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**SPECTRAL CHARACTERIZATION AND EXCITED-STATE
INTERACTIONS BETWEEN RARE EARTH IONS DOPED IN
BOROSILICATE AND SOL-GEL GLASSES:
ENERGY TRANSFER UP-CONVERSION IN THE Pr-Sm SYSTEM.¹**

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SPECTRAL CHARACTERIZATION AND EXCITED-STATE INTERACTIONS BETWEEN RARE EARTH IONS DOPED IN BOROSILICATE AND SOL-GEL GLASSES: ENERGY TRANSFER UP-CONVERSION IN THE Pr-Sm SYSTEM.

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ABSTRACT

Spectroscopic properties of selected 4f-elements in a sol-gel and two high temperature silicate based glasses are reported. In particular, the spectral properties of the Eu^{3+} ion have been used to probe the local coordination environment of the f-elements in these glass matrices. Luminescence studies of the high temperature glasses indicated that the electric dipole allowed f-f transitions dominate the spectra which suggests that the local symmetry around the 4f-ions is low. Temperature-dependent spectroscopic studies of the sol-gel glasses indicated that the f-elements retain a "solution-like" environment prior to thermal processing. After heat treatment, an increase in the emission intensities of the electric-dipole transitions is accompanied by a concomitant decrease in the magnetic-dipole allowed transitions. Moreover, excited state interactions has also been observed in the high temperature glasses that contain certain multiple f-elements. In Pr-Sm systems, exclusive excitation of the Sm^{3+} ion with a 514 nm argon ion laser line provides a higher-energy emission band (ca. 490 nm) from the Pr^{3+} ion ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) transition. This energy up-conversion is attributed to energy transfer from the $^6\text{H}_{13/2}$ level of the Sm^{3+} ion to the $^3\text{H}_6$ state of the Pr^{3+} ion. Following a second photon absorption, the Pr^{3+} ion is excited to the emitting $^3\text{P}_0$ level.

INTRODUCTION

Luminescence studies of f-elements in glassy matrices has attracted a considerable interest, due to the possible implication in solid-state laser and related optical applications [1, 2]. Understanding the local environment around the optically active ion is crucial for materials engineering, since the performance of such optical devices largely depends on the nature of the bonding interaction between the f-ions and the glass matrices [3]. In this regard, the Eu^{3+} ion is an ideal optical probe. One feature is that the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission band is non-degenerate and splitting or broadening reflects a dissimilar bonding environment. Another luminescence feature that provides information on the local environment is the "hypersensitive" $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. In the Eu^{3+} ion, an increase in the relative intensity of this electric-dipole allowed ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) transition is linked to deviations from an inversion symmetry. We have taken advantage of these spectroscopic features to monitor the "structural" variations in the local bonding environments in both high temperature borosilicate and sol-gel derived glasses.

In addition, the Pr^{3+} ion energy-level scheme is especially useful for applications involving fluorescence arising from two-step photo-excitation and energy up-conversion [4]. Laser and energy up-conversion properties have been documented in praseodymium(III) doped crystals and glasses. Examples include Pr^{3+} ion doped in LaCl_3 glasses that showed "up-converted" emission at 20930 cm^{-1} following excitation at 17050 cm^{-1} [5]. Two- and three-ion cooperative up-conversion has also been noted for the Pr^{3+} ion in LaF_3 , where emission from the $^1\text{S}_0$ high-energy excited level has been observed when a radiative energy capable of exiting to the much lower, $^3\text{P}_0$,

level is used [6].

In this paper, we present spectroscopic studies involving the Eu^{3+} ion as a probe to the local coordination environment of f-elements doped in high temperature borosilicate glasses and a sol-gel matrix. In addition, we present spectroscopic investigations on the excited-state interactions between multiple f-ions in the high temperature glasses. In particular, we report the nature of the energy transfer up-conversion that has been observed in the Pr-Sm system.

EXPERIMENTAL

Two high temperature glasses were studied in this work. The lower melting calcium borosilicate glass (850 °C) had a composition of: SiO_2 (50 %); B_2O_3 (18%); Na_2O (24%); CaO (3%). The higher melting (1400 °C) lead borosilicate had the following nominal weight percentages: SiO_2 (30 %); B_2O_3 (6 %); Al_2O_3 (13%); PbO (3%) and La_2O_3 (10- 15 %). Both glasses were prepared by dissolving the f-element oxide in the molten glasses. Platinum containers were used for the dissolution procedure.

The sol-gel samples were prepared via acid-hydrolysis (0.1 N HNO_3) and condensation of tetramethoxysilane (TMOS). The lanthanide was introduced in the initial stage of the process by dissolving the nitrate salt in water. The top of the glass cylinder containing the mixture was partly covered to reduce volatilization during the condensation process. Densification provided a clear glass after several days.

