Optical Transitions of Ho^{3+} in a Lead Silicate Glass

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The presence of a high concentration of the heavy and easily polarized Pb^{2+} ion has been found to perturb in a significant way the optical properties of glasses doped with trivalent lanthanide ions (Ln^{3+}). Lead metaphosphate glasses containing Nd^{3+} exhibit extremes in several of their spectroscopic properties [1], and silicate glasses of molar composition 38% PbO–62% SiO_2 doped with Eu^{3+} show a strong dependence of the intensities of the $4f^6 \rightarrow 4f^6$ transitions on the energy of the upper levels and an unusual low luminescence quantum yield [2]. In this note we report the optical properties of the same 38% PbO–62% SiO_2 glass doped with Ho^{3+}. The stimulated emission cross sections of the potential laser transitions ($^5F_4$, $^5S_2$) $\rightarrow$ $^5I_8$ and $^5F_5 \rightarrow {}^5I_8$ are relatively high due to a narrow effective linewidth, caused by the presence of Pb^{2+} as network modifier.

Experimental

The molar composition of the lead silicate glass under investigation was 37.5% PbO, 61.5% SiO_2 and 1.0% Ho_2O_3. Appropriate quantities of PbO and SiO_2 (both Carlo Erba RPE) and Ho_2O_3 (Riedel De Haen reagent grade) were mixed in Pt crucibles. Several batches were melted and annealed following a procedure previously reported [2].

The samples were then cut to a 1.5 mm thickness and polished for optical measurements. Absorption and luminescence spectra were measured at 293 and 80 K with the equipment previously described [2]. Additional luminescence spectra were recorded at 293 K using a Perkin-Elmer 650-40 spectrofluorimeter. The excitation wavelength was always $\lambda = 446$ nm. The luminescence spectra were not corrected for the response of the photomultiplier for $\lambda > 700$ nm.

The refractive index $n_d = 1.76$ of the glass was measured using standard techniques.

TABLE 1. Oscillator strengths P in the absorption spectrum of the 37.5% PbO–61.5% SiO_2–1.0% Ho_2O_3 glass at 293 K and intensity parameters Ω_λ. The ground level of Ho^{3+} is $^5I_8$

Excited level	Baricenter (cm^{-1})	$P \times 10^6$	
		Exp.	Calc.
$^5I_7$	5102	1.29	0.519 md 1.20 ed
$^5I_6$	8547	0.600	0.864
$^5F_5$	15516	2.07	2.37
$^5S_2$, $^5F_4$	18587	3.37	3.08
$^5F_3$	20601	1.13	0.923
$^5F_2$, $^3K_8$	21166	0.935	0.112 md 1.33 ed
$^5G_6$	22123	21.9	22.1
$^5G_5$, $^3G_5$	23923	2.25	2.37
$^5G_4$, $^3K_7$	25862	0.245	0.005 md 0.500 ed
$^3H_6$, $^3H_5$, $^5G_2$	27701	6.25	4.96

$\Omega_2 = (5.2 \pm 0.2) \times 10^{-20}$ cm^2; $\Omega_4 = (1.8 \pm 0.3) \times 10^{-20}$ cm^2; $\Omega_6 = (1.2 \pm 0.5) \times 10^{-20}$ cm^2; r.m.s. = 6.01×10^{-7}.

Results and Discussion

The absorption spectra at 293 K of the lead silicate glass doped with Ho^{3+} are composed of ten $4f^{10} \rightarrow 4f^{10}$ transitions in the infrared and the visible region, and a steeply rising edge starting at about 330 nm. The bands are clearly inhomogeneously broadened; their positions, experimental oscillator strengths and assignments are reported in Table 1. At 80 K no further resolution of the bands is obtained, and the oscillator strengths of the various transitions show differences up to ±25% with respect to 293 K. The Judd–Ofelt phenomenological parameters Ω_λ (λ = 2, 4 and 6) were calculated with a least-squares fitting procedure from the oscillator strengths at 293 K, using the reduced matrix elements calculated by Weber *et al.* [3]. The results are reported in Table 1, together with the calculated oscillator strengths. The root mean square deviation (r.m.s.) is 15.3% of the average oscillator strength.

The values of the intensity parameters appear to be the lowest found to date for Ho^{3+} in oxide glasses [4–6]. Weber *et al.* [1] have found exceptionally low Ω_λ intensity parameters for Nd^{3+} in phosphate

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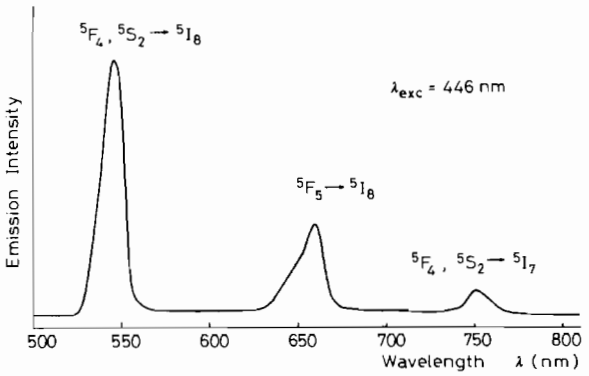

