Spectroscopic properties of trivalent samarium ions in glasses

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ABSTRACT

Optical absorption and luminescence spectra of the Sm^{3+} -doped fluorophosphate glasses $75\text{NaPO}_3\text{-}24\text{CaF}_2\text{-}1\text{SmF}_3$ and $75\text{NaPO}_3\text{-}24\text{BaF}_2\text{-}1\text{SmF}_3$, the phosphate glass $75\text{NaPO}_3\text{-}24.5\text{ZnO-}0.5\text{Sm}_2\text{O}_3$ and the fluoride glass ZBLAN:Sm^{3+} have been recorded. The dipole strengths of the transitions in the absorption spectrum are parameterized in terms of three phenomenological Judd-Ofelt intensity parameters Ω_λ ($\lambda = 2, 4$ and 6). The determination of intensity parameters for Sm^{3+} has inherent difficulties due to very large number of energy levels lying close to each other. In this case, we can take advantage of the property that both the dipole strengths and the squared reduced matrix elements of overlapping transitions are additive. The relation between the spectral intensities and the glass composition is discussed.

Keywords: samarium, rare earths, lanthanides, glasses, absorption spectroscopy, luminescence, Judd-Ofelt theory.

1. INTRODUCTION

The trivalent lanthanide ions are popular doping ions for various types of glasses. This interest is not only due to the interesting spectroscopic properties of these ions, but also to the potential of lanthanide-doped glasses as laser materials¹. Over the years, a vast amount of data on the spectroscopic properties of trivalent lanthanide ions in glasses were collected². The majority of the studies were devoted to Nd^{3+} , Pr^{3+} and Er^{3+} as the spectroscopically active centers. Much less studies are dealing with trivalent samarium³⁻¹². Although the trivalent samarium ion exhibits a strong luminescence in the visible spectral region (orange), the complicated electronic structure of the $4f^5$ configuration is responsible for this neglect. The very large number of energy levels lying close to each other renders the interpretation of the absorption spectra rather cumbersome. Tricks are needed to extract reliable intensity parameters.

In this paper, we discuss the spectroscopic properties of trivalent samarium in four different glass matrices: the fluoride glass $53\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}3\text{AlF}_3\text{-}3\text{LaF}_3\text{-}20\text{NaF-}1\text{SmF}_3$ (ZBLAN:Sm^{3+}), the fluorophosphate glasses $75\text{NaPO}_3\text{-}24\text{CaF}_2\text{-}1\text{SmF}_3$ and $75\text{NaPO}_3\text{-}24\text{BaF}_2\text{-}1\text{SmF}_3$, and the phosphate glass $75\text{NaPO}_3\text{-}24.5\text{ZnO-}0.5\text{Sm}_2\text{O}_3$.

2. EXPERIMENTAL DETAILS

The sample of the 1% Sm^{3+} doped ZBLAN glass (53 mol% ZrF_4 , 20 mol% BaF_2 , 20 mol% NaF , 3 mol% AlF_3 , 3 mol% LaF_3 and 1 mol% SmF_3) was prepared using methods described elsewhere¹³. The starting reagents for the glass preparation were ZrO_2 , BaF_2 , NaF , Al_2O_3 , La_2O_3 and Sm_2O_3 in appropriate ratios. The oxides were transformed into the fluorides during a fluorination step with NH_4HF_2 . Ammonium hydrogen fluoride was added to the reaction mixture in excess ($2\times$ the stoichiometric ratio). The reaction mixture was heated in a platinum crucible at 300 °C for several hours. Complex metallic ammonium fluorides are formed and subsequently decomposed by heating to 420 °C. At this temperature the excess NH_4HF_2 is also removed. The resulting powder was melted in a dry argon atmosphere (glove box) at 500 °C. The batch was further heated to 750 °C to refine the melt. Refining is necessary to remove the OH groups. The glass was cast into a brass mould which was preheated to 270 °C and the batch was annealed at this temperature for one day. The fluorophosphate

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glasses were prepared by melting the required amounts of sodium metaphosphate (NaPO_3) and the fluoride compounds in a platinum tube at a temperature of ca. 900 °C. After melting, heating was continued for 15 minutes to homogenize the melt. Then, the melt was cast in a brass mould (preheated to 250-300 °C). In order to remove strain, the glass samples were annealed for four hours in an oven at 270 °C. The phosphate glass $75\text{NaPO}_3\text{-}24.5\text{ZnO-}0.5\text{Sm}_2\text{O}_3$ was prepared in an analogous way as the fluorophosphate glasses. Finally, the glass samples were cut and polished. The glasses show the typical yellow color of the Sm^{3+} ion¹⁴. The physical properties of the glasses used in this study are summarized in Table 1.

Table 1: Refractive index (n), density (ρ) and Sm^{3+} concentration of the glasses used in this study.