The spectroscopic investigations were conducted using Argon-ion laser (Coherent Models 90 and 306) as the excitation source. The luminescence spectra were recorded with a double, 2 m spectrophotometer (Raman Model HG.2S, Jobin-Yvon/Instrument SA), having a resolution of 0.5 cm^{-1} at 514.5 nm. Emission from the sample was detected by a photon counting system, which employed a photomultiplier tube (Hamamatsu R636) and a multichannel analyzer (Nicolet 1170) interfaced with a personal computer. Data analysis was conducted with a "SpectraCalc" software (Galactic Industries)

RESULTS

The emission spectra of the Eu^{3+} ion doped in the two high temperature and sol-gel glasses are shown in Figure 1. In the high temperature glasses photo-excitation with 514 nm radiation provides emission (Figure 1a) originating from the $^5\text{D}_0$ excited state to the various $^7\text{F}_i$ ground manifolds. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is observed at 578.5 nm. Three weak, but well resolved bands are also evident for the magnetic-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions at 586, 591, and 596 nm. The most intense band in this spectrum corresponds to the electric-dipole allowed $^5\text{D}_0 \rightarrow ^5\text{F}_2$ transition. The dominance of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, indicates a lack of an inversion center for the local symmetry of the Eu^{3+} ion. The complete splitting of the three Stark components of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition also suggests that the Eu^{3+} ions are in low-symmetry bonding sites in the glass matrix.

Spectroscopic studies have also been conducted in sol-gel matrix in order to compare the Eu^{3+} ion bonding interactions with those in the melt-derived silicate glasses. In Figures 1b, c & d are shown the temperature-dependent emission spectra of a 10 % (wt %) Eu^{3+} doped in a sol-gel glass. The spectral profile and relative intensities of the various transitions show a dependence on the heating temperature, which provides insight into the bonding environment of the Eu^{3+} ion brought about by heating.

At room temperature the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition shows a single sharp band at 578.6 nm (Figure 1b). The overall spectral profile of this spectrum, as well as the ratio of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ to the

Figure 1. Emission Spectra of Eu^{3+} doped in: a) HT borosilicate glass; Sol-gel, (b) at room temperature; (c) heated at 400 °C; (d) heated at 800 °C

$^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, is very similar to the emission spectrum of $\text{Eu}(\text{NO}_3)_3$ in aqueous solution [7]. The strong similarity between the spectroscopic properties of $\text{Eu}(\text{NO}_3)_3$ in the sol-gel and in aqueous solution suggests that no major coordination changes have taken place around the lanthanide ion. The sol-gel matrix provides a local "aqueous micro-environment" for the encapsulated $\text{Eu}(\text{NO}_3)_3$ in the silanol network [8]. Significant spectral changes take place upon heating the sol-gel sample. All of the luminescence bands show broadening upon increasing the heating temperature. The intensity of the "environmentally sensitive", $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition increases with a concomitant decrease of the magnetic-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition with heat treatment at higher temperatures. The spectral broadening noted following heat treatment clearly indicates that a change in the local environment of the lanthanide ion takes place at these higher temperatures. The data provide evidence for the start of some bonding interaction between the rare earth ion and the silanol groups of the matrix. From the spectroscopic results we infer that the lanthanide-silanol interaction becomes dominant only after the removal of the counter ion (nitrate) and volatile components from the matrix through heat treatment and the process continues up to a temperature of ca. 800 °C.

Nevertheless, significant spectral differences between the melt-derived silicate glasses and the sol-gel matrices remain even after heating the latter to 800 °C; one being that the spectral broadening is more intense in the sol-gel glasses after heat treatment. As discussed above, the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition in the high temperature glasses (figure 1a) is sharper and greater splitting is observed for the various f - f transitions as compared to the heat treated sol-gel products (figure 1c). The data suggest that a more uniform local environment for the f-element is attained in the

high temperature melt-derived glasses than the heat treated sol-gel matrix.

In the sol-gel glasses, the lanthanide ion is uniformly distributed at the initial stage of the process, as indicated from the sharpness of the $^5D_0 \rightarrow ^7F_0$ transition (figure 1b). This suggests that the lanthanide is encapsulated within the silicate matrix, which behaves primarily as a non-interacting solvent. However, the removal of the counter anion and volatile components initiate bonding interactions between the lanthanide ion and the sol-gel matrix. The spectroscopic data clearly indicate that Eu^{3+} ions in the sol-gel matrix encounter minor differences in their surroundings when they interact with the silanol groups. As a consequence, spectral broadening and lack of splitting in the emission bands that originate from closely spaced multiple sites is observed. Thus, the lanthanide ions occupy several site symmetries when bonding interactions occur between the encapsulated f-ions and the sol-gel matrix at higher temperatures. The cause for the differences in site occupation is unclear at the moment even though similar broadening have been observed in the spectral profile of some actinide ions encapsulated in sol-gel matrices [9].

Excited-State Interaction

The high temperature borosilicate glasses doped with certain combinations of f-elements show special excited-state interactions. Among the lanthanide combinations that we have studied, the Pr-Sm interaction is particularly interesting as it leads to the observation of energy up-conversion. The emission spectrum of a Sm^{3+} doped borosilicate glass is shown in Figure 2a. All of the characteristic f - f transitions for this ion are observed when it is excited with the 514 nm argon ion laser. Three sharp, strong bands are observed at 17740, 16640, and 15425 cm^{-1} which correspond to the $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ transitions, respectively. Weak shoulders are observed at 17536, 16466 and 15260 cm^{-1} as stark components of these transitions. Emission is not observed when the 514 nm laser line is used to excite the Pr^{3+} ion doped borosilicate glass. The reason is that the Pr^{3+} ion does not have an excited level that matches (or nearly matches) the 514 nm excitation energy.

