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Journal of Luminescence 62 (1994) 95–100

JOURNAL OF
LUMINESCENCE

The fluorescence of Sm^{3+} in lithium molybdate borate glasses

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Received 29 October 1993; revised 31 March 1994; accepted 25 April 1994

Abstract

We report the fluorescence spectra of Sm^{3+} in $(Li_2B_4O_7)_{1-x}(MoO_3)_x$ glasses; fine structure of the $4G_{5/2}$–$6H_{x/2}$ ($x = 5, 7, 9, 11$) transitions and a slight increase of the oscillator strengths with x are connected with the local crystal field and hybridization effects, while an increasing fluorescence quenching with x appears to be related to a proportional increase of the $Mo_2O_7^{2-}$ cluster content.

1. Introduction

According to several contributions [1–3], at higher WO_3 and MoO_3 contents, clusters appear in molybdate and tungstate borate glasses which might be useful for the study of radiationless energy transfer mechanisms connected with the fluorescence of samarium and other rare earth ions. Both glass networks are rather similar, but comparative Raman studies [2,3] have shown that certain clusters which exist in the tungstate borate glasses do not appear in the molybdate borate glasses, which makes the latter a simpler and a reference system as far as cluster assisted fluorescence quenching or enhancement is concerned. Besides, for the tungstate glasses the quenching effects were obscured by an increase in the fluorescence transition oscillator strengths with increasing WO_3 content, which has been connected with the high electric polarisability of WO_3 [4,7] and which should not be so pronounced using the lesser dielectric MoO_3.

2. Experimental and results

The samples were prepared and the fluorescence intensity and the transmittance of the glasses (Fig. 1(a)) were taken [5,6]. For the transmittance we used a modified conventional double prism monochrometer (C.Leiss) together with a conventional halogen lamp (Osram) as source and a Valvo XP 1017 photomultiplier as a detector. For the fluorescence excitation we used the 5145 Å beam of an argon laser (Lexel 75-1), which was focused on the sample using a suprasil lens and which penetrated the sample at right angles with the fluorescence beam. The sample was located close to the entrance slit of a modified Jobin–Yvon M 225 double

