

Optical properties of fluorindate glasses doped with rare earth ions

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Multicomponent indium based fluoride glass singly doped with europium, terbium, holmium and thulium has been investigated using methods of optical spectroscopy. Owing to low energy of phonons available in the glass matrix, luminescent levels of rare earth ions are depopulated mainly by radiative transitions and nonradiative ion-ion interaction. The latter mechanism has been found to govern the relaxation dynamics of the 5D_2 , 5D_1 of europium, 5D_3 level of terbium, 5S_2 level of holmium and the 1D_2 , 1G_4 and 3H_4 levels of thulium when the activator concentration amounts to several mol%.

1. Introduction

Rare earth doped fluoride glasses have been studied extensively over past two decades. Owing to lower energy phonons as compared to oxide glasses, the multiphonon relaxation of excited states of rare earth ions in fluoride glass is strongly reduced thereby improving the luminescence efficiency. Following a discovery of fluoro-zirconate glass, referred to as ZBLAN [1], a number of other stable compositions have been reported. Among others, glasses based on indium and barium fluorides have been synthesised. One of them, based on fluorides of barium, indium, zinc, yttrium and thorium, referred to as BIZYT, deserves much attention [2], [3]. More recently, it has been found that the system $\text{InF}_3\text{-ZnF}_2\text{-BaF}_2\text{-SrF}_2$ may be stabilized by GaF_3 , GdF_3 , CaF_2 , NaF [4] to provide stable glasses of good optical quality. Optical spectra and upconversion phenomena in fluorindate glass doped with neodymium, thulium and erbium have been reported recently [5]–[7]. However, data concerning the excited state relaxation dynamics and processes contribution to the luminescence decay of indium based fluoride glasses doped with other rare earth ions are scarce.

In the present work, we investigate the influence of activator concentration on luminescence spectra and lifetimes of fluorindate glass doped with Eu^{3+} , Tb^{3+} , Ho^{3+} and Tm^{3+} with an intention to provide more detailed information on energy transfer processes involved. A set of experimental data gathered may be useful for an evaluation of optimal activator concentration in a material under study.

2. Experimental

The glass matrix under investigation has the following composition: $36\text{InF}_3-16\text{BaF}_2-20\text{ZnF}_2-20\text{SrF}_2-6\text{GaF}_3-2\text{NaF}$ (in molar %). In doped samples the InF_3 was substituted partially to obtain systems singly doped with luminescent ions of different concentrations. To prepare samples, anhydrous fluorides (99.99% purity, Aldrich) were mixed up and heated in an atmosphere of dry argon. Glasses were melted at 800°C in platinum crucibles, then poured into preheated copper moulds. Clear glass plates of about 2 mm in thickness were obtained. Optical absorption spectra were recorded with a Varian 2300 UV-VIS-NIR spectrophotometer. Luminescence has been excited with a third harmonic of a Nd:YAG laser or with a continuum optical parametric oscillator. The same sources were used to record luminescence decay curves. Luminescence was dispersed by a 1-meter double grating monochromator and detected with a photomultiplier with S-20 spectral response or with a cooled InSb detector. Luminescence spectra were recorded using a Stanford SRS 250 boxcar integrator connected to a personal computer. Luminescence decay curves were recorded and stored using a Tektronix TDS 3052 oscilloscope. All measurements were made at room temperature.

3. Results and discussion

Absorption spectra of fluorindate glasses singly doped with europium, terbium, holmium and thulium have been recorded at room temperature in 300 nm – 2100 nm spectral region. Based on these data the energy level schemes have been derived and depicted in Fig. 1. Luminescence spectra discussed below have been assigned with reference to energies of excited states as indicated in this figure.

