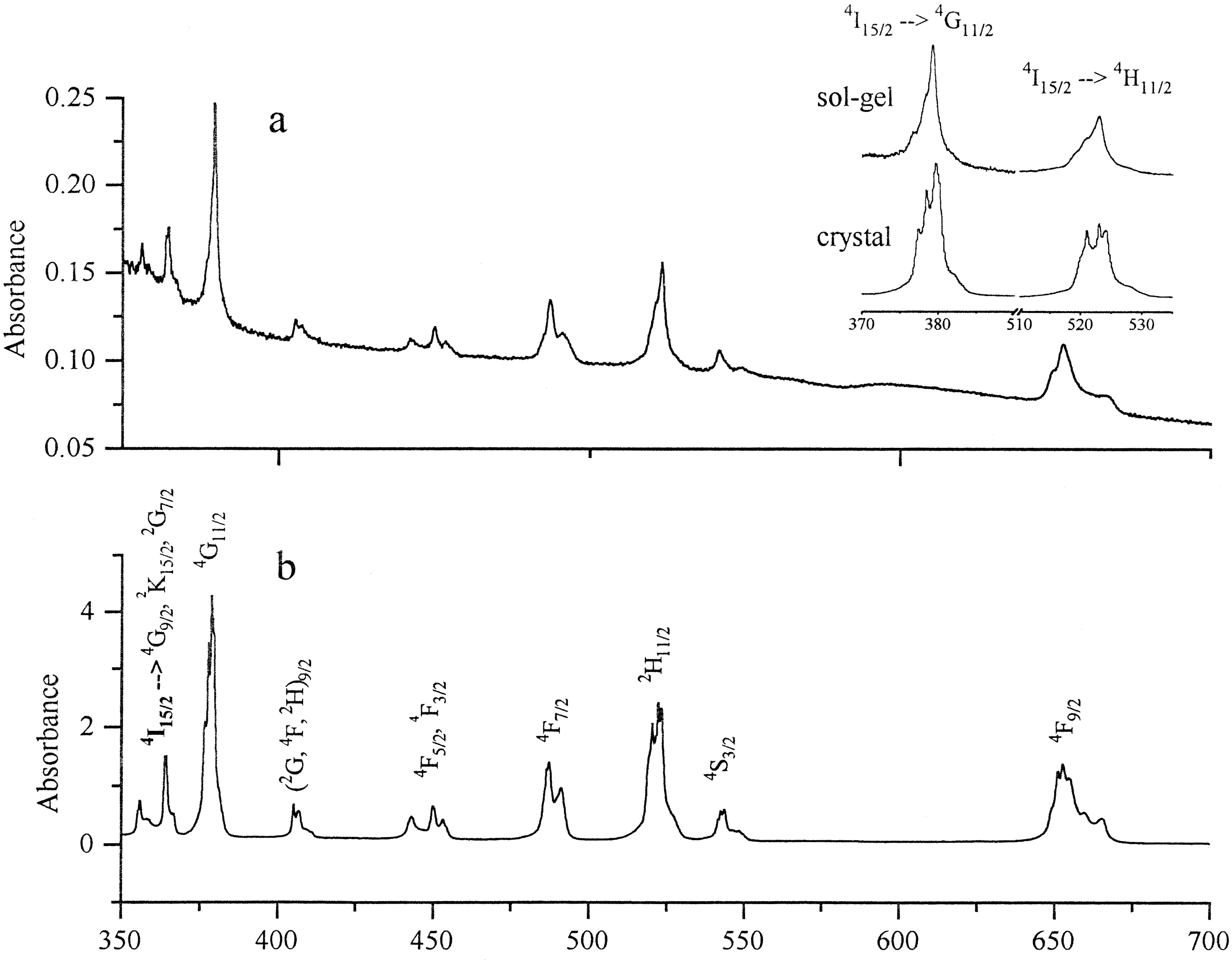

Fig. 1. Absorption spectra of $[Er_2(Ala, Ile)_4(H_2O)_8](Cl)_6$ incorporated into silica sol–gel (a) and single crystal (b).

