

FLUORESCENCE ENHANCEMENT IN Eu^{3+} DOPED FLUOROBORATE GLASSES CONTAINING A HIGHLY INHOMOGENEOUS SIZE DISTRIBUTION OF SILVER PARTICLES

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ABSTRACT

In this work we present and discuss the experimental observation of a fluorescence enhancement in Eu^{3+} doped fluoroborate glasses containing small silver particles, formed in the bulk of the amorphous medium. The observed enhancement depends considerably on the structure of the plasmon band due to the silver particles. In order to better elucidate this point, we have changed the characteristics of the plasmon band (form, peak position and intensity) through the action of a thermoreducing agent (Sb^{3+}). We also discuss the fact that changes in the chemical composition and inhomogeneities of the medium may contribute to the observed fluorescence enhancement.

1. INTRODUCTION

The nucleation and growth of small metallic particles in the bulk of isotropic media have, recently, gained a new interest which is the study of the effects of these small particles on the absorption and emission processes in molecules or ions diluted in these media [1, 2]. In the case, for example, of a Eu^{3+} doped fluoroborate glass, a factor of ~ 6 can be gained in the fluorescence of the Eu^{3+} ion if the glass material contains silver particles with an average diameter of 40Å and a particle concentration of $\sim 10^{18}\text{ cm}^{-3}$ [1]. As in the case of SERS (Surface Enhanced Raman Scattering), these effects can be rationalized in terms of the electro-magnetic interaction between the plasmons, localized in the small particles, and the molecules or ions [3, 6].

A fundamental point in these phenomena is to make the Mie resonance, i.e., the absorption by the plasmons, coincide with the absorption or emission by the molecules or ions. This is possible, in general, if one is able to control the nucleation and growth of the particles in a given medium. Once such a control is achieved one may then proceed by selecting the best material composition in order to complete the optimization of the fluorescence yield of the emitting species. In this case, theoretical considerations may show that a fluorescence gain of more than an order of magnitude may be expected. It is interesting to note that, within the context of the electromagnetic model, the basic mechanism responsible for this enhancement process has a great similarity with one of the mechanisms, namely, the Pseudo-Multipolar Interaction, responsible for the well known hypersensitive transitions in rare earth ions [7–9].

In the case of a volumetric distribution of metallic particles in amorphous media, the fluorescence enhancement problem may become a complex one due to the following reasons. Firstly, to control the peak position of the particle plasmon absorption band is not an easy task. Secondly, depending on this peak position, its intensity and the band width, then may be a considerable energy transfer from the fluorescent species to the metallic particles, i.e., a considerable quenching effect. Thirdly, after the sample has been prepared, there may remain metallic ions and/or atoms that have not participated in the formation of the particles and which may absorb in resonance with the fluorescent species. Their presence may also contribute to change the absorption edge of the amorphous medium, particularly at high concentrations ($> 1\%$, by weight). This can modify the populations of the excited fluorescent states and, consequently, the fluorescence yield. Finally, the effects of particle size and shape, and inhomogeneities in their distribution, may be of importance.

A careful and detailed experimental study is necessary for the elucidation of the fluorescence yield enhancement of rare earth ions in these composite media. This work is part of this project. Here we present and discuss an experimental observation of the Eu^{3+} fluorescence enhancement in a fluoroborate glass containing a highly inhomogeneous size distribution of silver particles.

2. EXPERIMENTAL

2.1 Sample Preparation and Instrumentation

The samples were prepared in essentially the same way as already described elsewhere [1]. The mixture contained in a platinum crucible was heated and melted at 1200°C for about 1 hour. The melt was then poured into a graphite mold pre-heated to 400°C for annealing purposes.