3.1. Europium

Energy level structure of trivalent europium in the transparency region of the matrix consists of two groups of levels. The low energy group contains the 7F_J ($J = 0, \dots, 6$) multiplets of the ground 7F term with energies lower than 5500 cm^{-1} . The high energy group is composed of the 5D_J ($J = 0, \dots, 3$) multiplets lying between 17000 cm^{-1} and 25000 cm^{-1} . Excitation of any 5D_J level brings about a luminescence spectrum associated with the ${}^5D_J-{}^7F_J$ transitions. Distribution of luminescence line intensities, as well as the overall luminescence efficiency depend on the properties of a matrix and on the rare earth concentration. In the limit of low activator concentration the relaxation of an excited state is governed by radiative transitions and competitive nonradiative relaxation which involves a creation of

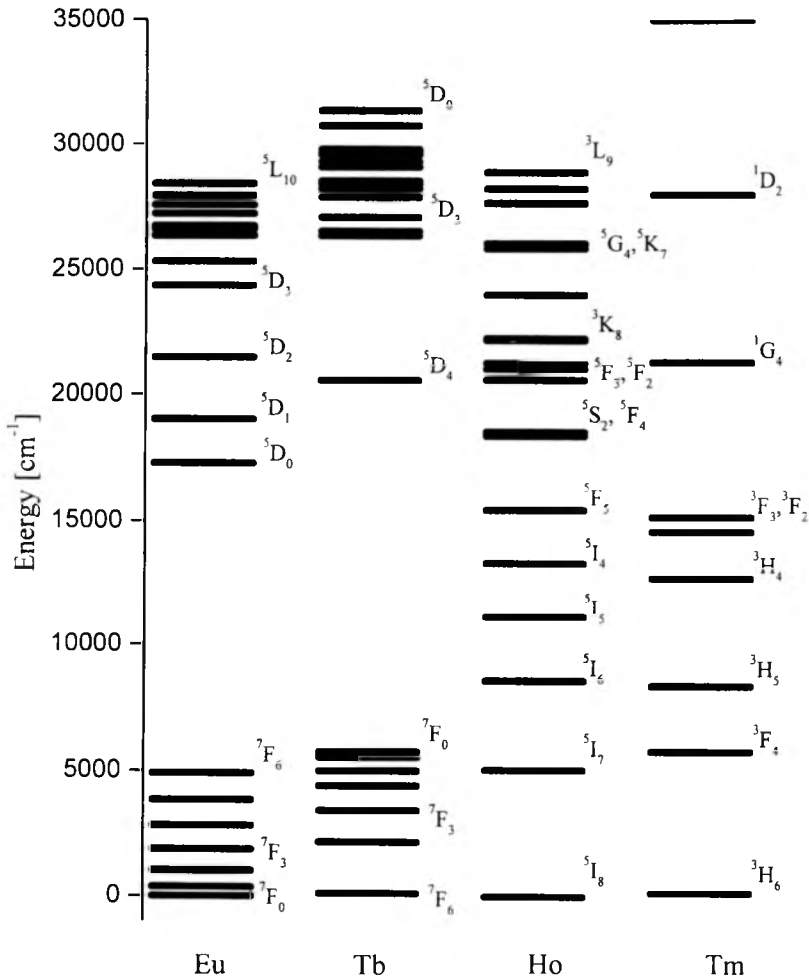


Fig. 1. Energy level schemes for Eu^{3+} , Tb^{3+} , Ho^{3+} and Tm^{3+} in fluoroindate glass.

phonons. The efficiency of the latter process decreases exponentially with increasing number of phonons needed to cover the energy gap between a luminescent level and the next lower level. Phonons available in the fluoroindate glass have relatively low energies ($< 500 \text{ cm}^{-1}$), therefore the contribution of multiphonon decay to the relaxation of excited states is strongly reduced with respect to oxide glass matrix. In Fig. 2, luminescence spectra recorded with fluoride glass samples containing 2% and 8% of Eu^{3+} are compared. The spectra were excited by a 459 nm line of an argon ion laser, resonant with the ${}^7F_0 - {}^5D_2$ transition. In the limit of low activator concentration the relaxation of an excited state is governed by radiative transitions and competitive nonradiative relaxation which involves a creation of phonons. Distribution of luminescence band intensities in spectrum recorded with a 8% Eu-doped sample is different. Bands associated with transitions from the ${}^5D_{1,2}$ levels