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SSDI 0022-2313(94)00032-8

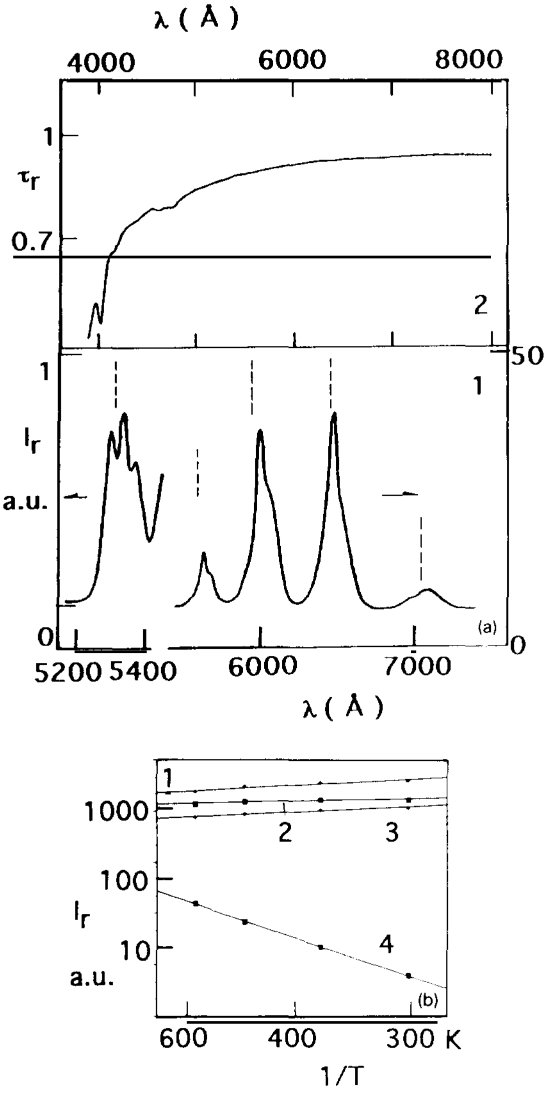

Fig. 1. (a) Fluorescence intensity I_r (1) and transmittivity $\tau_r(\lambda)$ (2) of Sm^{3+} in a $(Li_2B_4O_7)_{54}$ $(MoO_3)_{45}(Sm_2O_3)_1$ glass versus wavelength λ at 300 K. Broken lines: fluorescent transitions of Sm^{3+} in acid aqueous solution according to Ref. [13]. 1 (b) Maximum intensity of three transitions $^4G_{5/2} \rightarrow {}^6H_{n/2}$ and of $^4F_{3/2} \rightarrow {}^6H_{5/2}$ versus reciprocal temperature. 1, 2, 3, 4: 5965, 6456, 5627, 5275 Å, respectively; for line 4 $I_r = I_0 \exp(-\Delta E/kT)$; $\Delta E = 990\ \mathrm{cm}^{-1}$.

monochromator and the fluorescence was collected by an offside spherical mirror which itself was focused directly on the entrance slit. As detector we used the XP 1017 photomultiplier at − 10°C.

2.1. $(Li_2B_4O_7)_{1-y}(Sm_2O_3)_y$ glasses

As excitation by lasers often produces fluorescence line narrowing as only a subset of Sm ions are excited (FLN) [8–11], for the MoO_3-free glasses, the excitation intensity (4–100 mW) and the excitation wavelength (4765, 5145, 4880 Å) were varied. In no case the relative heights and positions of the peaks were changed notably ($< 1\%$) and the fluorescence intensity scaled with the excitation intensity. Small changes of the linewidths connected with different excitations, however, were suggested by deconvolution into Gaussian peaks [8]. Because of accuracy limits of the fitting procedure and because a variety of effects can contribute here, i.e., selective population by changing the bandwith of the excitation (FLN), energy diffusion, opening of new relaxation channels [9–11], we did not proceed further with these experiments. Also, virtually no changes were found when medium magnetic and electrical fields ($\leqslant 1$ T, $\leqslant 10$ kV/cm) were applied. Even the change in temperature (160–600 K) resulted in only small changes of the peak parameters. The relative shifts obtained were in the order of 0.1–1% i.e., they have to be interpreted with caution. According to [7,13] the observed peak positions themselves suggest the use of a $^{2S+1}L_J$ energy level scheme for Sm^{3+} in all glass samples, apparently subsplit by the (local) crystal field. The weakest line ($^4F_{3/2} \rightarrow {}^6H_{5/2}$), however, showed a larger and anomalous temperature dependence of the fluorescence intensity (Fig. 1(b)).

2.2. $(Li_2B_4O_7)_{1-x-y}(MoO_3)_x(Sm_2O_3)_y$ glasses

In order to compare the quantum yield Φ_j of the different transitions for various matrices, one has to correct the standardized fluorescence spectra. Fig. 1(a) shows an example, for the absorption α_0 of the excitation beam and for the absorption of the fluorescent beam α_f while they pass through the glass for a distance d_0, d. According to Ref [7], the corrected intensity I_c, that is the fluorescent intensity if the matrix were totally transparent at both wavelengths, is given by:

$$I_c \sim I_{\exp} f(\lambda_0, d_0) f(\lambda_f, d_f) \quad \text{with}$$

$$f(\lambda, d) = \alpha(\lambda)/(1 - \exp(-\alpha(\lambda) d)). \tag{1}$$

α_f, α_0 are numerically given by the Sm specific and the background absorption (Fig. 1(a), Table 1). After that, the local quantum yield is defined by:

