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Electronic spectroscopy of trivalent lanthanide ions in lead zinc borate glasses

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Abstract

New zinc borate glasses of composition $4PbO\cdot2ZnO\cdot5B_2O_3\cdot$ and $2PbO\cdot4ZnO\cdot5B_2O_3$ doped with Pr^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} were prepared. Absorption and luminescence spectra were measured and the Judd–Ofelt parameters were calculated. The spectroscopic behaviour appears to be strongly influenced by the presence of the highly polarizable Pb^{2+} ion. The values of stimulated emission cross sections for selected laser transition appear to be relatively high, suggesting that these materials can be considered as interesting candidates for optical applications. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxide glasses; Lanthanide ions; Judd–Ofelt theory; Optical spectroscopy

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1. Introduction

Zinc borate glasses have proved to be interesting hosts for lanthanide ions, both from a fundamental and an applied point of view. The $^5D_0\rightarrow{}^7F_0$ emission transition of Eu^{3+} in a $4ZnO\cdot3B_2O_3$ glass shows intense phonon sidebands assigned to Eu–O modes [1]. The near infrared laser transitions of Nd^{3+} and Er^{3+} in the same host are characterised by high stimulated emission cross sections [2]. Moreover, the optical spectra of zinc borate glass doped with Pr^{3+} have allowed to understand in detail the relaxation mechanisms of the $^1D_2$ and $^3P_0$ states [3]. It has been reported that for silicate [4], phosphate [5] and borate [6] glasses the presence of large amounts of Pb^{2+} greatly influences the spectroscopy of the lanthanide dopants, due to the strong and directional nature of the Pb–O bond. We found it interesting to extend our previous studies on zinc borate glasses to materials in which part of ZnO is replaced by PbO, with the aim of ascertaining if the influence of Pb^{2+} is also strong in these glasses.

2. Experimental details

$4PbO\cdot2ZnO\cdot5B_2O_3$ (4Pb2ZnB) and $2PbO\cdot4ZnO\cdot5B_2O_3$ (2Pb4ZnB) glasses doped with 2.5% of Pr^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} (with respect to Zn^{2+}) were prepared by melting appropriate quantities of ZnO, PbO, H_3BO_3 and the relevant lanthanide oxide in a platinum crucible at 900°C for 1 h and quenching the melts in a brass mould. The obtained glasses were annealed for 12 h at 380°C and carefully polished for the optical measurements.

Room temperature absorption spectra in the range 250–2800 nm (bandwidths of 1 and 3 nm in UV–VIS and NIR regions, respectively) were recorded using a Cary 5E double beam spectrophotometer. Low resolution luminescence spectra in the UV–VIS region were measured at room temperature using a conventional fluorimeter with spectral bandwidths of 5 nm for the excitation and also for the emission. NIR luminescence spectra were measured at room temperature using a He–Ne laser and a liquid nitrogen cooled Ge detector (bandwidth of 2.4 nm for the whole spectral range). The refractive indexes were measured at 632.8 nm using standard techniques.

3. Theoretical background

The absorption spectra of the Ln^{3+} ions in the glasses under investigation are composed of sets of inhomogeneously broadened $f\rightarrow f$ transitions (see Fig. 1 in the case of Nd^{3+}). According to the Judd–Ofelt theory [7–10], the

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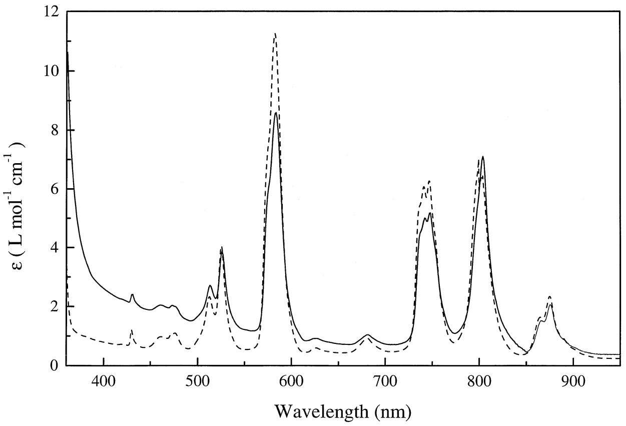