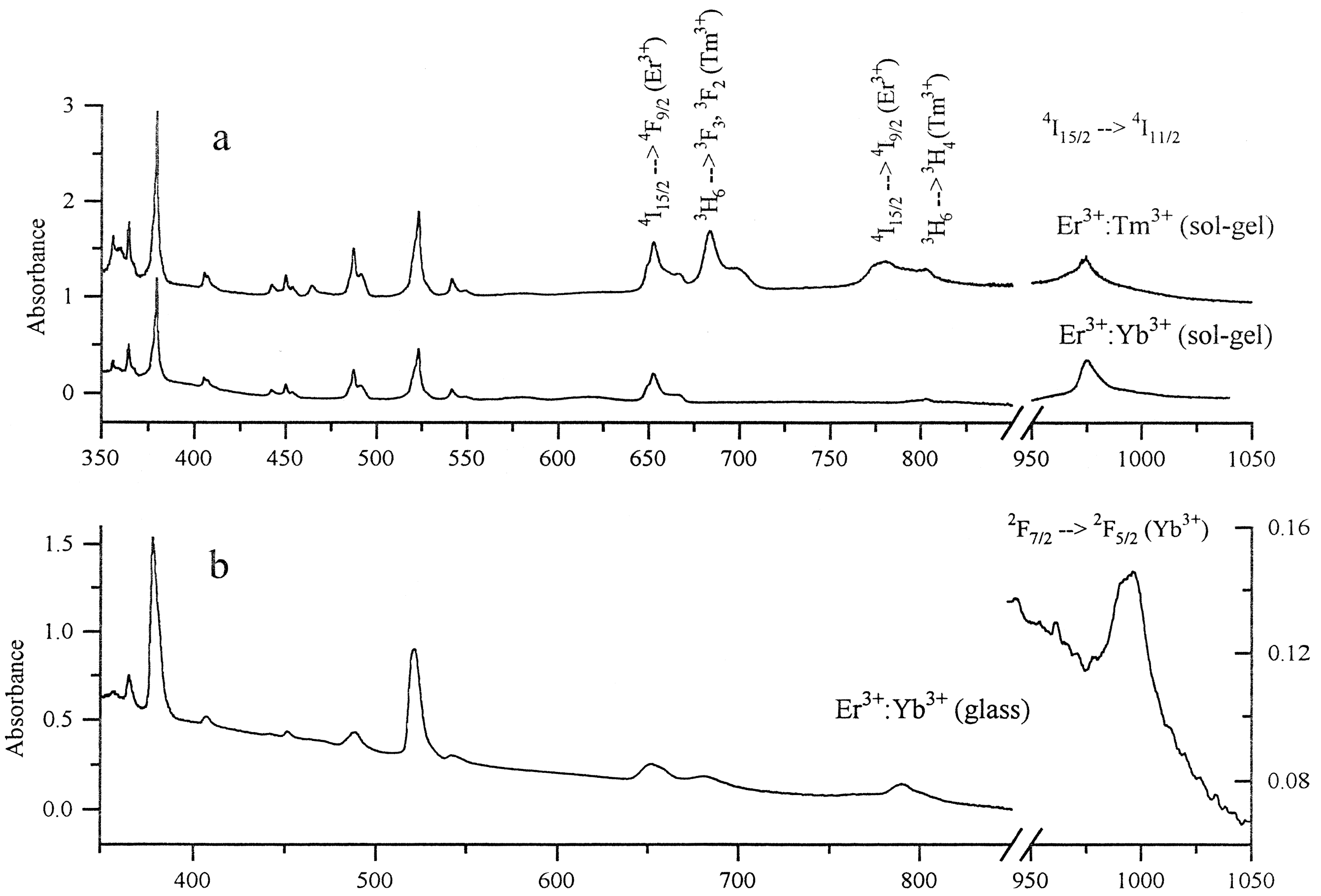

Fig. 2. Absorption spectra of Er^{3+}:Tm^{3+} and Er^{3+}:Yb^{3+} in silica glass.