$$\Phi^l_{\mathrm{loc}} = I^l_c/I_{\mathrm{em}} \quad l = 5,7,9,11. \tag{2}$$

where I_{em} is the sum over all emitted quanta. Fig. 2 shows the local quantum yield for the four transitions $^4G_{5/2} \rightarrow {}^6H_{x/2}(x = 5,7,9,11)$ as a function of the MoO$_3$-content. Note, that the 9/2 and 11/2 transitions do not scale with the other two transitions, suggesting a particular sensitivity of the corresponding oscillators to matrix changes just as found in the equivalent transitions in the tungstate glasses [7]. Some additional information is summarized in Table 1. One significant feature is the (linear) increase of the Sm-specific absorption with x, which again suggests an influence of the glass matrix on the oscillator strengths. Another interesting feature is the increasing brownish coloration, suggesting the appearance of some other kind of molybdate cluster(s) at higher MoO$_3$ contents, which may or may not contain different valence states of molybdenum Mo^{6+}, Mo^{5+}, as found for the analog tungstate glasses [1,32].

3. Discussion

3.1. $(Li_2B_4O_7)_{1-y}(Sm_2O_3)_y$ glasses

3.1.1. *Assignment of the transitions*

Fig. 3(b) shows the $^{2S+1}L_J$ energy level scheme of Sm^{3+} according to Refs. [12–15]. The notation used is not consistent with a local C_1 or C_2 [16] symmetry, disallowing more specific assignments of the observed transitions. We can state, however, that the splittings and degeneracies as proposed in Fig. 3(b) would be sufficient to explain all the observed features, for example, according to Fig. 3(b), the $^4F_{3/2} \rightarrow {}^6H_{5/2}({}^4G_{5/2} \rightarrow {}^6H_{5/2})$ transition could potentially be split into a triplet, as is found (Fig. 1(a)). Random variations of the nearest environments would result in equivalent variations of those levels and that would explain the Gaussian shape and the insensitivity to temperature of the deconvoluted fluorescence peaks. According to the known spectra of Sm^{+2} [17–19], the coexistence of Sm^{2+} can be ruled out here.

Table 1
Composition, Sm-specific absorption, density and color of the glasses

Li$_2$B$_4$O$_7$ [mol %]	MoO$_3$ [mol %]	Sm$_2$O$_3$ [mol %]	δ [g/cm^3]	α_{Sm} [m^{-1}, 4880 Å]	Color
100	0	0	2.13		transparent
99	0	1	2.23	5.6	transparent
94	5	1	2.27	6.7	transparent
89	10	1	2.30	8.3	transparent
79	20	1	2.37	10.4	transparent
70	30	0	2.40		brownish
69	30	1	2.45	15.2	brownish
59	40	1	2.54	18.3	brownish
54	45	1	2.59	21.9	brown

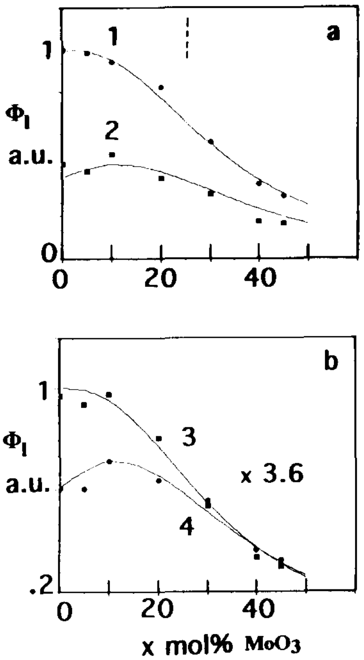

Fig. 2. Local quantum yield Φ_l versus MoO$_3$ content for the Sm^{3+}: $^4G_{5/2} \rightarrow {}^6H_{n/2}$ transitions with $n = 5,7,9,11(3,1,2,4)$. Multiply scale of 2(a) by 3.6 to match the scale of (b). —— fit to function: $F_1(x) = 1/(1 + 16.7x^{(7.5/3)})$; (1, 3); $F_2(x) = F_1(x)(1 + 2.4x - 2x^2)$; (2, 4); – – – borate anomaly (see text).