The situation changes when glasses containing both the Sm^{3+} and Pr^{3+} ions are excited with the 514 nm radiation. In Figure 2b is shown the emission spectra of the mixed Pr-Sm sample. Excitation with the 514 nm laser line provides all of the characteristics f - f transitions corresponding to the Sm^{3+} ion emission, as would be expected. However, a higher-energy emission (blue side of the excitation wavelength) corresponding to the Pr^{3+} ion $^3P_0 \rightarrow ^3H_4$ transition, is now evident in the spectrum.

Several mechanisms have been considered to understand this phenomenon. A conventional two-photon absorption (by the Pr^{3+} ion) is unlikely, an energy level lying approximately twice the laser photon-energy above the ground state is not present [7]. A two-step, sequential excitation process has also been ruled out due to the lack of up-conversion emission in samples prepared from the Pr^{3+} ion alone. Since the up-conversion emission has been observed only in samples containing both the Pr^{3+} and Sm^{3+} ions, it indicates that excited-state interactions between the two f-ions is important in the overall process.

Shown in Figure 3 is the dependence of the "up-converted" emission intensity on the flux of the exciting laser radiation; which depends quadratically on the flux. This quadratic dependence of the laser-induced fluorescence, at 490 nm, indicates the importance of energy transfer from an excited Sm^{3+} ion to the Pr^{3+} ion in observing the "up-converted" emission band [4]. We attribute the phenomenon to energy transfer from the $^6H_{13/2}$ level of the Sm^{3+} ion to the 3H_6 state of the Pr^{3+} ion. Following a second photon absorption, the Pr^{3+} ion is then excited to the emitting 3P_0 level.

Figure 2. Emission spectra of the Pr/Sm co-doped HT borosilicate glass: (a) Excited at 514 nm. Emission bands corresponding to the Sm^{3+} ion f-f transitions; (b) Up-conversion Emission corresponding to the Pr^{3+} ion $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition; Excited with 514 nm laser line; (c) Excitation with a 350 nm laser line.

Figure 3. Up-conversion emission intensity of the Pr-Sm system showing a quadratic dependence on the excitation flux.

Experimental evidence exists which support the idea that the energy transfer process takes place at these lower excited levels. For example, excitation of the Pr-Sm sample with 350 nm radiation provides emission corresponding only to the Sm^{3+} ion f - f transition; emission is not evident from the Pr^{3+} ion (Figure 2c). In a situation where an excited-state interaction takes place at higher

emitting levels, the sensitized emission should be independent of the excitation wavelength. However, the dependence of the sensitized emission upon the excitation wavelength (in the Pr-Sm system) suggests the Pr^{3+} ion is excited by a photon absorption following energy transfer from an excited Sm^{3+} ion. This implies that the process leading to the up-conversion emission involves a two-photon absorption. We suggest that the overall process progresses as follows. In the first step, the Sm^{3+} ion is excited to the $^4\text{F}_{3/2}$ level by 514 nm photon absorption. Following relaxation to the emitting $^4\text{G}_{5/2}$ level, the excited ion falls radiatively to the $^6\text{H}_{13/2}$ level. This level ($^6\text{H}_{13/2}$) is nearly in resonant with the $^3\text{H}_6$ level of the Pr^{3+} ion. Excitation of the Pr^{3+} ions to the $^3\text{H}_6$ level may occur through a non-radiative energy transfer mechanism. A second 514 nm photon absorption by the excited Pr^{3+} ions raises it to the emitting $^3\text{P}_0$ level, where the up-conversion emission originates. Efforts to fully understand the mechanism of the excited-state interaction and the efficiency of the energy transfer process in this high-phonon borosilicate matrix is under way in our laboratory.

CONCLUSIONS

The spectral properties of the Eu^{3+} ion have been used to probe the local coordination environment of the f-elements in two high temperature borosilicate and a sol gel matrices. In the high temperature glasses electric dipole allowed f - f transitions dominate the spectra, suggesting the local symmetry around the 4f-ions is low. Studies on the sol-gel glasses as a function of thermal treatments indicate that f-ions retain a solution-like environment prior to heating. An increase in the emission intensities of the electric-dipole allowed transitions is accompanied by a concomitant decrease in the magnetic dipole-allowed transitions after heating. Moreover, excited state interaction has been observed in the high temperature glasses containing multiple f-elements. In the Pr-Sm system, exclusively exciting the Sm^{3+} ion with a 514 nm argon ion laser provides a higher-energy emission band (ca. 490 nm) from the Pr^{3+} ion ($^3\text{P}_0 \rightarrow ^3\text{H}_4$) transition. The interaction involves an overall two photon absorption that leads to energy transfer up-conversion.

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