Fig. 1. Room temperature absorption spectra of the Nd^{3+} doped $4PbO\cdot 2ZnO\cdot 5B_2O_3$ (solid line) and $2PbO\cdot 4ZnO\cdot 5B_2O_3$ (dashed line) glasses.

oscillator strength, $P_{cal}(aJ;\ bJ')$, of an electric dipole absorption transition from the initial state $|aJ\rangle$ to the final state $|bJ'\rangle$ depends on three Ω_λ parameters (λ=2,4,6) as given by

$$P_{cal}(aJ;bJ') = \frac{8\pi^2 mc}{3h}\,\frac{\tilde{\nu}_p}{2J+1}\,\frac{(n^2+2)^2}{9n}\sum_{\lambda=2,4,6}\Omega_\lambda|\langle aJ\|U^{(\lambda)}\|bJ'\rangle|^2$$

where $\tilde{\nu}_p$ is the barycenter of the transition, n is the refractive index, m is the electron mass, c is the velocity of light, h is the Planck constant and $\langle\|U^{(\lambda)}\|\rangle$ are the double-reduced matrix elements of the unit tensor operators [7,10]. In the case of Pr^{3+} a modified procedure was employed [11] introducing a parameter α which takes into account the different degree of mixing of the manifolds with configurations of opposite parity.

The experimental oscillator strength, P_{exp} was obtained from the molar absorption coefficient ε [7]. The magnetic dipole contributions P_{md}, calculated as reported in Ref. [12], were subtracted from the P_{exp} in order to obtain the electric dipole contribution. The Ω_λ parameters were obtained by fitting by a least-squares method the electric dipole contributions of the P_{exp} of the observed transitions to the calculated ones, employing the matrix elements given by Carnall et al. [13].

The electric-dipole and magnetic-dipole contributions, A_{ed} and A_{md}, of the total spontaneous emission probability, A, were calculated with the equation [14]:

$$\begin{aligned} A(aJ;bJ') &= A_{ed} + A_{md} \\ &= \frac{64\pi^4\tilde{\nu}_p^3}{3h(2J+1)}\left[\frac{n(n^2+2)}{9}S_{ed} + n^3 S_{md}\right] \end{aligned}$$

where the electric-dipole line strength S_{ed} is given by

$$S_{ed} = e^2\sum_{\lambda=2,4,6}\Omega_\lambda|\langle aJ\|U^{\lambda}\|bJ'\rangle|^2$$

The A_{md} values were calculated using the procedure reported in Ref. [15].

The stimulated emission cross section of a laser transition was calculated using the equation [16]:

$$\sigma_p(aJ;bJ') = \frac{\lambda_p^4}{8\pi c n^2\,\Delta\lambda_{eff}}A(aJ;bJ')$$

where λ_p and $\Delta\lambda_{eff}$ are the peak wavelength and the effective linewidth of the emission band, respectively.

4. Results and discussion

The intensity parameters Ω_λ for the two glass series are presented in Table 1, together with the analogous results for the $4ZnO\cdot 3B_2O_3$ (ZnB) glass [2,17]. The r.m.s. values were about 10% of the experimental average oscillator strengths, therefore assuring the quality of the fits. As an example of the results of the fitting procedure, the measured and calculated oscillator strengths together with the barycenters of the transitions for the Nd^{3+} ion in the two different glasses are reported in Table 2.

