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Optical properties of Nd^{3+}-doped glasses

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Absorption and luminescence spectra are reported for Nd^{3+}-doped silicate, phosphate, borosilicate, and tellurite glasses. In particular, the host effect on radiative and nonradiative relaxations is investigated.

1. Introduction

Since discovery of laser emission in Nd^{3+}-doped glasses a great effort in studying optical properties of noncrystalline materials has been observed [1]. The excellent luminescence properties of this ion offer a broad optical applications in quantum electronics, optoelectronics and quite recently in luminescent solar concentrators [2]. In this paper we present a comparative study on Nd^{3+}-doped silicate, phosphate, borosilicate, and tellurite glasses. The Nd^{3+} ion transition intensity and, in particular, the hypersensitivity of the $^4G_{5/2}$ band are analyzed. The effect of glass composition on radiative and nonradiative transition is discussed.

2. Experimental

2.1. Glass samples

The compositions of basic glasses are the same as those in Cr^{3+}-doped glasses [3]. The glasses are doped with 3 wt% of Nd_2O_3.

2.2. Measurements

The apparatus used were described in the first paper of this series [3]. Emission spectra were excited with 514.5 nm line of argon ion laser (Tab. 1).

Table 1. Concentration of Nd(III) ions and refractive indexes

No.	Type	$\varrho \times 10^{20}$ [ions/cm^3]	n_D
52	K-Ba-silicate	2.96	1.54
62	Na-Cd-silicate	3.11	1.55
67	Phosphate	2.66	1.50
77	Tellurite	5.33	2.1
82	Borosilicate	2.55	1.52

3. Results and discussion

The absorption spectra of Nd^{3+}-doped silicate, phosphate, borosilicate, and tellurite glasses are shown in Fig. 1. The oscillator strengths of all measured glasses are listed in Tab. 2. The absorption spectra are similar and the principial difference is