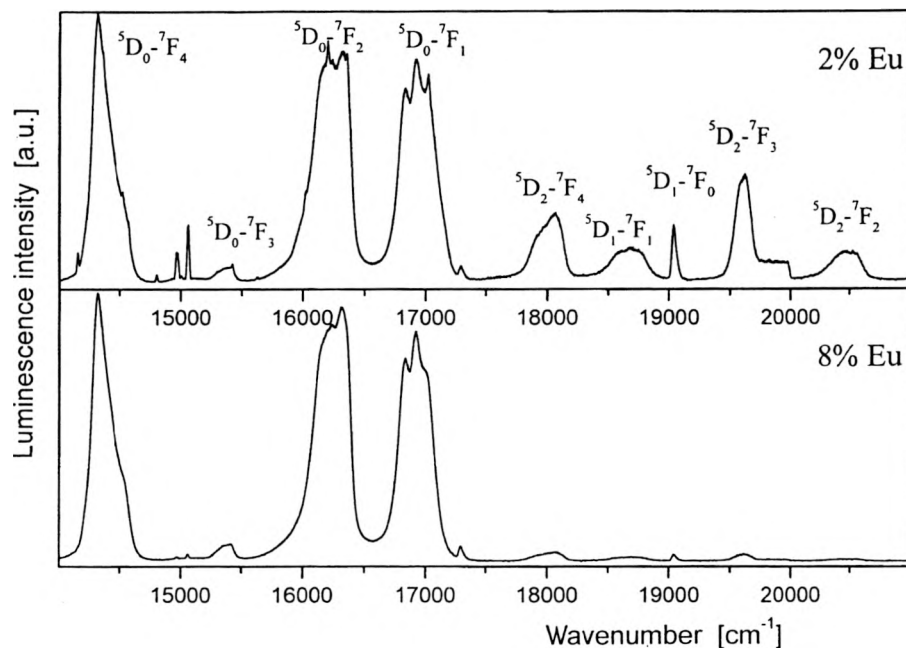


Fig. 2. Luminescence spectra recorded at 300 K with fluorindate glass containing 2% of Eu (upper) and 8% Eu (lower). Excitation into the 5D_2 level by a 459 nm line of an argon ion laser.

are negligibly small and the spectrum consists of bands assigned to the ${}^5D_0-{}^7F_J$ transitions. Influence of Eu concentration on luminescence spectrum is related to the contribution of activator-activator interaction to the relaxation of excited states. In this interaction the excitation may be removed by the so-called cross-relaxation process via intermediate levels in which an excited ion makes a downward transition and a coupled unexcited neighbour makes an upward transition. The rate of such nonradiative relaxation depends on separation between interacting ions and on energy mismatch between transitions involved. Strong quenching of luminescence is expected when transitions involved are resonant, whereas a weaker, temperature dependent quenching will be observed when the cross-relaxation is phonon-assisted. Examination of energy level scheme of Eu^{3+} reveals that the energy of the ${}^5D_2-{}^5D_0$ transition of about 4300 cm^{-1} is close to that of the ${}^7F_0-{}^7F_{5,6}$ transitions and the energy of the ${}^5D_1-{}^5D_0$ transition of about 1700 cm^{-1} matches that of the ${}^7F_0-{}^7F_3$ transition. Spectra shown in Fig. 2 give evidence that cross-relaxation processes are quite efficient in the system under study. In both processes the excitation is transferred to the 5D_0 level which decays radiatively because the energy level structure does not offer an upward transition close enough to be resonant and in addition the ${}^5D_0-{}^7F_6$ energy gap of about 12000 cm^{-1} is too large to involve multiphonon relaxation. It should be noted here that the energy separation between the 5D_2 , 5D_1 and 5D_0 levels is relatively small and these levels are coupled by multiphonon relaxation. To assess the rate of nonradiative relaxation samples containing considerably lower Eu concentrations should be examined.