A general shift of the barycenters of the absorption bands towards lower energy and a decrease of the inhomogeneous linewidth are observed as the lead content increases. As an example, the barycenter of the $^4I_{9/2}\rightarrow{}^2P_{1/2}$ transition of Nd^{3+} shifts monotonically toward lower energies as the amount of PbO is increased: on

Table 1
Judd–Ofelt intensity parameters Ω_λ (λ=2, 4, 6) for Ln^{3+} ions in the $4ZnO\cdot 3B_2O_3$, $2PbO\cdot 4ZnO\cdot 5B_2O_3$ and $4PbO\cdot 2ZnO\cdot 5B_2O_3$ glasses

Dopant ion	Ω_2(pm^2)	Ω_4(pm^2)	Ω_6(pm^2)
$4ZnO\cdot 3B_2O_3$			
$^aPr^{3+d}$	14.0±2.6	4.93±0.55	11.3±1.2
$^bNd^{3+}$	5.2	3.6	5.0
$^cHo^{3+}$	5.7	3.6	2.2
$^bEr^{3+}$	6.4	2.0	1.9
$2PbO\cdot 4ZnO\cdot 5B_2O_3$			
Pr^{3+e}	8.4±2.5	5.50±0.80	15.2±1.8
Nd^{3+}	4.65±0.55	4.75±0.81	5.67±0.36
Dy^{3+}	5.41±0.12	1.22±0.14	2.39±0.64
Ho^{3+}	4.65±0.25	3.38±0.40	2.22±0.22
Er^{3+}	5.77±0.20	1.73±0.28	1.72±0.10
$4PbO\cdot 2ZnO\cdot 5B_2O_3$			
Pr^{3+f}	2.8±2.4	3.8±1.1	13.2±2.6
Nd^{3+}	2.41±0.40	4.36±0.58	4.32±0.26
Dy^{3+}	3.58±0.11	1.43±0.12	1.77±0.06
Ho^{3+}	2.77±0.23	2.26±0.36	1.50±0.20
Er^{3+}	3.68±0.06	1.40±0.07	0.99±0.02

[a] A. Speghini et al., unpublished results.
[b] From Ref. [2].
[c] From Ref. [17].
[d] $\alpha=(2.04\pm 0.15)\cdot 10^{-5}$.
[e] $\alpha=(2.12\pm 0.16)\cdot 10^{-5}$.
[f] $\alpha=(2.07\pm 0.28)\cdot 10^{-5}$.

Table 2
Assignments and oscillator strengths P for the $f \rightarrow f$ transitions in the absorption spectra of Nd^{3+} in the doped $2PbO \cdot 4ZnO \cdot 5B_2O_3$ and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ glasses, the ground state of Nd^{3+} is $^4I_{9/2}$

Excited state	Barycenter (cm^{-1})	$P_{exp}/10^{-6}$	$P_{cal}/10^{-6}$
$2PbO \cdot 4ZnO \cdot 5B_2O_3$[a]			
$^4F_{3/2}$	11 416	2.62	2.92
$^4F_{5/2}$, $^2H_{9/2}$	12 477	8.72	9.37 (ed), 0.020 (md)
$^4F_{7/2}$, $^4S_{3/2}$	13 429	10.00	9.70
$^4F_{9/2}$	14 688	0.71	0.76 (ed), 0.004 (md)
$^2H_{11/2}$	15 907	0.22	0.21
$^4G_{5/2}$, $^2G_{7/2}$	17 171	24.11	24.20 (ed), 0.0004 (md)
$^2K_{13/2}$, $^4G_{9/2}$, $^4G_{7/2}$	19 211	8.96	7.23
$^4G_{11/2}$, $^2G_{9/2}$, $^2K_{15/2}$, $^2(D,P)_{3/2}$	21 346	2.23	1.64
$^2P_{1/2}$	23 188	0.53	0.74
$4PbO \cdot 2ZnO \cdot 5B_2O_3$[b]			
$^4F_{3/2}$	11 406	2.05	2.73
$^4F_{5/2}$, $^2H_{9/2}$	12 420	8.30	7.95 (ed), 0.021 (md)
$^4F_{7/2}$, $^4S_{3/2}$	13 410	7.62	7.91
$^4F_{9/2}$	14 662	0.53	0.63 (ed), 0.004 (md)
$^2H_{11/2}$	15 952	0.12	0.18
$^4G_{5/2}$, $^2G_{7/2}$	17 140	17.30	17.36 (ed), 0.0004 (md)
$^2K_{13/2}$, $^4G_{9/2}$, $^4G_{7/2}$	19 182	6.57	5.60
$^4G_{11/2}$, $^2G_{9/2}$, $^2K_{15/2}$, $^2(D,P)_{3/2}$	21 312	1.39	1.45
$^2P_{1/2}$	23 155	0.35	0.72