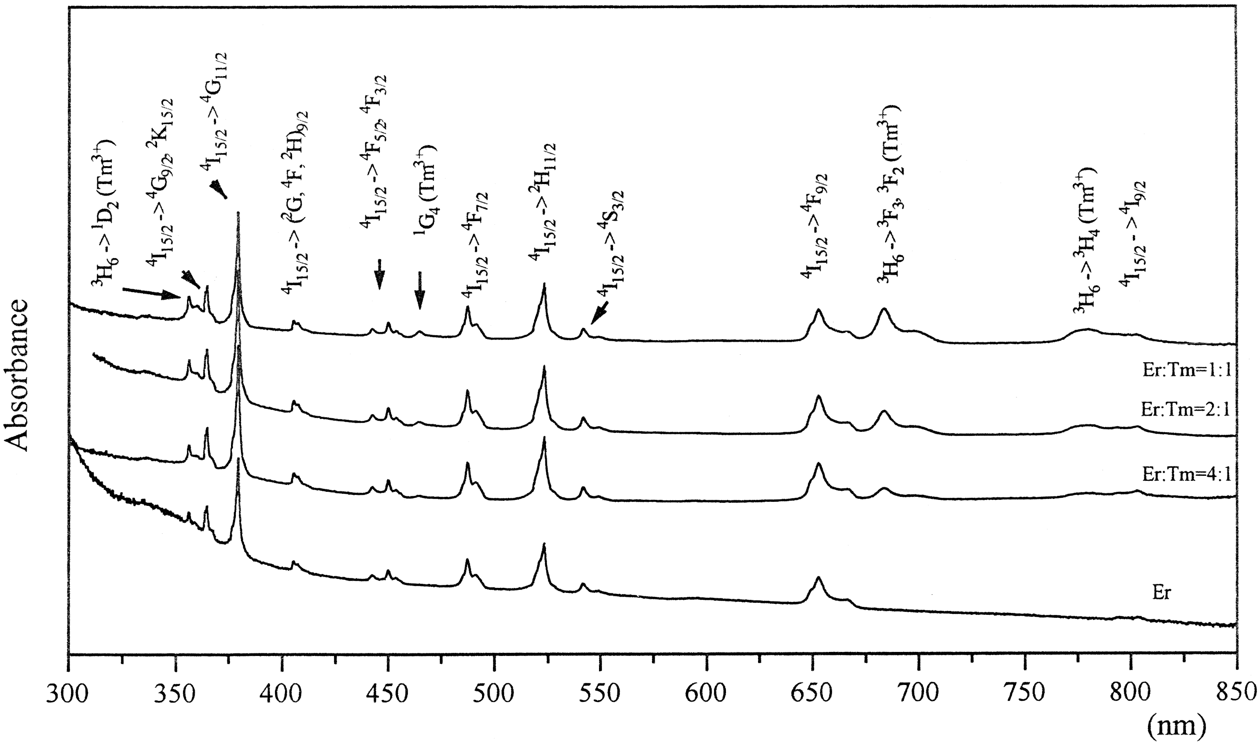

Fig. 3. Absorption spectra of silica sol–gels doped with Er^{3+} and co-doped with Tm^{3+} ions.

Table 1
Oscillator strength values for Er^{3+}, Tm^{3+} and Yb^{3+} co-doped gels[a]

Spectral range (nm)	Transition from $^4I_{15/2}$ level	Oscillator strength values ($P \times 10^8$)				
		Er/Tm 1:1		Er/Yb 1:2		Single crystal
		Ala $d=1.024$ cm	Ile $d=0.263$ cm	Ala $d=0.315$ cm	Ile $d=0.348$ cm	$cd=0.45$
249–258	$^4D_{7/2}$	245.38	–	–	–	–
258–261	$^2D_{5/2}$	55.68	–	–	–	–
271–277	$(^2H, {}^2G)_{9/2}$	35.34	–	–	–	–
361–369	$^4G_{9/2}$, $^2K_{15/2}$, $^2G_{7/2}$, $^1D_2$ (Tm^{3+})	119.28	115.83	87.71	85.69	374.51
369–388	$^4G_{11/2}$	163.57	152.07	281.75	279.45	930.62
398–415	$(^2G, {}^4F, {}^2H)_{9/2}$	17.47	18.04	36.44	38.33	116.33
435–459	$^4F_{5/2}$, $^4F_{3/2}$	27.25	29.11	54.13	55.93	179.00
480–500	$^4F_{7/2}$, $^1G_4$ (Tm^{3+})	98.41	97.77	64.76	63.53	301.48
505–535	$^2H_{11/2}$	73.43	77.23	139.78	141.68	493.82
535–556	$^4S_{3/2}$	13.31	16.62	24.41	26.84	83.00
633–676	$^4F_{9/2}$, $^3F_3$, $^3F_2$ (Tm^{3+})	144.88	149.23	89.78	131.69	305.22
775–833	$^4I_{9/2}$, $^3H_4$ (Tm^{3+})	68.25	68.25	13.46	50.81	38.76
926–1064	$^4I_{11/2}$	37.09	57.73	186.92	160.62	1255.24

