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Optical-physical-electrical properties of Er^{3+}:B_2O_3-BaO-RF glasses

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Abstract

This paper deals with preparation and characterization of Er^{3+}:B_2O_3-BaO-RF (RF=LiF, KF or NaF) glasses. From the measured absorption spectra of these glasses, the energy-level structure and spectral intensity parameters have been computed. Under a UV source, the Er^{3+}-doped glasses have displayed bright green colour due to the emission transition ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) at 530 nm. Based on the refractive indices (n_f, n_d and n_c) the non-linearity characteristic parameters have been evaluated to understand the dispersive powers in these glasses. Besides the estimation of densities and the related physical property parameters, the d.c. conductivity values have been measured to study their activation energy as a function of the change of alkali in the glass matrices. © 1998 Elsevier Science S.A.

Keywords: Optical properties; Er^{3+}; Fluoroborate glasses

1. Introduction

Over the past several years, extensive work has been done on a wide variety of glasses based on silicates, phosphates, halides and oxyhalides [1–7] for their use as different optical components in many designs. Doping them with rare earth ions has resulted in efficient and powerful lasing actions, particularly with rare earths such as Nd^{3+}, Tm^{3+} and Er^{3+} [8–11]. In our laboratory, we have been able to prepare several highly transparent borate glasses (B_2O_3-BaO) that are added with certain glass network modifiers (LiF, KF or NaF). Our study on these glasses shows that they have lower dispersion with a fairly high value of Abbenumber (≈55). Because of glass strength, transparency, and extended transmission range, they qualify to be good candidates for production of fibre optical glasses, besides their important use as laser glasses. According to Di Bartolo [12] and Fernandez et al. [13], application of Judd–Ofelt theory to absorption and fluorescence spectra becomes an essential method in the complete optical characterization of rare earth-doped liquids, glasses and crystalline materials. The aim of the present work is to undertake a systematic study on absorption, emission, physical properties and dc conductivities of Er^{3+}:B_2O_3-BaO-RF (RF=LiF, KF or NaF) glasses to understand the glass compositional effects on these properties.

2. Experimental

2.1. Glass preparation

The glass composition (in mol.%) of the samples prepared in the present study are given below:

Glass A $65B_2O_3^+14.8BaO+20LiF+0.2ErF_3$
Glass B $65B_2O_3^+14.8BaO+20KF+0.2ErF_3$
Glass C $65B_2O_3^+14.8BaO+20NaF+0.2ErF_3$

The glass batches of 6–8 g were prepared from commercially available chemicals with high purity of ErF_3 (Johnson Mathey, Cheshire, UK), $BaCO_3$, H_3BO_3, LiF, NaF and KF (local firms). The batches were melted in an electric furnace at 900–1000°C for about 30–60 min and were quenched between two polished plates for obtaining smooth surface glasses. The glasses formed were free from air bubbles and were in circular disc forms of 2–3 cm diameter having a uniform thickness of about 0.3 cm.

2.2. Spectral measurements

Absorption spectra of these three Er^{3+}-doped glasses were measured on a Perkin-Elmer 551 spectrophotometer at room temperature. The excitation and photoluminescence spectra of these glasses were also recorded at room temperature (300 K) on a Hitachi 650-10S spectrofluorometer using a 150-W xenon arc lamp as an excitation source.