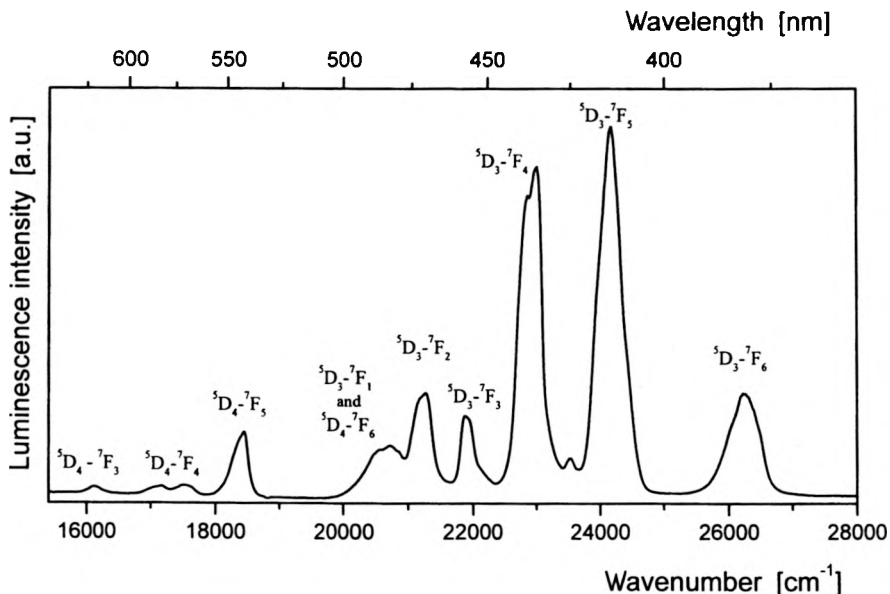


Fig. 3. Luminescence spectra recorded at 300 K with a fluorindate glass containing 0.1% of Tb. Excitation by a third harmonic of a Nd:YAG laser.

3.2. Terbium

Excitation of terbium doped glass with a third harmonic of a Nd:YAG laser brings about a reach luminescence spectrum in the 16000 cm^{-1} – 27000 cm^{-1} spectral range. Figure 3 shows the spectrum recorded with a 0.1%-doped sample. Assignment of bands has been made based on absorption data and decay kinetics. With increasing terbium concentration intensities of bands associated with transitions originating at the 5D_3 level decrease rapidly indicating the contribution of a self-quenching process. Figure 4 shows the time dependence of the 5D_3 luminescence intensity after short excitation for 0.1% and 1%-doped samples. Already in the 0.1%-doped sample the decay is not exponential indicating a contribution of ion–ion interaction, and the rate of luminescence quenching exceeds the rate of radiative decay in a 1%-doped sample. The self-quenching of the 5D_3 luminescence of terbium in crystals and glasses was investigated in the past. It was suggested that this phenomenon involved the cross-relaxation process in which an excited ion made the 5D_3 – 5D_4 transition and its unexcited neighbour made the 7F_6 – 7F_0 transition [8]. Recently, a new model which conserves the total parity has been proposed to account for the quenching by the cross-relaxation process mentioned above [9].

In contrast to the 5D_3 decay the 5D_4 luminescence is not influenced by the activator concentration in the limit of doping being investigated. Luminescence decay curves recorded with a 0.1%-doped sample and 1%-doped sample follow a single exponential time dependence with the same time constant of 4.44 ms. This value is considerably higher than 1.3 ms reported for a series of terbium doped fluorindate glasses containing alkali fluorides [10].