[a] Total lanthanide ions concentration in starting solutions 0.01 M dm^{-3}; d = sample thickness, $c=1$; $(\tau_\lambda \cdot 10^9)$ $\tau_2=3.71\pm0.20$, $\tau_4=3.36\pm0.32$, $\tau_6=3.20\pm0.19$.

broadening of the f–f transition bands make the resonance energy transfer from Er^{3+} to Yb^{3+} (or from Er^{3+} to Tm^{3+}) much more probable. Intensity analysis was performed and values of oscillator strengths were calculated from the Judd–Ofelt relation (in the form given by Carnall et al. [22]):

$$P = \sum_{\lambda=2,4,6} \tau_\lambda \sigma \left(f^N \Psi_J \| U^{(\lambda)} \| f^N \Psi'_{J'} \right)^2 / (2J+1)$$

where $U^{(\lambda)}$ are matrix elements of unit tensor operator of the order λ, $f^N \Psi_J$ and $f^N \Psi'_{J'}$ are the initial and final states of electronic transitions, J is the total quantum number, σ is the wave number of the $\Psi_J \rightarrow \Psi_{J'}$ transition in cm^{-1}. The oscillator strength values of f–f transitions for chosen molar ratios, calculated for gels and glasses are collected in Tables 1–3. Nonadequate intensity changes with concentration indicate the cluster forming phenomenon (Table 3). This fact can either influence the up-conversion intensity enhancement or make the concentration quenching through the energy transfer processes or cross-relaxation more effective, what is favored by the energy levels structure of the Er^{3+} ions. Calculating the oscillator strength values we assumed $c=1$ (c = molar concentration), because than the changes of P_{exp} and concentration are adequate. The concentration of active

Table 2
Oscillator strength values for Er^{3+}, Tm^{3+} and Yb^{3+} doped gels

Spectral range (nm)	Er^{3+} transition (from $^4I_{15/2}$ level)	Oscillator strength values ($P \times 10^8$)					
		Tm^{3+} ($^3H_6$)	Yb^{3+} ($^2F_{7/2}$)	Er Ile $d=0.339$[a]	Er Ala $d=0.233$[a]	Tm Ile $d=0.331$ cm	Yb Ile $d=0.229$ cm
249–258	$^4D_{7/2}$	–	–	1025.2 (68.33)	1071.70 (71.81)	–	–
258–261	$^2D_{5/2}$	–	–	–	–	–	–
271–277	$(^2H, {}^2G)_{9/2}$	–	–	–	–	–	–
361–369	$^4G_{9/2}$, $^2K_{15/2}$, $^2G_{7/2}$	$^1D_2$	–	272.65 (16.42)	256.69 (15.28)	–	–
369–388	$^4G_{11/2}$	–	–	606.80 (40.94)	571.28 (39.86)	–	–
398–415	$(^2G, {}^4F, {}^2H)_{9/2}$	–	–	82.00 (5.010)	77.20 (4.74)	–	–
435–459	$^4F_{5/2}$, $^4F_{3/2}$	–	–	128.16 (9.24)	120.64 (8.79)	–	–
480–500	$^4F_{7/2}$	$^1G_4$	–	232.68 (15.17)	219.05 (15.80)	5.18	–
505–535	$^2H_{11/2}$	–	–	296.23 (23.80)	278.88 (24.48)	–	–
535–556	$^4S_{3/2}$	–	–	67.65 (5.29)	63.69 (5.58)	–	–
633–676	$^4F_{9/2}$	$^3F_3$, $^3F_2$	–	230.63 (17.00)	217.12 (16.66)	22.27	–
775–833	$^4I_{9/2}$	$^3H_4$	–	29.73 (1.47)	27.14 (1.39)	12.86	–
926–1064	$^4I_{11/2}$	–	$^2F_{5/2}$	86.10 (25.61)	81.06 (35.25)	–	71.04
1087–1299	–	$^3H_5$	–	–	–	2.63	–