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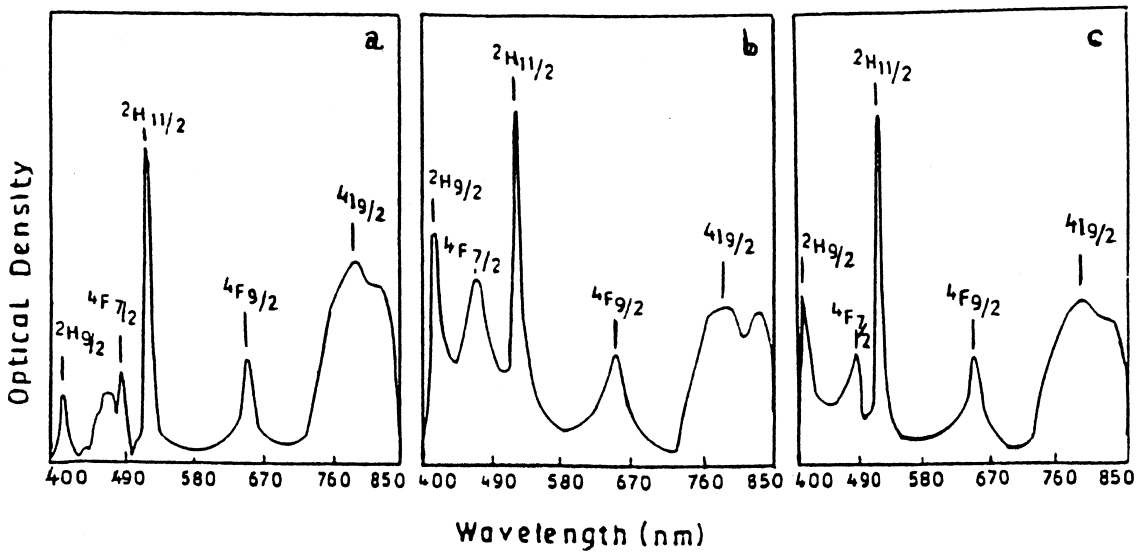

Fig. 1. Absorption spectra of Er^{3+}:B_2O_3-BaO-RF (RF = LiF, KF, NaF). (a) glass A; (b) glass B; (c) glass C. All transitions are from the $^4I_{15/2}$ ground level to the indicated levels.

2.3. d.c. conductivity

The conductivity measurements on these glasses were made using an electrometer amplifier (Keithly electrometer-617). In order to obtain good electrical contacts, the surfaces of the glass pieces were painted with silver paste by using amyl acetate as the solvent. During the d.c. measurements, the temperature was slowly varied from 300 to 550 K. Activation energies of erbium-doped glasses were evaluated from the measured conductivities using a simple Arrhenius type of equation [14].

3. Results and discussions

3.1. Absorption bands

The measured absorption band spectra of Er^{3+} glasses are shown in Fig. 1a–c and the assignment for the electronic transitions has been straightforward. The energies (cm^{-1}) of five absorption bands along with their assignments are presented in Table 1. The assigned levels are $^4F_{9/2}$, $^4I_{9/2}$, $^2H_{11/2}$, $^4F_{7/2}$, and $^2H_{9/2}$, and the energy level structural Racah (E^1, E^2, E^3), spin orbit (ξ_{4f}) and r.m.s deviation (σ_{rms}) parameters have been calculated by performing a least-square fit anlaysis [15,16], and the results are given in Table 1. E^1 and E^2 are found to be higher for glass B, with lower values of E^3 and ξ_{4f}, compared to the other two glasses (A and C). For this glass, the ionic nature was also found to be low, as shown in Table 1.

3.2. Glass bonding nature

Following the works of Sinha [17] and Reisfeld [18] the nephelauxetic ratio factor (β) and bonding parameter (δ%) have been evaluated. Depending upon the positive or negative nature of the δ values, the bonding nature could

Table 1
Absorption band energy (E, cm^{-1}), r.m.s. deviation (σ_{rms}, cm^{-1}), Racah (E^1, E^2, E^3, cm^{-1}), spin-orbit (ξ_{4f}, cm^{-1}), nephelauxetic (β) and bonding (δ) parameters of the three glasses

Absorption transitions $\psi_j \rightarrow \psi'_{j'}$	Glass A		Glass B		Glass C	
	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	12 654	12 650	12 800	12 813	12 606	12 610
$\rightarrow {}^4F_{9/2}$	15 439	15 771	15 404	15 543	15 475	15 881
$\rightarrow {}^2H_{11/2}$	19 281	19 277	19 115	19 105	19 337	19 333
$\rightarrow {}^4F_{7/2}$	20 570	20 571	20 278	20 258	20 655	20 657
$\rightarrow {}^2H_{9/2}$	24 089	24 092	23 916	23 912	24 353	24 352
σ_{rms}	±148.4		±63.0		±181.0	
E^1	7440.4		7647.1		7239.6	
E^2	71.7		85.4		59.8	
E^3	444.5		341.1		509.8	
ξ_{4f}	3984.6		2366.9		3527.7	
β	1.004		1.001		1.008	
δ%	−0.369		−0.122		−0.851	

Table 2
Different physical and non-linearity properties of Er^{3+}:B_2O_3-BaO-RF(R=Li, Na or K) glasses