3.1.2. *Temperature-induced changes of the spectra*

The slight temperature-induced shifts of the line positions (Fig. 1(b)) are usually connected with a change of the average static crystal field with

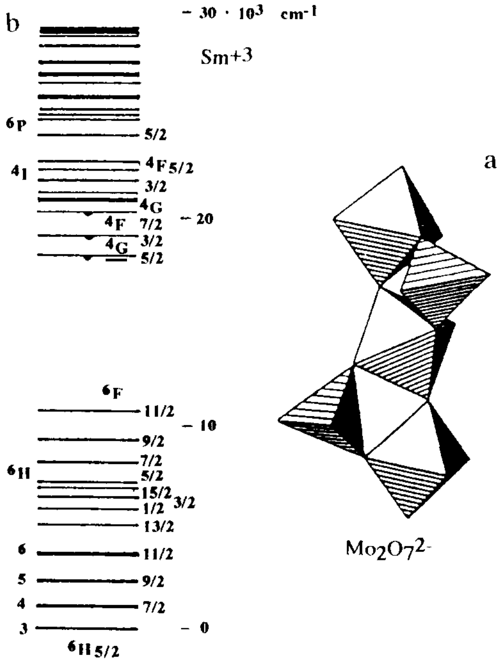

Fig. 3. $Mo_2O_7^{2-}$ cluster (a) and energy level scheme of Sm^{3+} (b) according to [12, 15, 16, 33, 34]. Numbers left side of level scheme: degeneracy of states.

thermal expansion [20, 21]. The reduction of fluorescence intensity with increasing temperature is usually ascribed to competing non-radiative multiphonon processes, which become increasingly important when the temperature is raised [22]. This does not, however, account for the anomalous temperature behaviour of the first small triplet $^4F_{3/2} \rightarrow {}^6H_{5/2}$ (Fig. 1(b)): here, by similarity argument, we adopt the interpretation given by Ref. [23] for the case of Er^{3+} in tellurite and germanate glasses; in that case the upper (fluorescence) level of this transition gets populated by fast thermalization of excited states. In particular, if the $^4G_{5/2}$ and the $^4F_{3/2}$ levels (Fig. 3) are close to thermal equilibrium, the occupancy of the higher $^4F_{3/2}$ state should be proportional to exp $(-\Delta E/kT)$, where ΔE is the $^4G_{5/2} - {}^4F_{3/2}$ level difference. Therefore, we use a logarithmic plot versus $1/T$ [29, 30]. From that plot we find $990\,cm^{-1}$ and from the scale of Fig. 3(b), $995\,cm^{-1}$. A small increase in linewidth with temperature apparently occurs in both cases, however, it is difficult to extract the true linewidths even after deconvolution as additional (nonresolved) transitions might be present. The temperature-induced broadening is higher as in equivalent crystals [24], which again suggests that increased variations in the local crystal field connected with the thermal expansion are responsible.

3.2. $(Li_2B_4O_7)_{1-x-y}(MoO_3)_x(Sm_2O_3)_y$ glasses

3.2.1. MoO_3 induced changes: variation of the oscillator strengths

The slight shifts of the line positions to higher wavelengths have been connected with an increase of the Sm-nearest neighbour interactions with x [7]. Also, the small increase of $\Phi_l(x)$ at low x and the increase of the Sm-specific absorption have been assigned to an increase of the respective oscillator strengths following the reduction of the Sm–O distances, i.e., increased mixing of electronic states leads to a further relaxation of the Laport selection rules, which in turn is thought to be induced by the average replacement of B by W (Mo) in the tungstate (or molybdate) glasses.