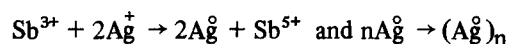
The high stability of the samples permits the realization of subsequent annealings without destroying the basis sample characteristics. Host composition was such that the weight of glass forming B_2O_3 and CaF_2 was $(\text{CaF}_2 + \text{B}_2\text{O}_3)/\text{CaF}_2 = 1.43$ and the doping concentrations, by weight, were $x \text{ Eu}_2\text{O}_3$ (with $x = 0.0$ and 3.0%), $y \text{ Ag}$ (with $y = 0.0$ and 3.0%) and $z \text{ Sb}_2\text{O}_3$ (with $z = 0.0$, 1.5 and 3.0%).

The absorption spectra were recorded with a Beckman Acta CV doublebeam spectrophotometer. All spectra were obtained using the sample without silver as the reference (corrected in weight in order to compensate the AgNO_3 lack).

In the excitation and fluorescence spectra the samples were excited by a Xenon lamp, XBO – 450 W, followed by a 0.5m monochromator (Spex minimate) for the wavelength selection. The spectra were recorded by a 1.2m Spex monochromator model 1269, with a slit width of $100\mu\text{m}$. The luminescence following excitation was detected by a water cooled R.C.A. C31034-02 photomultiplier, and the signal processed by a data mate lock-in amplifier Spex model DM-1; the out put results were displayed in a strip-chart recorder.

2.2 Electron Micrographs

Silver particles are presumably formed either by spontaneous precipitation or by the action of a thermo-reducing agent (Sb^{3+} in our case) according to the reactions [10]



In order to confirm the presence of the particles in our samples, we have performed an electron microscopy analysis.

Glass samples, in powder form, were mixed with ethanol and dropped on a copper grid covered with a thin double layer of collodion and amorphous carbon. The observations were made with a model 100 CXII JEOL electron microscope at 80KV. Care was taken in order to identify the possible formation of silver clusters due to the action of the electron beam. About 5 glass grains per sample were micro-graphed in an electron microscopic film FC orthochromatic $8.2 \times 11.8\text{cm}$.

In the selected photos the external contour of the glass grains and the silver particles were drawn by using an Image Analysis System – MOP – Videoplan. The results show that the particles are nearly spherical and that they are rather uniformly distributed inside the sample (figure 1). Also, a detailed analysis reveals that the particle size distribution is highly inhomogeneous. It is peaked at two different radii, 18 and 72\AA , as shown in figure 2 below. Their respective concentrations were estimated to be $\sim 10^{14}\text{cm}^{-3}$ and $3 \times 10^{15}\text{cm}^{-3}$.

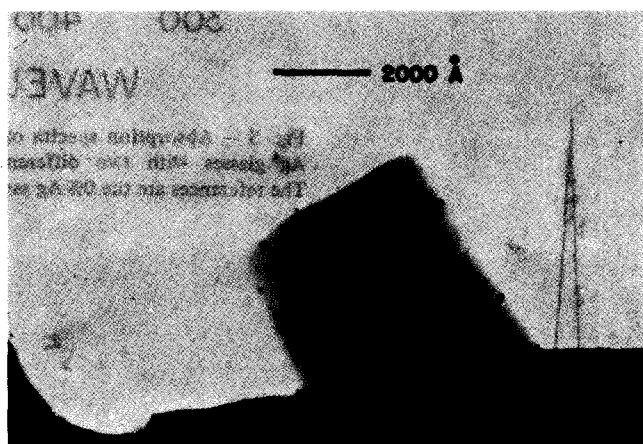


Fig. 1 – Conventional micrograph of silver particles in the sample with 1,5% of Sb_2O_3 and 3% of Ag. The observed particle radii varied from ~ 20 to 100\AA .