Parameters	Glass A	Glass B	Glass C
Average molecular weight, $\bar{M}$ (g)	75.05	81.46	78.24
Density, d (g cm^{-3})	2.01	2.08	2.10
Refractive indices:			
at 489 nm (n_f)	1.4858	1.4806	1.4760
at 589 nm (n_d)	1.4797	1.4746	1.4686
at 656 nm (n_c)	1.4772	1.4721	1.4661
Dispersive power ($1/\nu_d$)	0.0181	0.0180	0.0179
Non-linear refractive index, n_2, ($\not\approx 10^{13}$ esu)	1.270	1.242	1.214
Non-linear refractive index coefficient, γ ($\not\approx 10^{15}$ cm^2 w^{-1})	3.59	3.53	3.46
Dopant ion concentration, N ($\not\approx 10^{20}$ ions cm^{-3})	3.233	3.088	3.239
Inter ionic distance, r_i (nm)	1.457	1.479	1.457
Polaron radius, r_p (nm)	0.587	0.596	0.587
Glass electronegativity, Δx	2.447	2.466	2.453
Glass ionicity, I_c (%)	77.63	78.14	77.80
Field strength, ^{F} ($\not\approx 10^{16}$ cm^{-2})	0.226	0.263	0.261
Molar refractivity, R_M (cm^{-3})	10.58	10.97	10.35

be suggested. Since the δ parameter takes negative signs for the glasses studied, the erbium-doped glasses could be considered as ionic materials. The ionic nature of the glasses displayed the following trend, glass C>glass A> glass B.

3.3. Physical and non-linearity properties

From the measured densities (d), refractive indices (n) and also based on the average molecular weights ($\bar{M}$) of each glass, different related physical and non-linear properties have been computed and the data are tabulated in Table 2. Mathematical formulae for obtaining the above parameters have been taken from Refs. [19–21].

3.4. Spectral oscillator strengths

Spectral intensity of a band is determined in terms of a quantity known as oscillator strength (f_{exp}). The experimental oscillator strength is obtained as suggested in Ref. [22]. Although we had the optical density (OD) values, we had some difficulty in measuring the half bandwidths for the bands as has been indicated by an asterisk mark in Table 3. Among the five measured absorption bands, only three bands had the Gaussian shapes to evaluate f_{exp} values. As it was not possible to measure f_{exp} values for two of the bands, only the theoretical value f_{cal} could be presented in Table 3. Theoretical determination of oscillator strength for observed bands was carried out by the Judd–Ofelt method [23–26].

3.5. Hypersensitive transition

For erbium-doped glasses, ($^4I_{15/2}\rightarrow{}^2H_{11/2}$) was the hypersensitive band, which satisfies the selection rule $\Delta L=2$ and $\Delta J=2$. The oscillator strengths of the observed bands are mostly monitored by the Judd–Ofelt parameter (Ω_2) [23,24]. From our results presented in (Table 3) and Fig. 1a–c, it can be seen that the hypersensitive ($^4I_{15/2}\rightarrow{}^2H_{11/2}$) has been the most intense one compared to other bands. In all three glasses, Ω_2 is two to three times higher than Ω_4 and Ω_6 values, respectively.

Table 3
Optical density (OD, arbitrary units), absorption band intensities (f_{exp} and f_{cal}, $\times 10^6$) and Judd–Ofelt intensity (Ω_λ, $\times 10^{20}$ cm^2) parameters of Er^{3+}:B_2O_3-BaO-RF(R=Li, Na or K) glasses

Absorption transitions ($\psi_j\rightarrow\psi'_{j'}$)	Glass A			Glass B			Glass C		
	OD	f_{exp}	f_{cal}	OD	f_{exp}	f_{cal}	OD	f_{exp}	f_{cal}
$^4I_{15/2}\rightarrow{}^4I_{9/2}$	1.17	—*	2.54	0.96	—*	1.93	0.93	—*	3.86
$\rightarrow{}^4F_{9/2}$	0.68	15.75	15.74	0.72	18.35	18.35	0.66	22.98	22.98
$\rightarrow{}^2H_{11/2}$	1.74	45.45	45.45	1.95	46.33	46.33	0.82	52.37	52.37
$\rightarrow{}^4H_{7/2}$	0.60	15.31	15.31	0.93	22.66	23.66	0.67	21.30	21.30
$\rightarrow{}^2H_{9/2}$	0.48	—*	4.91	1.32	—*	9.40	0.96	—*	7.64
Ω_2		28.50			30.69			29.95	
Ω_4		12.30			8.70			19.13	
Ω_6		10.39			18.86			14.07	

Some difficulty was encountered measuring the half bandwidths for the bands indicated by an asterisk.