[a] r.m.s. $= 1.2 \cdot 10^{-6}$.
[b] r.m.s. $= 6.8 \cdot 10^{-7}$.

passing from ZnB to 2Pb4ZnB and from 2Pb4ZnB to 4Pb2ZnB we observe a red-shift of (22±2) cm^{-1} and (33±2) cm^{-1}, respectively (see Table 2 and Ref. [2]). This behaviour is due to the nephelauxetic effect [18], that is caused by an overlap of the charge clouds of the ligands (in this case, oxygen atoms) and the partly filled 4*f* shell of the Ln^{3+} ion. This effect constitutes a measure of the covalency of the Ln–O bond. In lead zinc borate glasses, the covalency of the Ln–O bond increases as the lead content increases, as reported for lead germanate glasses [19].

For a given Ln^{3+} ion, the values of the Ω_λ parameters decrease significantly on passing from the ZnB matrix to 2Pb4ZnB and 4Pb2ZnB (see Table 1), though in a different way depending on λ. In fact, Ω_2 is the parameter which is more influenced. This behaviour is similar to that reported for lead germanate glass [19], for which it was observed that the variation of Ω_λ must correlate with structural effects and, therefore, with the crystal field (CF) parameters. One possible explanation of this behaviour is based on the nature of Pb^{2+} [20]. This ion is easily polarised and forms strong covalent Pb–O bonds. Therefore, the oxygen electrons should be less available for the coordination of Ln^{3+} ion and the CF around the sites should decrease. But in this case the covalency of the Ln–O bond is also expected to decrease, which is in contradiction with the observed nephelauxetic effect. An alternative explanation is that the average symmetry of the lanthanide ions increases due to the formation of strong, directed Pb–O bonds, thereby drastically reducing the magnitudes of the CF parameters and therefore the intensity parameters. This explanation is corroborated by the fact that the asymmetry ratio R of the emission intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions of the Eu^{3+} doped lead zinc borate glasses decrease as the amount of PbO increases [21].

The behaviour of the Ω_6 parameter as a function of the number of 4*f* electrons is shown in Fig. 2. Ω_6 decreases monotonically throughout the lanthanide series for both hosts. In the same host we can assume that the distributions of site symmetries around the Ln^{3+} are identical, as the CF parameters. Considering that the Ξ quantities [10], depending on the radial integrals between the 4*f* configuration and excited states configurations and the energy differences between these, decrease monotonically

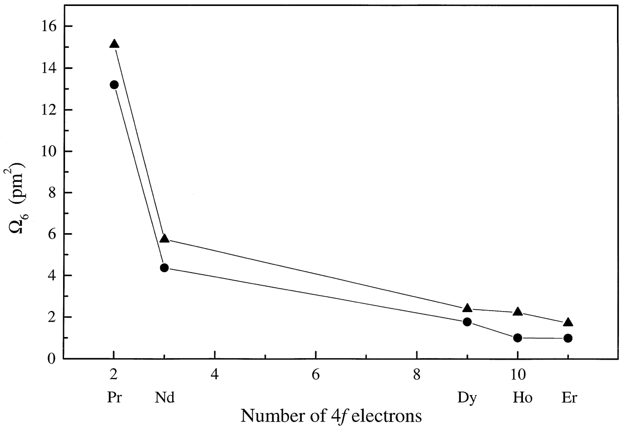

Fig. 2. Variation of the Judd–Ofelt parameter Ω_6 along the lanthanide series for the $2PbO \cdot 4ZnO \cdot 5B_2O_3$ (▲) and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ (●) glasses (the lines are included to guide the eye).

along the lanthanide series [22], the behaviour of Ω_6 indicates that the static contribution to the intensity mechanism is predominant while the vibronic one is unimportant [10,19].