3.2.2. MoO_3-induced changes: Fluorescence quenching

The local quantum yield versus x curves for the four main peaks show that we have always a fluorescence decay at higher x. Since the oscillator strengths increase with a change of matrix, see Table 1 and Ref. [7], the decrease of the quantum yields should be due to fluorescence quenching. As the maximum of $\Phi_l(x)$ for the 9/2 and 11/2 transitions at low x suggests a superposition of two effects of almost equal magnitude, for a description of $\Phi_l(x)$ in terms of fluorescence quenching alone we should start with the 7/2, 5/2 transitions. Here, we may assume a negligible change of oscillator strengths. For the fluorescence quenching description one has a choice to adopt intrinsic (matrix induced) or extrinsic (impurities, clusters) causes. Little is known about the electronic states of the molybdateglass matrix and in particular about those of its clusters. If, however, the MoO_3 substitution itself would introduce acceptor states for non-radiative transitions, we would have strong fluorescence quenching already at small MoO_3

contents; however, at small x, $\Phi_l(x)$ is almost constant. Therefore, and since intentional impurities are absent, MoO_3 clusters are more likely to act as acceptors. Fluorescence quenching by both multipole based energy transfer and impurity assisted resonant energy transfer, can be compiled into one formula for the reduced fluorescence intensity [25,26], i.e.:

$$I_r = I_e/I_0 = (1 + \beta(c/c^*)^{\theta/3})^{-1} = F(c)$$

$$c^* = 3/4\pi(R^*)^{\theta/3}, \tag{3}$$

where R^* is the critical transfer distance, β a mechanism dependent constant, c the acceptor concentration, I_e, I_0 the fluorescence intensity with and without acceptor, θ mechanism dependent exponent: $\theta = 3$ the (assisted) radiationless resonant energy transfer, $\theta = 6$ the dipole–dipole interaction, $\theta = 8$ the dipole–quadrupole interaction, $\theta = 10$ the quadrupole–quadrupole interaction.

It has been proposed that the expected cluster concentrations c_i can be written as a power of the number of tungsten atoms i involved, $c_i \sim x^i$ and thus also as a power of the number m of their MoO_3–(WO_3) units: $c \sim x^m$ [1]. Assuming the exponent m to be integer and combining this with Eq. (3), we expect as exponent of x: $m\Theta/3$; i.e. for $m = 1$ we would find $m\Theta = 3, 6, 8, 10$; for $m = 2$ we would find $m\Theta = 6, 12, 16, 20$ and for $m = 3$ we would have $m\Theta = 9, 18, 24, 30$, etc. As the optimal fit of Eq. (1) to $\Phi_l(x)$ gives a θ of 7–8 (Fig. 2), we have a choice of assigning the fluorescence quenching to $m = 1$, $\theta = 8$ (MoO_3 as impurity, dipole–quadrupole interaction) or $m = 2$–3, $\theta = 3$ (2.5 (MoO_3) as impurity, assisted resonant energy transfer).

As it has been shown that already 1 mol% Cu [27], but not that amount of WO_3 can completely quench the Sm^{3+} fluorescence, the first choice, taking the glass forming MoO_3 as an acceptor is again to be ruled out.

On the other hand, a $Mo_2O_7^{2-}$ cluster (Fig. 3(a)), which has been claimed to exist in molybdate glasses from the interpretation of Raman spectra [3], would indeed involve 2–3 formula units of MoO_3 [33,34].

If this analysis is correct, we would expect to fit the other two transitions 9/2, 11/2 (Fig. 2) by taking into account the (linear) matrix induced increase in oscillator strength; this we can implement by replacing I_0 in Eq. (3) by $I_0(x)$ with

$$I_0(x) = I_0(1 + ax + bx^2 + \dots) \quad \text{to give}$$

$$I_r = I_0(x)\, F(c(x))/I_0. \tag{4}$$

While the linear part of the expansion is directly related to the linear increase of the oscillator strength, the small curvature bx^2 could arise from the Sm^{3+} self-quenching, as this effect runs through a maximum at about 2 weight% Sm [31]; i.e. we expect a curvature when the Sm-content is changed around 2 weight% or when the density of the glasses is changed with x while the Sm content is fixed. Indeed, according to Table 1, the density increases somewhat with x. Overall, we find that a fit to Eq. (4) is possible.