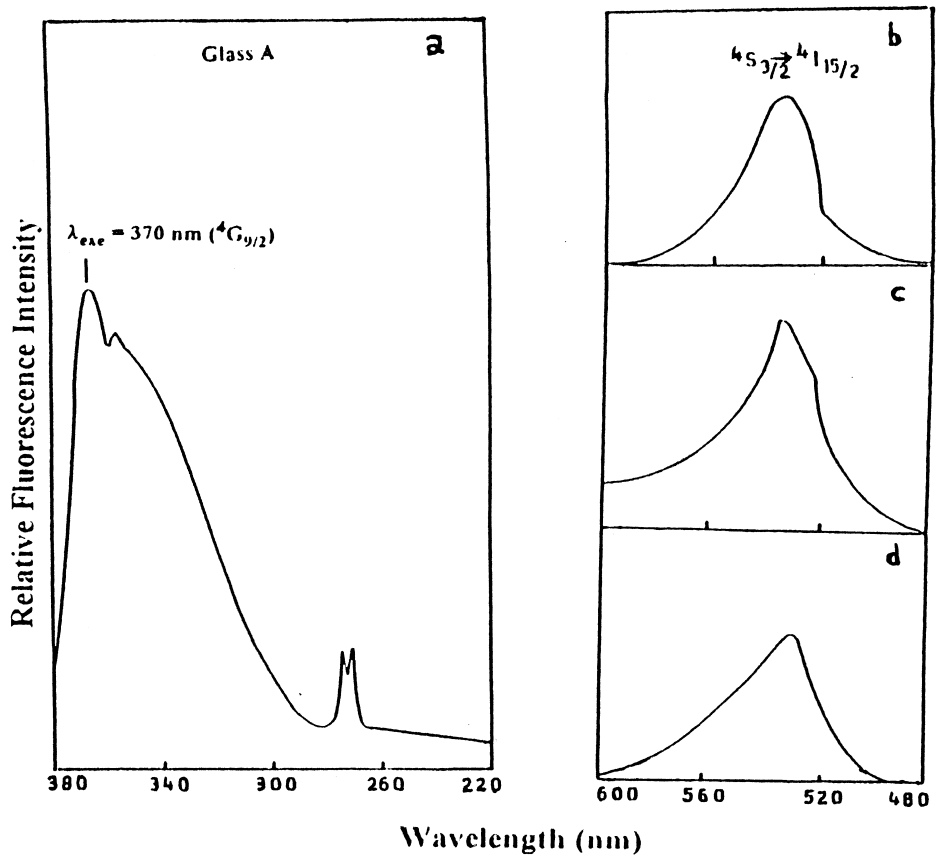

Fig. 2. (a) Excitation spectrum. (b–d) Photoluminescence spectra fo Er^{3+}:B_2O_3-BaO-RF (RT=LiF, KF, NaF). (b) Glass A; (c) glass B; (d) glass C.

3.6. Fluorescence spectra

The excitation spectrum for glass A is shown in Fig. 2a and the photoluminescence spectrum for the three glasses in Fig. 2b–d. From the excitation spectrum, the excitation wavelength λ_{exc}=370 nm ($^4G_{9/2}$) is determined as that which was required to record the photoluminescence spectra of erbium-doped glasses showing a bright green emission at 530 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$). To understand the radiative properties of this emission transition, it is necessary to use Judd–Ofelt parameters. To characterize the above transition, we have to compute radiative parameters (A, A_T, β_R and T_R) for the following emission transitions $^4S_{3/2} \rightarrow {}^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$, and these have been presented in Table 4. The procedures used in evaluating these parameters were similar to that given in Ref. [27]. The data given in this table describe the glass compositional influence on the properties investigated.