The spontaneous transition probabilities A from some excited states of Nd^{3+}, their branching ratios β and radiative lifetimes τ_{rad} calculated from the Ω_λ parameters are reported in Table 3. A general decrease of the A values and a slight increase of the τ_{rad} values is observed as the amount of PbO is increased, due to the decrease of the Ω_λ parameters. The presence of Pb^{2+} does not influence dramatically the branching ratios. In particular, for the transitions originating from the $^4F_{3/2}$ the β values depend on Ω_4 and Ω_6 but not on Ω_2 [16]. Since the Pb^{2+} ion affects prevalently Ω_2, the amount of PbO does not have a relevant influence on β. The β value of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is similar to that reported by Weber et al. for halide and silicate glasses [16].

The infrared laser transitions $^4F_{3/2} \rightarrow {}^4I_{11/2}$ of Nd^{3+} and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions in the ZnB and lead zinc borate hosts are compared in Figs. 3 and 4. For Nd^{3+} a decrease of $\Delta\lambda_{eff}$ on passing from ZnB to 2Pb4ZnB and 4Pb2ZnB is observed. From the luminescence spectra of Eu^{3+} doped 4Pb2ZnB and 2Pb4ZnB glasses, we have observed that the linewidth of the $^5D_0 \rightarrow {}^7F_0$ transition decreases as the amount of lead increases [21], and therefore a smaller inhomogeneous broadening and energy site-distribution is induced by increasing amounts of PbO in the host. Moreover, the presence of lead decreases the CF around the Ln^{3+} ion (see above) and therefore the Stark splitting of the $f \rightarrow f$ transitions. The decrease of $\Delta\lambda_{eff}$ could be due to both these effects. The case of Er^{3+} is different, because $\Delta\lambda_{eff}$ increases on passing from ZnB to 2Pb4ZnB, and decreases on passing from 2Pb4ZnB to 4Pb2ZnB (see Fig. 4); $\Delta\lambda_{eff}$ has nearly the same value for the zinc borate host glass and for the one with the higher lead content. In this case presumably the CF splitting and the inhomogeneous broadening vary in an opposite way with the PbO concentration.

Table 3
Calculated spontaneous transition probabilities A, branching ratios β and radiative lifetimes τ_{rad} for emission from excited states of Nd^{3+} in the $2PbO \cdot 4ZnO \cdot 5B_2O_3$ and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ glasses

Initial state	Final state	A(s^{-1})	β	τ_{rad} (ms)
$2PbO \cdot 4ZnO \cdot 5B_2O_3$				
$^4F_{5/2}$	$^4F_{3/2}$	0.3	~0	
	$^4I_{15/2}$	142.6	0.067	
	$^4I_{13/2}$	772.5	0.363	
	$^4I_{11/2}$	459.6	0.216	
	$^4I_{9/2}$	751.6	0.353	
				0.470
$^4F_{3/2}$	$^4I_{15/2}$	25.8	0.005	
	$^4I_{13/2}$	500.1	0.099	
	$^4I_{11/2}$	2525.0	0.501	
	$^4I_{9/2}$	1992.0	0.395	
				0.198
$^4I_{15/2}$	$^4I_{13/2}$	18.9	0.265	
	$^4I_{11/2}$	39.3	0.551	
	$^4I_{9/2}$	13.1	0.184	
				14.020
$4PbO \cdot 2ZnO \cdot 5B_2O_3$				
$^4F_{5/2}$	$^4F_{3/2}$	0.2	~ 0	
	$^4I_{15/2}$	124.4	0.06	
	$^4I_{13/2}$	710.5	0.345	
	$^4I_{11/2}$	464.3	0.226	
	$^4I_{9/2}$	759.4	0.369	
				0.486
$^4F_{3/2}$	$^4I_{15/2}$	22.5	0.005	
	$^4I_{13/2}$	436.5	0.092	
	$^4I_{11/2}$	2301.0	0.483	
	$^4I_{9/2}$	2006.0	0.421	
				0.210
$^4I_{15/2}$	$^4I_{13/2}$	16.6	0.266	
	$^4I_{11/2}$	34.4	0.551	
	$^4I_{9/2}$	11.4	0.183	
				15.985