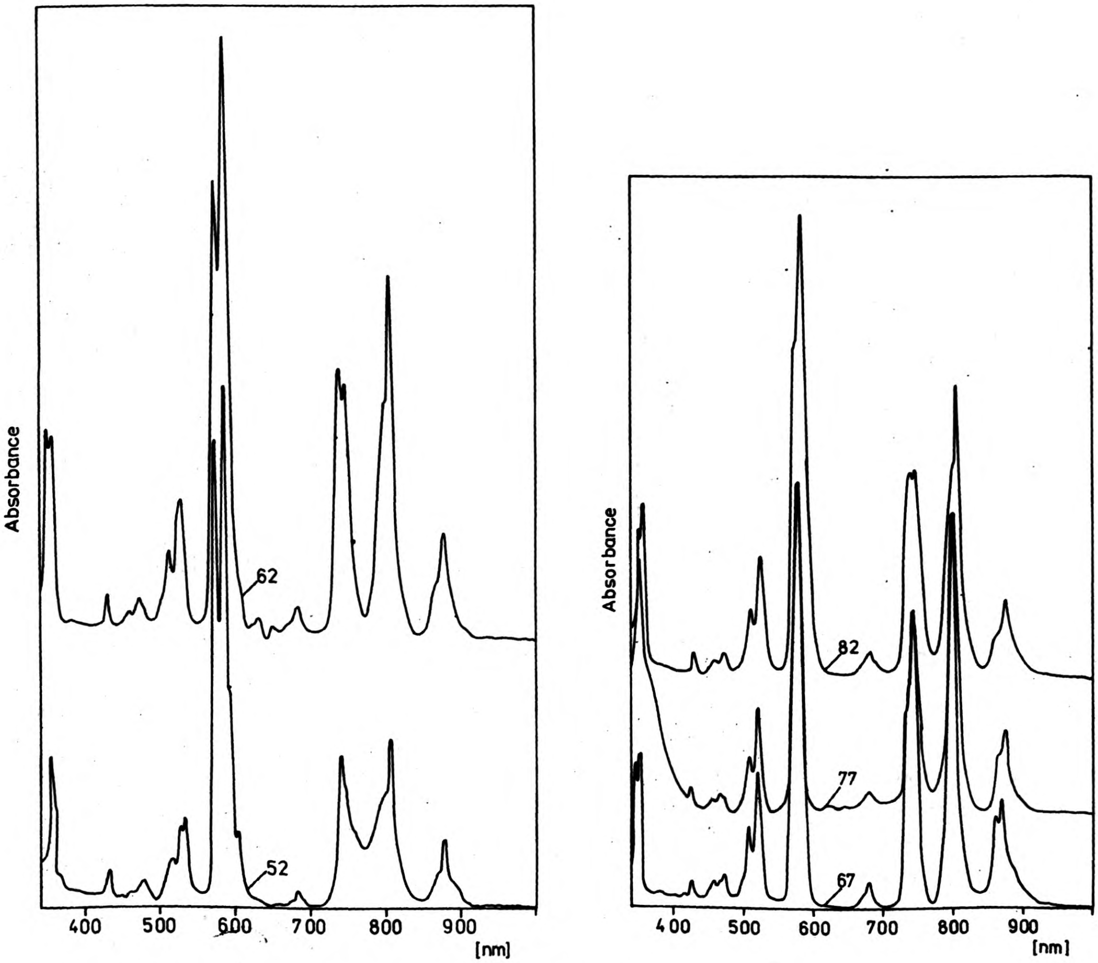

Fig. 1. Absorption spectra of 3 wt% Nd_2O_3-doped glasses

noticed for the $^4G_{5/2}$ band which is changed most intensively. From the data in Table 2, it is clear that oscillator strength of that band increased along the series: silicate < phosphate < borosilicate < tellurite. The intensity of particular f–f transition is given by the Judd–Ofelt expression [4], [5]

$$P_{JJ} = A \sum_{\lambda = 2,4,6} \Omega_\lambda \langle J \| U^\lambda \| J' \rangle^2 \quad (1)$$

Table 2. Measured oscillator strengths

Band	Wavelengths [nm]	Oscillator strengths $P \times 10^8$				
		62	52	67	82	77
$^2L_{15/2}$, $^4D_{1/2}$, $^2I_{11/2}$, $^4D_{5/2}$, $^4D_{3/2}$	370–343	801.45	473.22	625.90	804.92	–
$^2D_{5/2}$	442–420	39.44	24.31	29.27	26.24	92.82
$^4G_{11/2}$, $^2D_{3/2}$, $^2G_{9/2}$, $^2K_{15/2}$	488–448	83.91	58.45	118.57	103.03	92.82
$^4G_{9/2}$, $^4G_{7/2}$, $^2K_{13/2}$	548–492	418.88	253.96	422.50	461.40	705.91
$^2G_{7/2}$, $^4G_{5/2}$	618–556	1605.96	1114.26	1152.21	1623.26	2329.24
$^4F_{9/2}$	698–664	28.97	22.95	33.10	31.63	53.55
$^4S_{3/2}$, $^4F_{7/2}$	774–718	431.38	208.06	518.60	494.09	718.70
$^2H_{9/2}$, $^4F_{5/2}$	844–776	464.47	225.44	519.65	465.80	759.14
$^4F_{3/2}$	912–848	131.78	67.82	140.63	152.45	226.42

where

$$A = (n(n^2+2)^2/9)\frac{8\pi^2 mc}{3h}, \tag{2}$$

and

$$\Omega_\lambda = \Sigma_{p,t}|A_{tp}|^2 \Xi^2(t,\lambda)(2t+1)^{-1}. \tag{3}$$

Using as a basis for the intensity analysis the set of oscillator strength given in Table 2, we have performed the least squares fitting of Ω_λ parameters. These parameters involve information on microscopic features of the environment. They are summarized in Table 3. It can be noticed that most remarkable variation is observed for the Ω_2 parameter. The set of empirically determined Ω_λ parameters may be used to predict the transition probabilities in emission.