3.7. UV and IR transmission

In the UV region, glass A was found to allow UV radiation up to 320 nm, glass B up to 335 nm, and glass C

Table 4
Transition probability (A_E, s^{-1}), relaxation rate (A_T, s^{-1}), branching ratio (β_R, %), radiative lifetime (T_R, μs), emission cross section ($\sigma_p\Delta\lambda$, cm^3) of the fluorescent transitions of Er^{3+}:B_2O_3-BaO-RF(R=Li, Na or K) glasses

Absorption transitions ($\psi_j \rightarrow \psi'_{j'}$)	Glass A		Glass B		Glass C	
	A	β_R (%)	A	β_R (%)	A	β_R (%)
$^4S_{3/2} \rightarrow {}^4F_{9/2}$	0.4844	0	0.8529	0	0.6448	0
$\rightarrow {}^4I_{9/2}$	403.54	4	60 920	3	553.73	4
$\rightarrow {}^4I_{11/2}$	252.22	2	427.60	2	334.50	2
$\rightarrow {}^4I_{13/2}$	3099.9	28	5569.5	28	4102.1	28
$\rightarrow {}^4I_{15/2}$	7471	66	13 429	67	988	66
$A_T=\Sigma A$	11 226		20 036		14 872	
$T_R=(A_T)^{-1}$	89		50		67	
$\sigma_p^E\Delta\lambda$	3.79×10^{26}		6.85×10^{26}		4.97×10^{26}	

up to 360 nm. Among these three alkali-containing glasses, glass A with LiF could be rated a better glass as it has an extended UV transmission compared to the other two glasses. In the IR region, also, glass A has shown an enhanced IR transmission up to 4.5 μm, whereas glasses B and C have shown transmissions up to 4.3 and 4.2 μm, respectively.

3.8. Activation energy

The inverse temperature dependence of the measured d.c. conductivity is illustrated in Fig. 3 for all three glasses. Each one of the graphs shows two distinct regions: one at higher temperatures and the other at temperatures near RT, indicating two types of thermally activated processes. From the slopes of the graphs the activation energies in the higher temperature regions were evaluated:

glass A (Li^+) = 0.432 eV, glass B (K^+)
= 0.496 eV, glass C (Na^+) = 0.798 eV

From the activation energy values, it can be inferred that glass A has a higher conductivity than that of glasses B and C.

4. Conclusion

Glass A (20 mol.% LiF) has shown better results both in its absorption and emission spectra. Physical properties and activation energy values determined from d.c. conductivities clearly encourage us to suggest glass A to be a better optical material for its production in bulk in order to observe lasing action as well as possessing strength, transparency and extended transmission range.

References

[1] R. Reisfeld, C.K. Jørgensen, Lasers and Excited States of Rare Earths, Springer Verlag, Berlin, 1977.
[2] J. Lucas, Mater. Sci. Forum. 3 (1987) 19.
[3] J.A. Duffy, J. Non-Crystalline Solids 35 (1989) 109.
[4] L. Wetenkamp, G.F. West, H. Jobben, J. Non-Crystalline Solids 25 (1992) 140.
[5] F. Auzel, Proc. IEEE 61 (1973) 758; Phys. Rev. 13 (1976) 2809.