Glass	n	ρ (g cm ⁻³)	conc. Sm^{3+} (mol L ⁻¹)
ZBLAN: Sm^{3+}	1.495	4.43	0.32
$75\text{NaPO}_3\text{-}24\text{CaF}_2\text{-}1\text{SmF}_3$	1.486	2.66	0.28
$75\text{NaPO}_3\text{-}24\text{BaF}_2\text{-}1\text{SmF}_3$	1.506	3.14	0.26
$75\text{NaPO}_3\text{-}24.5\text{ZnO-}0.5\text{Sm}_2\text{O}_3$	1.525	2.90	0.29

The density of the glass samples were determined by Archimedes' method, using CCl_4 as the immersion liquid. The refraction index n_D was measured on a Abbé refractometer (ATAGO 3T). The optical path length was measured to the nearest 0.01 cm. Absorption spectra were recorded at room temperature on a Shimadzu UV-3100 spectrophotometer. Luminescence spectra were recorded with a home-built apparatus. A water-cooled 450 W xenon lamp was used as the excitation source. Wavelength selection was achieved by a Sciencetech Model 9050 monochromator. Luminescence light was measured at an angle of 90° with respect to the excitation beam. The emission light was analyzed by a McPherson monochromator (1200 lines/mm) and detected by a single-photon counting detector (photomultiplier and Stanford Research Systems SR400 Two Channel Gated Photon Counter). The emission spectra are not corrected for the instrument spectral sensitivity. Wavelength calibration was done by using the emission lines of a mercury lamp. Luminescence spectra can be recorded between 350 nm and 750 nm.

3. THEORETICAL BACKGROUND

The intensities of the transitions can be characterized by the dipole strength D :

$$D = \frac{1}{108.9 \times C \times d} \int \frac{A(\bar{\nu})}{\bar{\nu}} d\bar{\nu}, \quad (1)$$

where C is the concentration of the lanthanide ion (mol L⁻¹), d is the optical path length (cm), A is the absorbance ($A = -\log(I/I_0)$) and $\bar{\nu}$ is the wavenumber (cm⁻¹). We are conscious of the fact that we do not use S.I., but the C.G.S. system. In spectroscopy, the S.I.-units are not easy to handle and their use often obscures simple relations between different quantities. The dipole strength is expressed in D^2 (Debye²). According to the Judd-Ofelt theory^{15,16}, the intensity of induced electric dipole transitions can be described in terms of three phenomenological intensity parameters Ω_λ ($\lambda = 2, 4$ and 6):

$$D = \frac{10^{36}}{2J+1} \frac{(n^2+2)^2}{9n} e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle J \parallel U^{(\lambda)} \parallel J \right\rangle^2. \quad (2)$$

The factor 10^{36} is used for the conversion between D^2 units and $\text{esu}^2 \text{ cm}^2$ ($1 D = 10^{-18} \text{ esu cm}$). The elementary charge e is $4.803 \times 10^{-10} \text{ esu}$. The degeneracy of the ground state is equal to $2J+1$. The factor $(n^2 + 2)^2 / 9n$ takes into account that the lanthanide ion is not in a vacuum, but in a dielectric medium (n is the refractive index of the glass). Finally, the $|J \langle U^{(\lambda)} \rangle J|^2$ are the squared reduced matrix elements. We used in our Judd-Ofelt parameterization the matrix elements reported by Carnall and coworkers¹⁷ for samarium ions in aqueous solution. We can use these matrix elements, because the matrix elements are virtually host independent. For the calculation of the luminescence properties we used the matrix elements reported by Carnall *et al.* for samarium ions in LaF_3 ¹⁸. The Ω_λ parameters can be determined by a standard-least squares fitting method.

Figure 1. Absorption spectrum of trivalent samarium ions in the fluorozirconate glass ZBLAN (at ambient temperature)

4. RESULTS AND DISCUSSION

The absorption spectra for the different glass compositions were recorded at room temperature. Room temperature spectra are necessary for application of the Judd-Ofelt theory, because this theoretical model assumes that all crystal-field levels of the ground state are equally populated. This condition is fairly well fulfilled at room temperature, if the crystal-field splitting is not too large (a few hundred cm^{-1}). In all the glasses, samarium is present in the tripositive oxidation state (Sm^{3+}). The absorption spectrum of ZBLAN:Sm^{3+} is shown in figure 1. The Sm^{3+} ion has a $4f^5$ electron configuration which is characterized by 198 $^{2S+1}L_J$ free-ion levels. In the presence of a low-symmetric crystal field, these free-ion manifolds split

into a total of 1001 crystal-field levels (Kramers doublets). In the glasses, the crystal-field fine structure is not resolved due to inhomogeneous line-broadening, and only absorption bands between $^{2S+1}L_J$ manifolds are observed. Only a limited number of the 198 $^{2S+1}L_J$ manifolds can be observed experimentally. Moreover many of the manifolds are lying so close to each other that it is not possible to determine their barycenters. For instance, in the absorption spectrum of ZBLAN:Sm³⁺ only 17 discrete absorption bands can be observed, belonging to a total of 46 $^{2S+1}L_J$ levels. For the other glasses, even less transitions are observed, because their UV-cutoff is shifted to longer wavelengths.