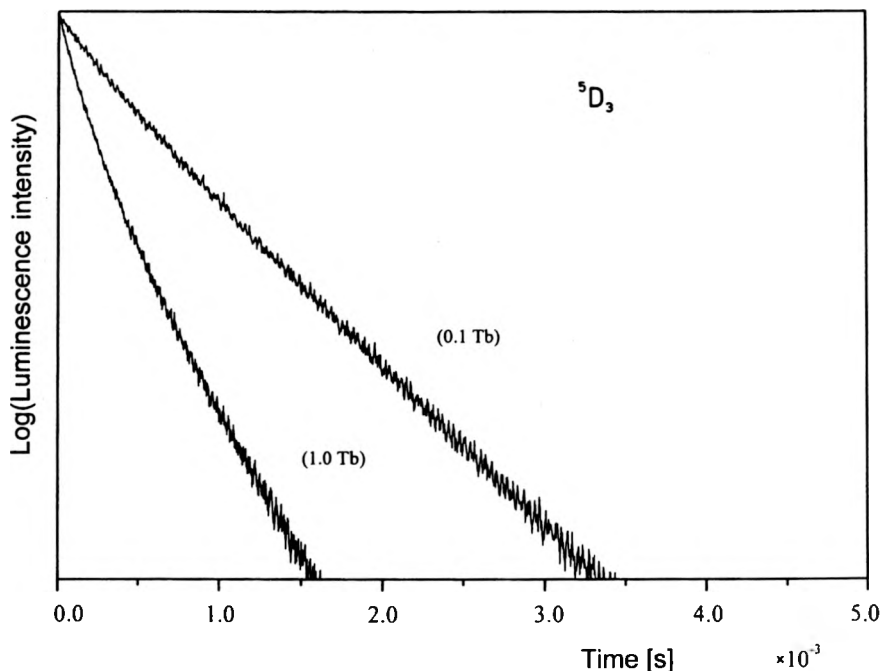


Fig. 4. Decay curves of luminescence originating in the 5D_3 level of Tb^{3+} recorded with samples containing different amounts of terbium.

3.3. Holmium

Results of investigation of holmium doped glass are considered as preliminary since luminescence decay curves are not yet available. As a first step the optical absorption spectra have been recorded at room temperature in the 4000 cm^{-1} – 25000 cm^{-1} spectral region. Areas under absorption bands have been calculated numerically and the values of oscillator strengths have been derived. For each of the experimental bands theoretical oscillator strengths have been expressed in terms of phenomenological intensity parameters as given by the theory of Judd and Ofelt. Next, the set of calculated oscillator strengths has been fitted to that derived experimentally. In

Table 1. Measured and calculated oscillator strengths for Ho^{3+} in fluoroindate glass.

Transition (from 5I_8)	Energy ν [cm^{-1}]	Oscillator strength $P \cdot 10^6$	
		Measured	Calculated
5I_7	5150	151	152
5I_6	8600	85	110
5I_5	11100	21	20
5F_5	15550	326	315
${}^5S_2, {}^5F_4$	18600	443	404
${}^5F_3, ({}^5F_2, {}^3K_8), {}^5G_6$	21600	1124	1124
5G_5	24050	287	318

Table 1, the results are given for intensity parameters $\Omega_2 = 1.28 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 3.00 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 2.02 \times 10^{-20} \text{ cm}^2$ which gave the best fit. With these data radiative transition rates and luminescence branching ratios for an emission originating in several excited states of Ho have been calculated and gathered in Tab. 2.

Table 2. Calculated radiative transition rates A_r , luminescence branching ratios β and corresponding radiative lifetimes τ_{rad} for Ho^{3+} in fluorindate glass.

Transition	Wavelength λ [nm]	A_r [s^{-1}]	τ_{rad} [μs]	β
${}^5F_4 - {}^5F_5$	3226	4	247	—
5I_5	1333	135	247	0.03
5I_6	1000	265		0.07
5I_7	744	377		0.09
5I_8	538	3275		0.81
${}^5S_2 - {}^5F_5$	3226	1	442	—
5I_5	1333	38		0.02
5I_6	1000	157		0.07
5I_7	744	879		0.39
5I_8	538	1189		0.52
${}^5F_5 - {}^5I_5$	2273	7	442	—
5I_6	1449	89		0.04
5I_7	966	406		0.18
5I_8	643	1762		0.78
${}^5I_5 - {}^5I_6$	4000	5	7194	0.04
5I_7	1681	76		0.54
5I_8	901	58		0.42
${}^5I_6 - {}^5I_7$	2899	16	5714	0.09
5I_8	1163	159		0.91
${}^5I_7 - {}^5I_8$	1942	68	14706	1.00

Figure 5 shows luminescence spectra recorded at room temperature in the $8000 \text{ cm}^{-1} - 16000 \text{ cm}^{-1}$ spectral region with samples containing 0.5% and 6% of holmium. For lower activator concentration the spectrum consists of one strong line associated with the ${}^5S_2 - {}^5I_7$ transition and considerably less intense line associated with the ${}^5S_2 - {}^5I_6$ transition. Line intensity ratio corresponds to luminescence branching ratios, presented in Tab. 2. For higher Ho content transitions originating at the 5F_5 , 5I_5 and 5I_4 levels were observed as well. These levels are not populated by multiphonon relaxation because corresponding energy gaps are large compared to energy of phonons. They are excited in heavily doped sample by cross-relaxation processes, which remove part of the 5S_2 excitation.