[a] These values are calculated as a consequence of $^4G_{11/2}/^4F_{7/2}$ ratio and confronted with values of aquoion transitions; d = sample thickness, $c=1$. Er Ile: $(\tau_\lambda \cdot 10^9)$ $\tau_2=2.13\pm0.23$, $\tau_4=2.47\pm0.38$, $\tau_6=2.49\pm0.21$; Er Ala: $\tau_2=2.01\pm0.22$, $\tau_4=2.32\pm0.36$, $\tau_6=2.34\pm0.20$.

Table 3
Oscillator strength values for Er^{3+}, Tm^{3+} and Yb^{3+}doped glasses

Spectral range (nm)	Transition (from $^4I_{15/2}$ level)	Oscillator strength values ($P\times10^8$)							
		Ala				Ile			
		Er+Tm	Er+Yb			Er+Tm	Er+Yb		
		$d=0.302$[a] 1:1	$d=0.281$ 1:2	$d=0.407$ 1:5	$d=0.25$ 1:10	$d=0.386$ 1:1	$d=0.026$ 1:2	$d=0.334$ 1:5	$d=0.239$ 1:10
249–258	$^4D_{7/2}$	–	–	–	–	–	–	–	–
258–261	$^2D_{5/2}$	–	–	–	–	738.18?	–	–	–
271–277	$(^2H, ^2G)_{9/2}$	–	–	–	–	536.00	–	–	–
361–369	$^4G_{9/2}, ^2K_{15/2}, ^2G_{7/2}, ^1D_2$ (Tm^{3+})	119.27	49.01	25.56	13.85	96.36	53.88	24.55	16.94
369–388	$^4G_{11/2}$	360.96	368.24	194.95	129.43	331.73	367.33	188.43	125.78
398–415	$(^2G, ^4F, ^2H)_{9/2}$	18.78	13.99	8.41	–	15.08	17.00	4.33	2.55
435–459	$^4F_{5/2}, ^4F_{3/2}$	14.44	16.72	7.24	–	22.14	–	4.87	–
480–500	$^4F_{7/2}, ^1G_4$ (Tm^{3+})	63.78	36.07	15.66	12.23	31.33	27.07	17.17	7.00
505–535	$^2H_{11/2}$	193.71	179.44	95.36	63.54	169.29	180.90	96.52	60.69
535–556	$^4S_{3/2}$	12.00	–	–	–	10.35	27.53	12.82	10.29
633–676	$^4F_{9/2}, ^3F_3, ^3F_2$ (Tm^{3+})	110.87	30.27	24.21	–	91.61	30.45	25.14	19.98
775–833	$^4I_{9/2}, ^3H_4$ (Tm^{3+})	62.70	4.61	–	–	63.59	–	–	–
926–1064	$^4I_{11/2}$	8.32	229.64	95.86	283.13	34.34	410.24	289.33	168.24
1429–1613	$^4I_{13/2}$	9.24	–	–	0.87	–	–	0.93	–

[a] d = sample thickness (cm).

ions in the glasses, calculated approximately by comparison of P_{exp} values with that calculated by Carnall [22] for aquoions, reveal 45% increase of intensity in glasses in relation to aquoions ($^4I_{15/2}\rightarrow{}^4G_{11/2}$ — 592aq; — 606 in gels). These values are, however, lower than these in erbium molybdates and tungstates — 2660 and 2726, respectively. The results of the intensity analysis correlated with the energy transfer efficiency, determined from the lifetime measurements mainly in the mixed Er:Tm and Er:Yb systems, can help in explanation of complexity of the energy transfer and cross-relaxation processes, and finally make possible to reveal the mechanisms which enhances the up-conversion and is responsible for the most effective up-conversion process.