Table 2: Measured and calculated dipole strengths for the transitions in the absorption spectrum of the glass matrix ZBLAN:Sm³⁺ (*).

Transition ← $^6H_{5/2}$	$\bar{\nu}$ /cm ⁻¹	D _{exp} /10 ⁻⁶ Debye ²	D _{calc} /10 ⁻⁶ Debye ²	D _{exp} - D _{calc} /10 ⁻⁶ Debye ²	D _{calc} / D _{exp}
$^6H_{15/2}, ^6F_{3/2}, ^6F_{1/2}$	6710	589	589	0	1.00
$^6F_{5/2}$	7240	479	481	-2	1.00
$^6F_{7/2}$	8100	520	570	-50	1.10
$^6F_{9/2}$	9230	354	305	+49	0.86
$^6F_{11/2}$	10580	41	42	-1	1.02
$^4G_{5/2}$	17850	2	2	0	1.00
$^4F_{3/2}$	19010	2	2	0	1.00
$^4I_{13/2}, ^4I_{11/2}, ^4M_{15/2}, ^4I_{9/2}, ^4G_{7/2}$	20980	153	66	+87	0.43
$^4I_{15/2}, ^4M_{17/2}, ^4G_{9/2}$	22750	21	8	+13	0.38
$^4G_{11/2}, ^4L_{15/2}, ^4K_{11/2}, ^6P_{3/2}, ^4F_{7/2}$	25020	371	336	+35	0.90
$^4L_{13/2}, (^6P, ^4P)_{5/2}$					
$^4F_{9/2}, ^4K_{13/2}, ^4L_{17/2}, ^6P_{7/2}, ^4D_{1/2}$	26810	57	65	-8	1.14
$^4H_{7/2}, (^4D, ^6P)_{5/2}, ^4D_{3/2}$	27700	83	68	+15	0.82
$^4H_{11/2}, ^4D_{7/2}, ^4H_{9/2}, ^4K_{15/2}$	29140	38	32	+6	0.84
$^4G_{5/2}, ^4G_{9/2}, ^4G_{7/2}, ^4H_{13/2}$	30190	8	5	+3	0.62
$^4P_{3/2}, ^2L_{15/2}, ^4G_{11/2}$	31590	23	22	+1	0.96
$^4P_{5/2}$	32850	7	3	+4	0.43
$(^4I, ^4F)_{9/2}$	34560	2	1	+1	0.50

(*) The Judd-Ofelt parameters used for the intensity calculation are: $\Omega_2 = (2.15 \pm 0.21) \cdot 10^{-20} \text{ cm}^2$, $\Omega_4 = (3.05 \pm 0.19) \cdot 10^{-20} \text{ cm}^2$ and $\Omega_6 = (1.56 \pm 0.12) \cdot 10^{-20} \text{ cm}^2$. The R.M.S. value is $33 \cdot 10^{-6} \text{ Debye}^2$.

The initial level for all the transitions is the $^6H_{5/2}$ ground state of Sm^{3+} . The first excited state $^6H_{7/2}$ is only ca. 1100 cm^{-1} above the ground state, but no transitions starting from this level could be detected. The absorption peaks are due to transitions from the $^6H_{5/2}$ level to the various excited $^{2S+1}L_J$ levels. The majority of the transitions in the spectra originate from induced electric dipole (ED) interactions with the selection rule $\Delta J \leq 6$. Some transitions contain contributions from the magnetic dipole (MD) interactions with the selection rule $\Delta J = 0, \pm 1$. An example is the $^4G_{5/2} \leftarrow ^6H_{5/2}$ transition at ca. 17850 cm^{-1} . The most intense transitions are found in the near infrared at energies lower than 10000 cm^{-1} . These are transitions to the $^6H_{15/2}$ and to the 6F_J manifolds. The high intensity of these transitions is expected because the transitions are spin-allowed ($\Delta S = 0$). All the transitions in the visible and in the UV spectral region are spin-forbidden, except the intense transition $^6P_{3/2} \leftarrow ^6H_{5/2}$ around 25000 cm^{-1} .