The emission spectra of Nd^{3+}-doped silicate, phosphate, borosilicate, and tellurite glasses are shown in Fig. 2. The fluorescence of Nd^{3+} ion originates totally from the $^4F_{3/2}$ level. The peaks corresponding to the $^4F_{3/1} \rightarrow {^4I_{9/2}}$ and $^4F_{3/2} \rightarrow {^4I_{11/2}}$ transitions are located at 11100–11700 cm^{-1} and 9000–9800 cm^{-1}, respectively.

The fluorescence lifetimes and fluorescence branching ratios are listed in Table 4. It can be noticed that the measured lifetime was the longest in silicate glasses and the shortest in tellurite glass.

As it is know the reciprocity of fluorescence lifetime is determined by the sum of radiative and nonradiative transition probabilities

$$\tau^{-1} = k_R + k_{NR} \tag{4}$$

where k_R is the radiative rate constant which may be determined from Eq. (1), k_{NR} is the nonradiative rate constant associated with the multiphonon relaxation interionic interaction. The multiphonon transition rate for lanthanide (III) ions may be

Table 3. Ω_λ parameters

Glass no. / Parameter Ω_λ	52	62	67	77	82
$\Omega_2 \times 10^{20}$ cm^{-1}	3.20±0.07	4.31±0.08	3.01±0.26	3.87±0.17	4.58±0.16
$\Omega_4 \times 10^{20}$ cm^{-1}	1.84±0.06	3.08±0.07	2.46±0.23	3.74±0.29	2.92±0.15
$\Omega_6 \times 10^{20}$ cm^{-1}	1.49±0.09	3.12±0.11	4.32±0.34	3.18±0.14	3.75±0.21

Table 4. Radiative transition probabilities, fluorescence branching ratios, radiative and experimental lifetimes

Transition	λ [nm]	52		62		67		77		82	
		A [s^{-1}]	β_c	A [s^{-1}]	β_c	A [s^{-1}]	β_c	A [s^{-1}]	β_c	A [s^{-1}]	β_c
$^4F_{3/2} \rightarrow {^4I_{9/2}}$	0.88	440	0.47	783	0.43	644	0.36	2644	0.46	731	0.40
$\rightarrow {^4I_{11/2}}$	1.06	426	0.45	854	0.47	949	0.53	2625	0.46	909	0.50
$\rightarrow {^4I_{13/2}}$	1.35	76	0.08	162	0.09	201	0.11	474	0.08	182	0.10
$\rightarrow {^4I_{15/2}}$	1.88	3	0.004	8	0.004	9	0.005	22	0.004	9	0.005
		945		1887		1803		5765		1831	
Radiative luminescence lifetimes of $^4F_{3/2}$ level [μs]		1058		553		554		173		546	
Experimental lifetimes [μs]		270		230		76		82		41	

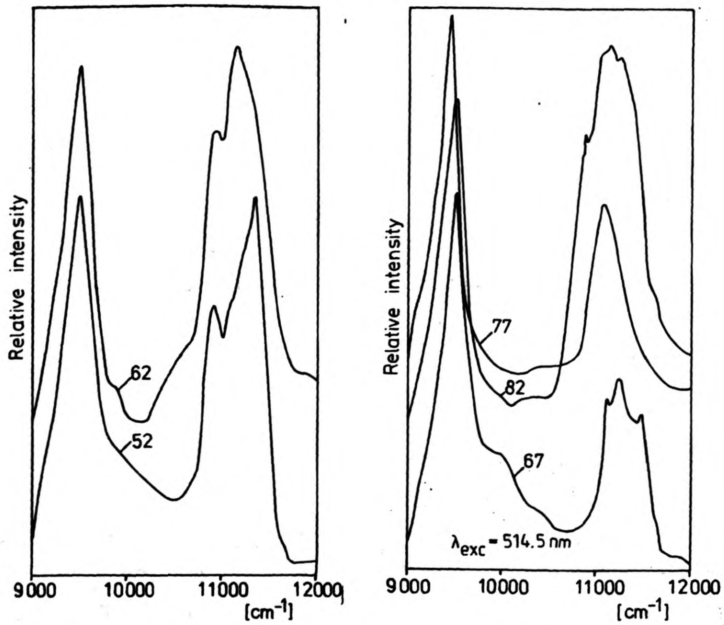

Fig. 2. Fluorescence spectra of Nd (III)-doped glasses

calculated from the expression for weak coupling limit called the energy gap law [6]