3.4. Thulium

Optical properties of trivalent thulium in fluorindate glass have been analysed in the framework of the Judd–Ofelt theory. Theoretical oscillator strengths have been

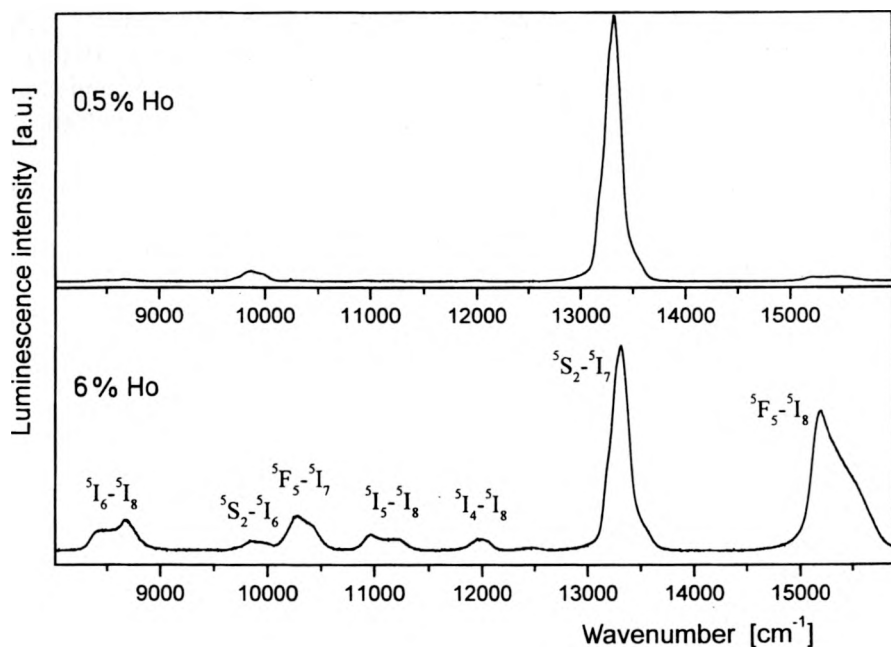


Fig. 5. Luminescence spectra recorded at 300 K with fluoroindate glass containing 0.5% of Ho (upper) and 6% Ho (lower). Excitation into the 5F_3 level by a 488 nm line of an argon ion laser.

Table 3. Measured and calculated oscillator strengths for Tm^{3+} in fluoroindate glass.

Transition (from 3H_6)	Energy ν [cm^{-1}]	Oscillator strength $P \cdot 10^8$			
		Without 3H_5		With 3H_5	
		Measured	Calculated	Measured	Calculated
3F_4	5850	165	167	165	169
3H_5	8300	—	—	164	137
3H_4	12850	191	182	191	192
${}^3F_3, {}^3F_2$	14700	317	322	317	343
1G_4	21300	69	50	69	50
1D_2	28000	231	208	231	209

Table 4. Values of the phenomenological parameters Ω_i [$10^{-20} cm^2$] for Tm^{3+} in fluoroindate glass.

Ω_i	Without 3H_5	With 3H_5
Ω_2	1.68	1.71
Ω_4	1.77	1.74
Ω_6	1.30	1.43

expressed in terms of three phenomenological Ω parameters and fitted to experimental oscillator strengths, which were derived from optical absorption spectra. Results

of the fitting procedure are given in Tab. 3, and the Ω parameters obtained are given in Tab. 4. In one of the calculation procedures the ${}^3H_6 - {}^3H_5$ transition containing a magnetic dipole contribution has been excluded but a minor improvement of the fit quality has been achieved only. Using the Ω parameters the radiative transition rates and luminescence branching ratios have been calculated. Results of calculation are collected in Tab. 5. Relaxation of excited states has been examined experimentally with glass samples containing 0.1% and 5% of Tm. Decay curves of luminescence originating at the 1D_2 and 1G_4 levels are shown in Fig. 6 and those originating at the