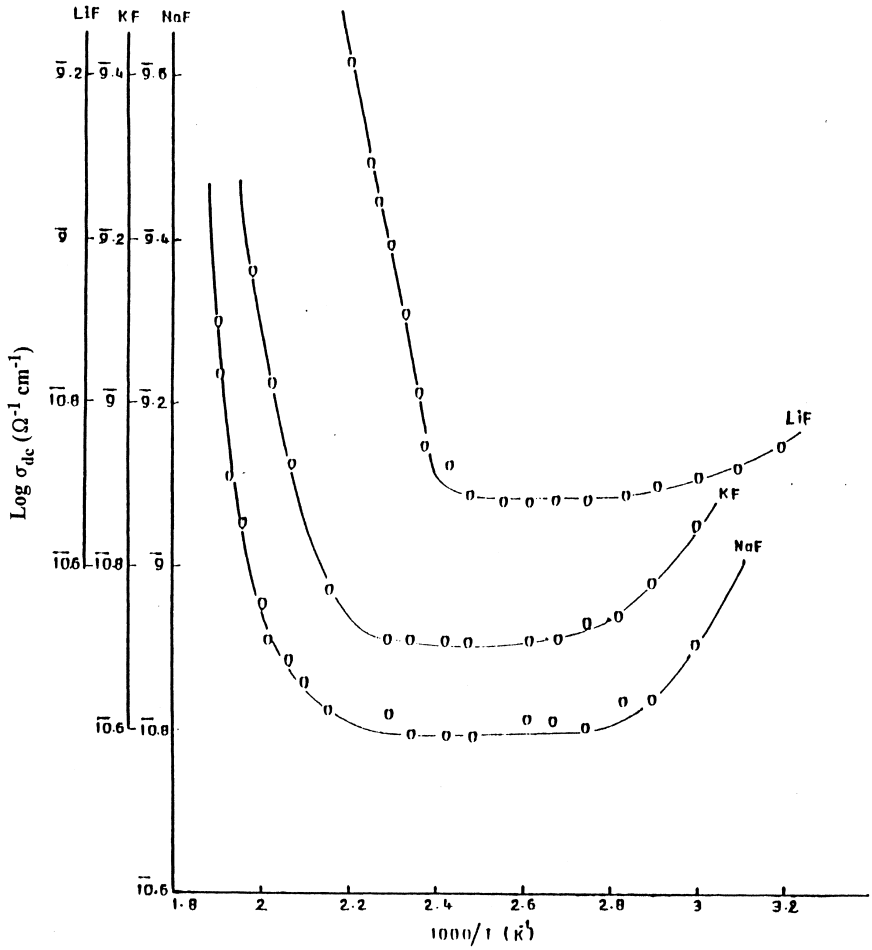

Fig. 3. Variation of conductivity σ_{dc} with temperature for Er^{3+}:B_2O_3-BaO-RF (RT=LiF, KF, NaF) glasses.

[6] L.R. Pederson, D.R. Baer, G.L. McVay, M.H. Enghelhard, J. Non-Crystalline Solids 86 (1986) 369.
[7] G. Amarnath, S. Buddhudu, J. Non-Crystalline Solids 143 (1992) 252.
[8] K. Annapurna, S. Buddhudu, J. Phys. D (Appl. Phys.) 226 (1993) 302; J. Solid State Chem. 93 (1991) 454.
[9] G.F. Imbush, R. Kopelman, Laser Spectroscopy of Solids, in: K.M. Yen, P.M. Selzen (Eds.), Topics in Applied Physics, Springer Verlag, Berlin, 1977.
[10] K. Tanimura, M.D. Shinn, W.A. Sibley, Phys. Rev. B 30 (1984) 2429.
[11] R. Cases, M.A. Chamarro, R. Alcala, V.D. Rodriguez, J. Lumin. 48 (1991) 509.
[12] B. Di Bartolo, Optical Interactions in Solids, Wiley, New York, 1968.
[13] J. Fernandez, M.A. Illarramendi, J. Lucas, J.L. Adam, J. Non-Crystalline Solids 131 (1991) 1230.
[14] H.A.A. Sidek, I.T. Collier, R.N. Hampton, G.A. Saunders, B. Bridge, Phil. Mag. B 59 (1989) 221.
[15] Y. Subramanyam, Ph.D. Thesis, S.V. University Tirupati, India 1988.
[16] E.Y. Wong, J. Chem. Phys. 38 (1963) 976.
[17] S.P. Sinha, Structure Bonding 22 (1975) 83; Spectrochim. Acta 22 (1966) 57.
[18] R. Reisfeld, Structure Bonding 22 (1975) 124.
[19] Y. Zhao, K. Kosula, J.S. Sakka, J. Mater. Sci. 22 (1987) 4103.
[20] A. Paul, Chemistry of Glasses, Chapman and Hall, London, 1982.
[21] N.L. Boling, A.J. Glass, J. Quantum. Electron. 14 (1984) 601.
[22] M.J. Weber, in: D.C. Brown (Ed.), High Peak Power Nd:Glass Laser System, Springer Verlag, Berlin, 1981.
[23] B.R. Judd, Phys. Rev. 127 (1962) 750.
[24] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[25] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4412, 4424, 4443, 4447, 4450.
[26] W.T. Carnall, H. Crosswhite, H.M. Crosswhite, Energy level-structure and transition probability of trivalent lanthanides and LaF_3, Argonne National Laboratory, Argonne, IL, USA, 1977.
[27] W.M. Yen, in: I. Zschokke (Ed.), Optical Spectra of Glasses, D. Reidel, The Netherlands, 1986.