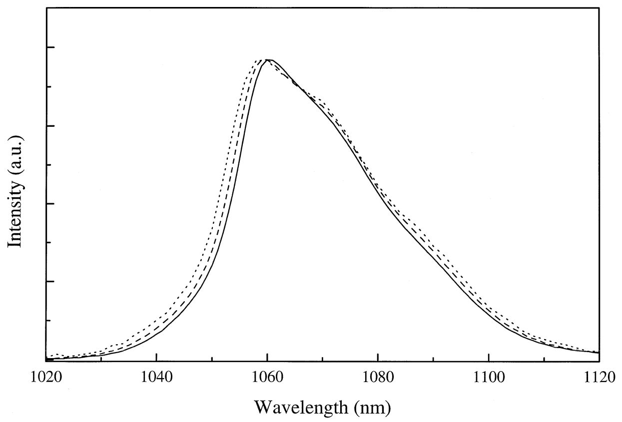

Fig. 3. Room temperature NIR emission spectra of the Nd^{3+} doped $4ZnO \cdot 3B_2O_3$ (dotted line, from Ref. [17]), $2PbO \cdot 4ZnO \cdot 5B_2O_3$ (dashed line), $4PbO \cdot 2ZnO \cdot 5B_2O_3$ (solid line) glasses for laser excitation at 632.8 nm.

The corresponding values of the stimulated emission probability σ_p are reported in Tables 4 and 5 for the three

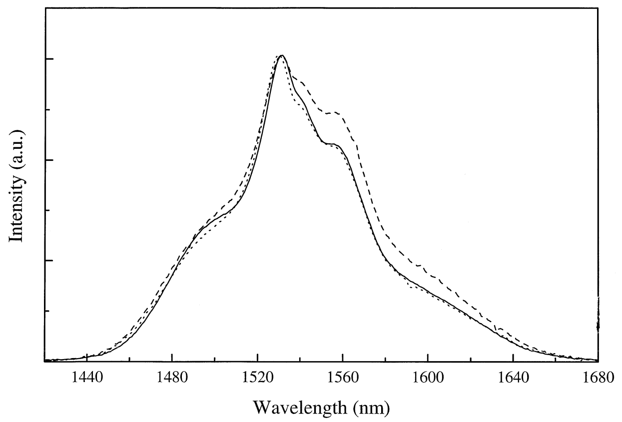

Fig. 4. Room temperature NIR emission spectra of the Er^{3+} doped $4ZnO \cdot 3B_2O_3$ (dotted line, from Ref. [2]), $2PbO \cdot 4ZnO \cdot 5B_2O_3$ (dashed line), $4PbO \cdot 2ZnO \cdot 5B_2O_3$ (solid line) glasses for laser excitation at 632.8 nm.