Fig. 4 shows the luminescence spectra of chosen systems in the range of $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$

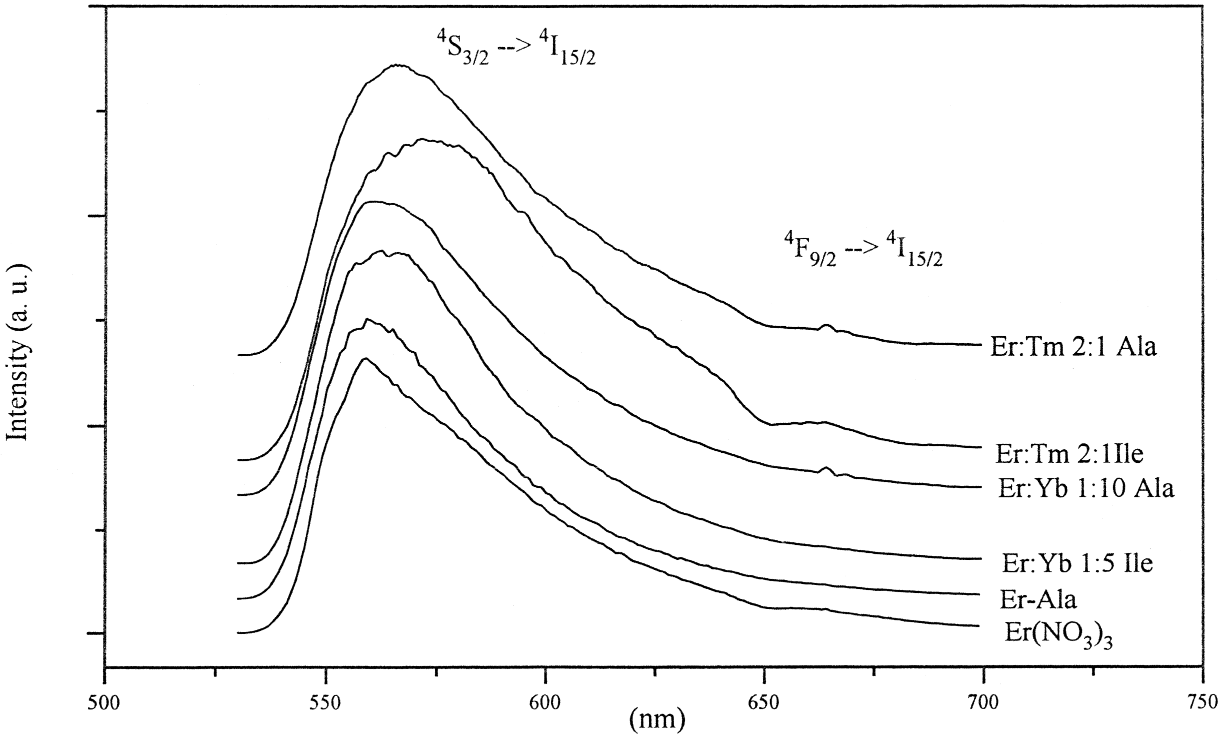

Fig. 4. Emission spectra of Er^{3+} doped glasses and co-doped with Yb^{3+} and Tm^{3+} ions.

transitions, obtained using 488 nm line of an argon ion laser (directly into $^4F_{7/2}$ level). The green up-conversion emission was not detected, when excited by 647.1 nm line of krypton laser, neither for glasses doped with organic complexes nor for that doped with inorganic salt. Moreover, the glasses prepared by heating in an N_2/CCl_4 atmosphere (900°C) did not exhibit the up-conversion emission, too. The up-converted emission from the $^4S_{3/2}$ and $^2H_{9/2}$ levels was not detected also for Tm^{3+} and Yb^{3+} co-doped glasses. Please note that $^4I_{15/2}\rightarrow{}^4I_{11/2}$ erbium absorption band is wider for Tm^{3+} co-doped systems than for Yb^{3+} ones (Fig. 2). In the latter $^2F_{7/2}\rightarrow{}^2F_{5/2}$ Yb^{3+} absorption band entirely overlaps the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ band of erbium (Fig. 2b).

The results presented above can be explained in the following way: either up-conversion excitation is less efficient than concentration quenching (and next series of glasses with lower concentration of active ions should be synthesized) or the dimer structure which is still present in gels becomes destroyed during conversion to glass and a new form is created. In fact, in mixed Er:Yb and Er:Tm glasses, multiphonon relaxation competes with cross-relaxation and energy transfer processes. Which of them could dominate, depends on the way used for preparation of gels and glasses. Thus, other concentrations of active ions and some modification of technology should be taken into account in the future investigations.

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