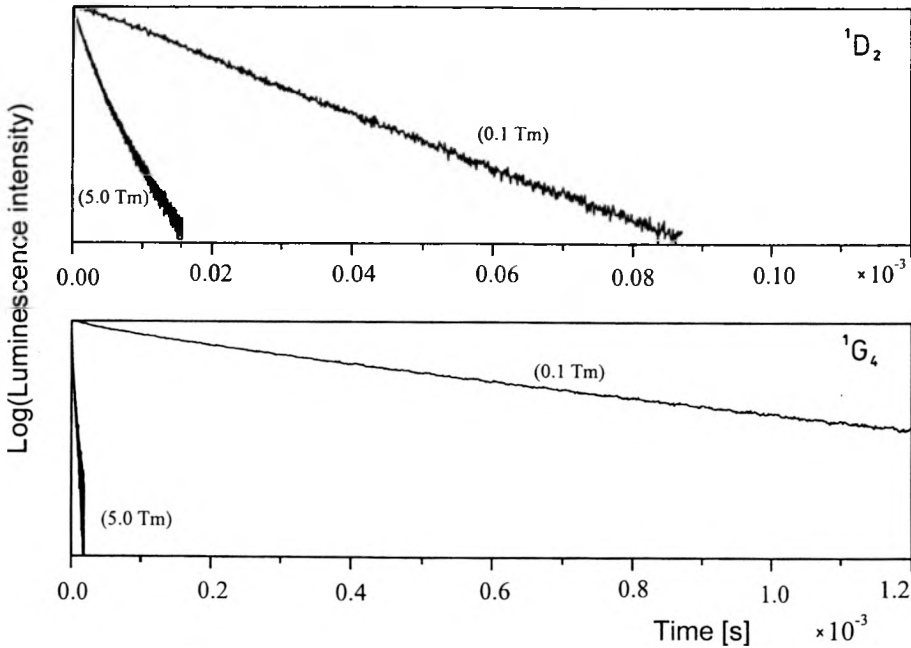


Fig. 6. Decay curves of luminescence originating in the 1D_2 level (upper) and the 1G_4 level (lower) of Tm^{3+} recorded with samples containing different amounts of thulium.

3H_4 and 3F_4 levels are shown in Fig. 7. For lower Tm concentration all decays follow a single exponential time dependence with lifetimes of 48 μs (1D_2), 634 μs (1G_4), 1.7 ms (3H_4) and 4.4 ms (3F_4). Considering the time dependence of decays and large energy gaps between luminescent levels, lifetimes given above are supposed to be close to radiative lifetimes. It can be seen in Tab. 3 that calculated radiative lifetimes do not differ drastically from experimental data except for the 3F_4 level, which decays faster than expected. With increasing Tm concentration the luminescence decays become accelerated and the corresponding decay curves deviate from a single exponential time dependence. In a 5% Tm-doped sample the 1D_2 decay at its final stage may be approximated by a time constant of 5 μs . Several cross-relaxation processes via the 1G_4 , 3F_3 , 3F_2 and 3H_4 levels may be involved in the quenching. The cross-relaxation is even more efficient in the case of the 1G_4 level since its lifetime recorded with a 5% Tm-doped sample is about 4 μs only. Another

Table 5. Calculated radiative transition rates A_r , luminescence branching ratios β and corresponding radiative lifetimes τ_{rad} for Tm^{3+} in fluorindate glass.

Transition	Wavelength λ [nm]	A_r [s^{-1}]		τ_{rad} [μs]		β
		Without ${}^3\text{H}_5$	With ${}^3\text{H}_5$	Without ${}^3\text{H}_5$	With ${}^3\text{H}_5$	
${}^1\text{D}_2 - {}^3\text{H}_6$	357	6345	6369	72	73	0.46
${}^3\text{F}_4$	451	5449	5528			0.40
${}^3\text{H}_5$	508	79	86			0.01
${}^3\text{H}_4$	660	769	818			0.05
${}^3\text{F}_3$	746	413	416			0.03
${}^3\text{F}_2$	781	587	581			0.04
${}^1\text{G}_4$	1493	80	80			0.01
${}^1\text{G}_4 - {}^3\text{H}_6$	470	491	493	854	815	0.42
${}^3\text{F}_4$	647	108	115			0.09
${}^3\text{H}_5$	769	418	454			0.36
${}^3\text{H}_4$	1183	107	115			0.09
${}^3\text{F}_3$	1493	37	40			0.03
${}^3\text{F}_2$	1639	10	10			0.01
${}^3\text{F}_2 - {}^3\text{H}_6$	658	505	556	1098	1025	0.55
${}^3\text{F}_4$	1070	221	226			0.24
${}^3\text{H}_5$	1449	180	189			0.20
${}^3\text{H}_4$	4255	25	5			0.01
${}^3\text{F}_3$	16667	<1	<1			—
${}^3\text{F}_3 - {}^3\text{H}_6$	685	1570	1665	573	542	0.90
${}^3\text{F}_4$	1143	45	50			0.03
${}^3\text{H}_5$	1587	128	128			0.07
${}^3\text{H}_4$	5714	2	2			—
${}^3\text{H}_4 - {}^3\text{H}_6$	778	647	686	1375	1304	0.89
${}^3\text{F}_4$	1429	60	62			0.08
${}^3\text{H}_5$	2198	20	19			0.03
${}^3\text{H}_5 - {}^3\text{H}_6$	1205	158	166	6250	5988	0.99
${}^3\text{F}_4$	4082	2	1			0.01
${}^3\text{F}_4 - {}^3\text{H}_6$	1709	123	125	8104	8000	1.00