Table 4
Peak wavelength λ_p, effective linewidth $\Delta\lambda_{eff}$, and stimulated emission cross section σ_p for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of Nd^{3+} in the zinc borate glasses under investigation

Glass	λ_p(nm)	$\Delta\lambda_{eff}$(nm)	σ_p(pm^2)
$4ZnO \cdot 3B_2O_3$ [a]	1060	37.9	2.64
$2PbO \cdot 4ZnO \cdot 5B_2O_3$	1060	35.3	3.65
$4PbO \cdot 2ZnO \cdot 5B_2O_3$	1060	33.6	3.23

[a] From Ref. [2].

doped zinc borate glasses. For Nd^{3+}, the highest σ_p value is relative to the glass with intermediate amount of PbO, whose presence decreases the Ω_λ parameters and also the spontaneous emission probabilities with respect to the ZnB glass. On the other hand, σ_p increases as $\Delta\lambda_{eff}$ decreases. The higher refractive index and the lower $\Delta\lambda_{eff}$ of the sample with a higher amount of PbO do not compensate the decrease of the spontaneous emission probabilities. The values of σ_p are similar or higher than those reported for other borate glasses [23], for which typical values of stimulated emission cross sections for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ of Nd^{3+} are in the range 2.1–3.2 pm^2. For Er^{3+} the situation is different, because it is the ZnB host that shows the highest value of σ_p (see Table 5). Once again, the value of σ_p depends on a subtle balance of factors, especially Ω_λ and $\Delta\lambda_{eff}$, that operate in opposite directions. In the case of Er^{3+}, the most relevant factor in the decrease of σ_p with the amount of lead is the decrease of the Ω_λ parameters. For comparison purposes, typical values of σ_p for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} in laser glasses are in the range 0.4–1.2 pm^2 [24].

5. Conclusions

The $\Delta\lambda_{eff}$ values of the laser transitions vary with the nature of the host. Therefore, it is possible to maximise the value of the stimulated emission cross section by choosing an appropriate composition of the glass.

High concentrations of Pb^{2+} reduce significantly the linewidth of the optical transitions, because this ion tends to decrease the disorder of the host and gives rise to a weaker crystal field around the dopant [26]. On the other hand, a weaker crystal field is responsible for lower values of the transition probabilities. As shown in Tables 4 and 5, the values of the stimulated emission cross sections derive from the balance of different factors that operate in opposite directions when the host composition is changed. This explains the observation that, in the case of Nd^{3+}, the host containing less Pb^{2+} (2Pb4ZnB) shows the maximum value of σ_p with respect to the $4ZnO \cdot 3B_2O_3$ glass and the host containing more Pb^{2+} (4Pb2ZnB). The high values of σ_p make these host glasses particularly interesting as materials for optical amplifiers and lasers, especially in the eye-safe region. However, glasses with a relatively high linear refractive index (1.863 and 1.790 for 4Pb2ZnB and 2Pb4ZnB, respectively) usually show also a high non-linear refractive index [25]. For high power lasers, a high non-linear refractive index could induce self-focusing phenomena and consequently serious damage of the optical components. On the other hand, such glasses could be used in fiber and waveguide devices with optical confinement, because in this case self-focusing do not occur, or even better, as an all optical switching device, e.g. Kerr lensing effect for generation of ultrashort pulses, where a high non-linear refractive index is desired [25]. It is well known that the B–O vibration can quench the Nd^{3+} or Er^{3+} luminescence through multiphonon relaxation [23]. For this reason it is interesting to investigate the vibrational spectra of these hosts. These results lie beyond the scope of this paper and will be reported elsewhere [21].

Table 5
Peak wavelength λ_p, effective linewidth $\Delta\lambda_{eff}$, and stimulated emission cross section σ_p for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ of Er^{3+} in the zinc borate glasses under investigation

Glass	λ_p(nm)	$\Delta\lambda_{eff}$(nm)	σ_p(pm^2)
$4ZnO \cdot 3B_2O_3$ [a]	1530	77.5	0.78
$2PbO \cdot 4ZnO \cdot 5B_2O_3$	1531	87.4	0.70
$4PbO \cdot 2ZnO \cdot 5B_2O_3$	1532	78.0	0.56

[a] From Ref. [2].

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