As we expect a similar cluster formation also in the equivalent Lithiumboratetungstate glasses, we expect to apply this fitting procedure also to Sm^{3+} and Eu^{3+} in tungstate borate glasses, at least when the charge transfer states which frequently occur in those glasses [1–8] do not contribute to the fluorescence quenching significantly. This fit is also possible, but apparently we have to allow for two different neighbourhoods for the fluorescent ions, one of which is unaffected by the clusters, i.e. would give a constant reduced quantum yield and the other involves some cluster acceptor state:

$$I_r = I_0(x)\,(\alpha F(c(x)) + (1 - \alpha)F_0)/I_0. \tag{5}$$

The result for $\Phi_l(x)$ of a Eu^{3+} fluorescent transition in a tungstate glass is shown in Fig. 4. Specifically, in Fig. 4(a) both contributions are superimposed, the change in oscillator strength included; in Fig. 4(b), the oscillator strength is normalized to 1 in order to show that a $\Phi_l(x)$ curve is obtained like that for the molybdate glasses (Fig. 2). This suggests the presence of clusters in the tungstate glasses, too, but the number density of the $W_2O_7^{2-}$ clusters would be considerable smaller ; the borate anomaly, which is supposed to occur around $x = 20$ mol% [32], however, appears to be more pronounced. The assumption of two different neighbourhoods for Sm^{3+} might appear remote at first sight, but an equivalent situation has been encountered with Cu acceptors in borate–tungstate glasses [28].

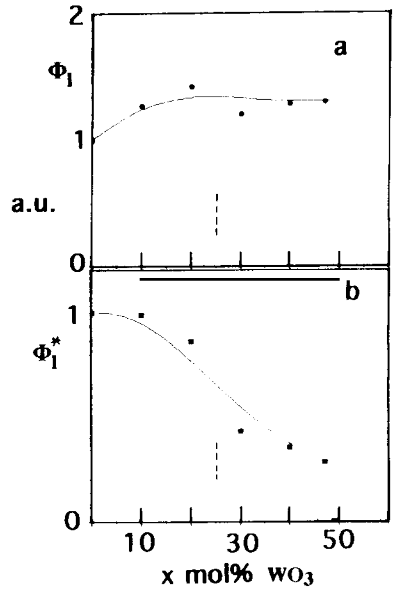

Fig. 4. Local quantum yield Φ_l (a) and local quantum yield with normalized oscillator strengths Φ_l^* (b) of $Eu^{3+}({}^5D_0 \to {}^7F_2)$ in tungstate borate glasses versus WO_3 content :—— fit to function $F_1(x)$ (b) and $I_r = (0.6F_1(x) + 0.4)\,(1 + 2.75x)$ (a); ---- borate anomaly (see text).

4. Conclusions

From the analysis of the fluorescent transitions of Sm^{3+} in lithium borate molybdate glasses we infer an enhancement of the oscillator strengths with increasing MoO_3 content, probably due to an increased hybridization of the 4f electronic states with the states of the sourrounding matrix ions, analog to effects found in lithium borate tungstate glasses. We also infer an increased fluorescence quenching with increasing MoO_3 content which we relate to a certain MoO_3 cluster, these clusters are likely to exist also in the tungstate glasses; according to Raman data this cluster is probably $Mo_2O_7^{2-}$ ($W_2O_7^{2-}$). We do not find direct evidence for the presence of charge transfer states in the molybdate glasses although those frequently occur in lithium borate tungstate glasses.

Acknowledgements

The authors thank R. Braunstein for stimulating discussions. This work was supported in part by the Deutsche Forschungsgemeinschaft.

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