Table 3: Judd-Ofelt intensity parameters of samarium-doped glasses

Glass composition	$\Omega_2 / 10^{-20} cm^2$	$\Omega_4 / 10^{-20} cm^2$	$\Omega_6 / 10^{-20} cm^2$
ZBLAN:Sm ³⁺	2.15±0.21	3.05±0.19	1.56±0.12
75NaPO ₃ -24CaF ₂ -1SmF ₃	2.18±0.32	3.80±0.28	2.15±0.18
75NaPO ₃ -24BaF ₂ -1SmF ₃	2.23±0.25	3.82±0.23	2.18±0.15
75NaPO ₃ -24.5ZnO-0.5Sm ₂ O ₃	2.35±0.23	3.87±0.20	2.26±0.13

From the spectra, the experimental dipole strengths were derived and these were used to determine the Judd-Ofelt intensity parameters Ω_λ ($\lambda=2, 4$ and 6). In the case of overlapping transitions, the matrix elements of the corresponding transitions were summed. It is allowed to sum the reduced matrix elements, because the reduced matrix elements are additive and they can act independently of each other. Indeed the total intensity of an absorption band is equal to the sum of the intensities of the overlapping transitions. In theory, it should be possible to determine the different contributions to the total absorption band separately by means of fitting Gaussian curves under the absorption band. However, in samarium-doped glasses the overlap is so severe that it is simply impossible to unambiguously assign $^{2S+1}L_J$ labels to the overlapping transitions. That the energy levels overlap to a large extent in the spectral region above 20000 cm^{-1} , is evident from literature data dealing with Sm^{3+} in crystalline host matrices, for instance SmODA²⁰ and SmOF²¹. The spectral assignments, the experimental and calculated dipole strengths for samarium ions in the glass ZBLAN:Sm³⁺ are given in Table 2. The intensity results for the other glasses are analogous, so that we restrict ourselves to reporting only the Ω_λ parameters (Table 3). The agreement between the calculated and the experimental dipole strengths is quite well. The errors on the intensity parameters are small: especially the Ω_6 parameter is well defined. The Judd-Ofelt theory gives thus a framework in which the intensities of the f-f transitions of trivalent samarium can be adequately described.

If we compare the Judd-Ofelt parameters for the different Sm^{3+} doped glasses, no large variations are found. The intensity parameters of the fluorophosphate and the phosphate glasses are very close to each other. Moreover, if we take the errors on the parameters into account, it is acceptable to that these three glasses have identical parameters¹⁹. Only for ZBLAN:Sm³⁺, the intensity parameters are smaller. This is quite expectable, since the transitions of the other lanthanide ions also show very low intensities in the fluoride glasses. For all the samarium-doped glasses we studied, we found the following trend for the values of the intensity parameters: $\Omega_6 < \Omega_2 < \Omega_4$. This differs from the trend observed for Nd^{3+} in comparable glasses²². We found: $\Omega_2 < \Omega_4 < \Omega_6$ for the fluorophosphate and fluoride glasses, whereas the trend for the phosphate glasses was $\Omega_4 < \Omega_2 < \Omega_6$. But for all the parameters we find that the parameter values increase in the order fluoride < fluorophosphate < phosphate glasses. In contradistinction to Nd^{3+} , there are not enough literature data available to make a thorough comparison of the intensities of Sm-doped glasses. When comparing our results with those of Boehm *et al.*³, it is obvious that the intensities are much higher in borate, germanate, tellurite and in other phosphate glasses than in our glasses. Only Sm^{3+} in

oxyfluoroborate glasses exhibits weaker spectral transitions¹². The Ω_λ parameters we obtained for the ZBLAN:Sm³⁺ glass are comparable with the values of the parameters in other fluoride glasses^{5,7}.

When the glasses are irradiated by blue, violet or ultraviolet light, an intense orange luminescence is observed. The luminescence spectrum of ZBLAN:Sm³⁺ is shown in figure 2. When any of the energy levels above $^4G_{5/2}$ is excited, there is a fast non-radiative relaxation to this emitting level. Consequently, the same luminescence spectrum is obtained regardless the excitation wavelength (same relative intensities). However, the absolute intensities are dependent on the excitation wavelength. The most intense luminescence is observed by exciting the samples at 400 nm (25000 cm⁻¹). This is excitation to the $^6P_{3/2}$ level. The orange luminescence color is due to the intense $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition at ca. 16700 cm⁻¹.

Figure 2. Luminescence spectrum of ZBLAN:Sm³⁺ at ambient temperature. The excitation wavelength is 400 nm.

5. CONCLUSIONS

This paper described the spectroscopic properties of the trivalent samarium ion doped into fluoride, fluorophosphate and phosphate glasses. The intensities of the transitions in the optical absorption spectrum can adequately be described by three phenomenological intensity parameters (Ω_2 , Ω_4 , Ω_6) using the Judd-Ofelt theory. Because many transitions overlap, it is necessary to integrate all the transitions contribution to one absorption band together. The corresponding reduced matrix elements have to be summed. All the glasses show a strong orange luminescence, typical for the Sm³⁺ ion.

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