Fig. 1. Luminescence spectrum at 293 K of the 37.5% PbO–61.5% SiO_2–1.0% Ho_2O_3 glass with λ_{exc} = 446 nm.

glasses containing high concentrations of PbO (corresponding to the metaphosphate composition or higher in PbO) and attributed this behaviour to the high polarizability of Pb^{2+} and the directional nature of the Pb–O bond. This is clearly possible also for the glass under investigation even if these considerations are not consistent with our results for Eu^{3+} in the same lead silicate matrix [2]. In this last case the intensity parameters depend on the energy of the upper levels involved in the transitions and, when expressed as T_λ, are higher than the corresponding values for a lead-free silicate glass [7]. This peculiar behaviour of Eu^{3+} in the lead silicate matrix has been attributed to a strong mixing of the $4f^6$ states with low-lying states of opposite parity, probably of charge-transfer nature [2].

The luminescence spectrum at 293 K of the lead silicate glass doped with Ho^{3+}, after excitation in the $^5G_6$ level, is reported in Fig. 1. The spectrum does not change at 80 K. The three bands are assigned to the transitions $(^5F_4, {}^5S_2) \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $(^5F_4, {}^5S_2) \rightarrow {}^5I_7$ in increasing wavelength order, if the thermal population of $^5F_4$ is taken into account [4].

The radiative transition probabilities A and the branching ratios β for emission from the excited levels $^5F_4$, $^5S_2$ and $^5F_5$, calculated from the Ω_λ intensity parameters, are reported in Table 2 for the lead silicate glass doped with Ho^{3+}. The branching ratios are very similar to the values determined for other oxide glasses [4–6] and reasonably similar to those for fluoride glasses [8–10] and are not strongly influenced by the different values of the intensity parameters.

From the calculated radiative emission probabilities and the luminescence spectrum, the peak stimulated emission cross sections σ_p [11, 12] have been evaluated for the potential laser transitions $(^5F_4, {}^5S_2) \rightarrow {}^5I_8$ and $^5F_5 \rightarrow {}^5I_8$. The level $^5F_4$ lies roughly 100 cm^{-1} above $^5S_2$ [13] and laser emission is possible from both levels [14]. In Table 3 the values of σ_p are reported together with the peak

TABLE 2. Calculated radiative transition probabilities A, branching ratios β and radiative lifetimes τ_R for emission from excited levels of Ho^{3+} in the 37.5% PbO–61.5% SiO_2–1.0% Ho_2O_3 glass

Initial state	Final state	A (s^{-1})	β	τ_R (ms)
$^5F_4$	$^5I_8$	3383.0	0.801	
	$^5I_7$	390.4	0.092	
	$^5I_6$	279.3	0.066	
	$^5I_5$	137.7	0.033	
	$^5I_4$	23.2	0.005	
	$^5F_5$	13.7	0.003	
				0.24
$^5S_2$	$^5I_8$	1311.0	0.531	
	$^5I_7$	901.6	0.365	
	$^5I_6$	169.3	0.068	
	$^5I_5$	42.1	0.017	
	$^5I_4$	46.0	0.019	
	$^5F_5$	0.5	0.001	
				0.40
$^5F_5$	$^5I_8$	1816.0	0.763	
	$^5I_7$	455.7	0.191	
	$^5I_6$	101.3	0.043	
	$^5I_5$	8.1	0.003	
	$^5I_4$	0.1	0.001	
				0.42

TABLE 3. Peak wavelength λ_p, effective linewidth $\Delta\lambda_{eff}$ and stimulated emission cross section σ_p of some laser transitions of Ho^{3+} in the 37.5% PbO–61.5% SiO_2–1.0% Ho_2O_3 glass at 293 K

Transition	λ_p (nm)	$\Delta\lambda_{eff}$ (nm)	$\sigma_p \times 10^{20}$ (cm^2)
$(^5F_4, {}^5S_2) \rightarrow {}^5I_8$	550.3	15	0.343
$^5F_5 \rightarrow {}^5I_8$	664.0	19	0.658

wavelengths λ_p and the effective linewidths $\Delta\lambda_{eff}$. The values of σ_p are relatively high, despite the low intensity parameters, and are comparable with the highest values for the glasses in the 48% ZrF_4–23% BaF_2–8% AlF_3–20% RF–1% HoF_3 series (RF = LiF–NaF or NaF–KF pair) [10]. The effective linewidth appears in the denominator of the expression for σ_p and the low values of $\Delta\lambda_{eff}$, due to the reduced ligand field around the Ho^{3+} ion caused by the strong and covalent Pb–O bonds [1], are important in determining the cross sections.

As a conclusion, the 37.5% PbO–61.5% SiO_2–1.0% Ho_2O_3 glass shows some optical properties similar to those of fluoride glasses and is characterized by low values of the Judd–Ofelt parameters, by narrow emission linewidths and by relatively high stimulated emission cross sections of the $(^5F_4, {}^5S_2) \rightarrow {}^5I_8$ and $^5F_5 \rightarrow {}^5I_8$ potential laser transitions.

The high value of the refractive index is also effective in increasing the peak cross sections for the aforementioned transitions.

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