important process in which an excited Tm ion undergoes the ${}^3\text{H}_4 - {}^3\text{F}_4$ transition and its coupled neighbour undergoes the ${}^3\text{H}_6 - {}^3\text{F}_4$ transition removed efficiently the excitation of the ${}^3\text{H}_4$ level. It can be seen in Fig. 6 that the Tm concentration influences the ${}^3\text{F}_4$ lifetime, too. The reason of this quenching is not clear because there are no cross-relaxation schemes involved. One possible explanation is migration accelerated energy transfer to traps such as defects or unintentional impurities.

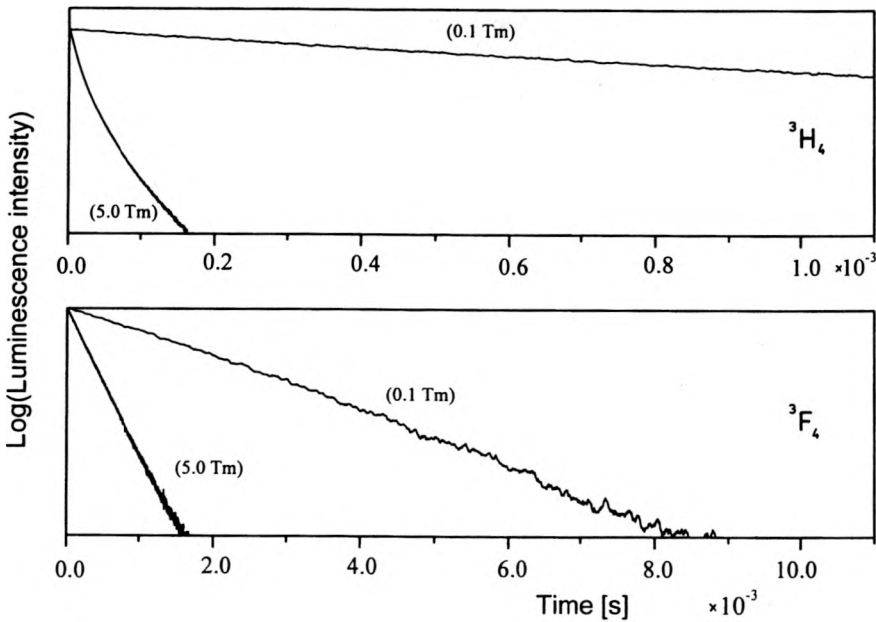


Fig. 7. Decay curves of luminescence originating in the 3H_4 level (upper) and the 3F_4 level (lower) of Tm^{3+} recorded with samples containing different amounts of thulium.

4. Conclusions

Owing to low energy of phonons in the fluorindate glass under study an efficient luminescence may be recorded with samples containing Eu, Tb, Ho and Tm. Processes governing a population build up and relaxation of excited states consist of radiative transitions, multiphonon relaxation and ion-ion nonradiative energy transfer. The latter process contributes critically to the relaxation of the majority of luminescent levels in systems being investigated. Consequently, a discrimination of unwanted luminescence channels or enhancement of desired emission lines can be accomplished by a proper choice of activator concentration.

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