$$k_{NR}^{mp} C \exp\left[-\frac{\Delta E}{\hbar\omega_{max}}(\ln\frac{\Delta E}{E_M}-1)\right] \tag{5}$$

where C is the constant characterizing the host, ΔE is the energy distance between the energy levels involved, $\hbar\omega_{max}$ is the maximum energy phonon frequency

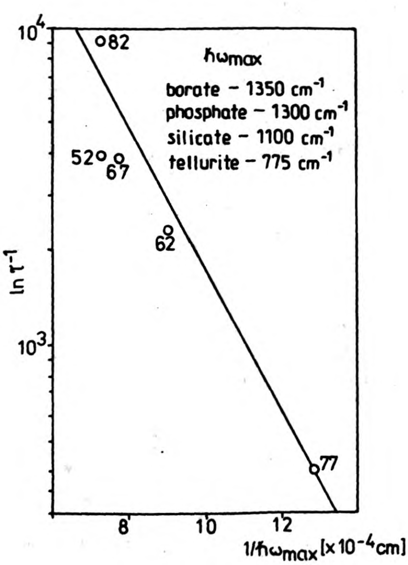

Fig. 3. Dependence of nonradiative rate on $(\hbar\omega_{max})^{-1}$

of host, and E_M is the half Stokes shift. Since the Nd (III)-doped glasses were investigated at low concentration limit, the contribution arising from the concentration quenching of Nd (III) fluorescence can be neglected. So k_{NR} is determined by multiphonon relaxation.

From Equation (5) it follows that

$$\ln k_{NR} \sim (\Delta E/\hbar\omega_{max}).$$

Since the energy gap ΔE for emitting level ${}^4F_{3/2}$ is constant it can be expected that $\ln k_{NR} \sim (\hbar\omega_{max})^{-1}$. The dependence $\ln k_{NR}$ vs. $(\hbar\omega_{max})^{-1}$ is plotted in Fig. 3. To this end we have assumed that the dominant contribution to the decay rate of the ${}^4F_{3/2}$ state at small concentration limit is influenced by nonradiative multiphonon relaxation.

3. Concluding remarks

In this paper optical investigations of Nd (III)-doped silicate, phosphate, borosilicate and tellurite glasses are presented. Its purpose was to compare the radiative and nonradiative relaxation of Nd (III) in these glasses to get information on the most appropriate candidate for luminescent solar concentrator.

We have performed the intensity analysis according to Judd and Ofelt and found that the intensities of *f–f* transitions increase along the series: silicate < phosphate < borosilicate < tellurite. The most pronounced variation was noted for the hypersensitive transition ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$.

Using the set of Ω_λ parameters the radiative lifetimes have been determined and theoretical branching ratios calculated. They are consistent with the experimental ratios. The dependence of k_{NR}^{-1} on the maximum phonon energy $\hbar\omega_{max}$ in glasses plotted from the fluorescence lifetimes measured for all glasses appeared to be linear.

It allows us to conlude that nonradiative multiphonon relaxation determines the luminescence properties of Nd (III) ion in glasses. The shortest decay times have been stated for tellurite glass. High oscillator strengths for this ion in tellurite glass distinguish plausibly this material. Some disadvantage is associated with a too high refractive index which may restrict the application of this glass to very thin narrow plates.

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Оптические свойства стекол активированных ионами Nd^{3+}

Описаны спектры силикатных, фосфатных, боросиликатных и теллуритных стекол активированных ионами Nd^{3+}. Проведено исследования влияния среды на лучательные и безлучательные переходы.