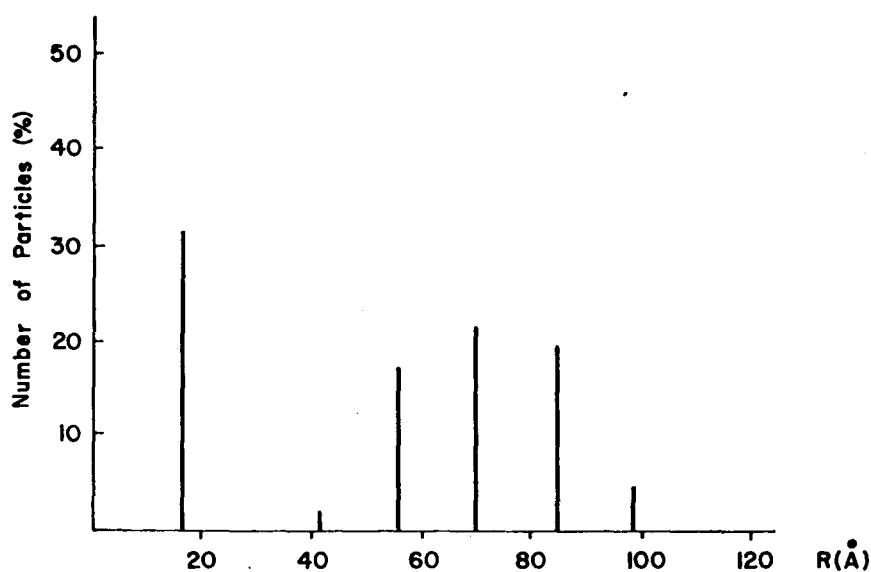


Fig. 2 – Size distribution of silver particles observed from figure 1. The distribution is peaked at the radii values 18 and 72\AA .

2.3 Fluorescence Enhancement Results

Figure 3 shows the absorption spectra of the samples with (a) 1.5% and (b) 3% of Sb_2O_3 , where in both cases the Ag concentration is 3% (by weight). In both spectra two peaks are observed and their relative intensities are inverted from one case to the other. Also, the position of the lower energy peak ($\sim 425\text{nm}$) remains practically unchanged while the higher energy one moves from 350 to 325nm when the Sb_2O_3 concentration is doubled.

An important result for our discussion is shown in figure 4. As we increase annealing temperature and time on the samples, the higher absorption peaks shown in figure 3 present a well resolved double band structure. As it will be discussed later, this suggests a correlation with the particle size distribution shown in figure 2.

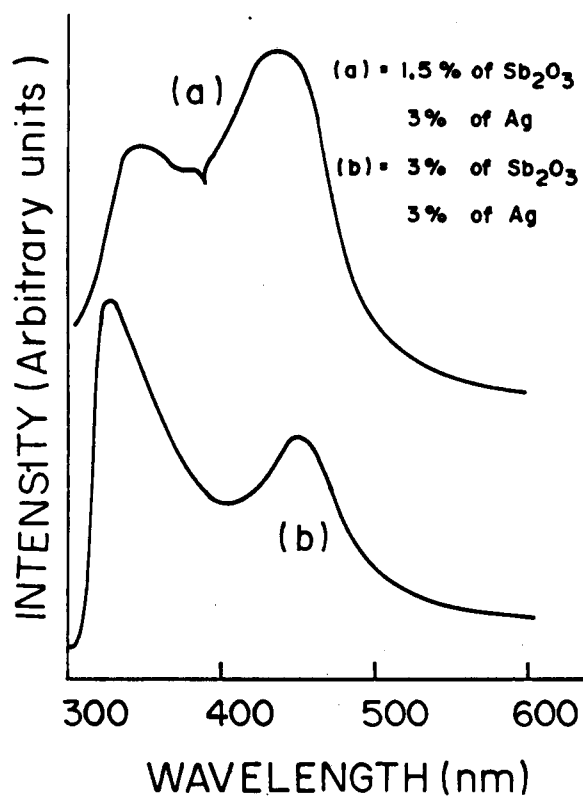


Fig. 3 - Absorption spectra of $\text{CaF}_2 - \text{B}_2\text{O}_3$, 3% Eu_2O_3 and 3% Ag glasses with two different antimony oxide concentrations. The references are the 0% Ag samples.

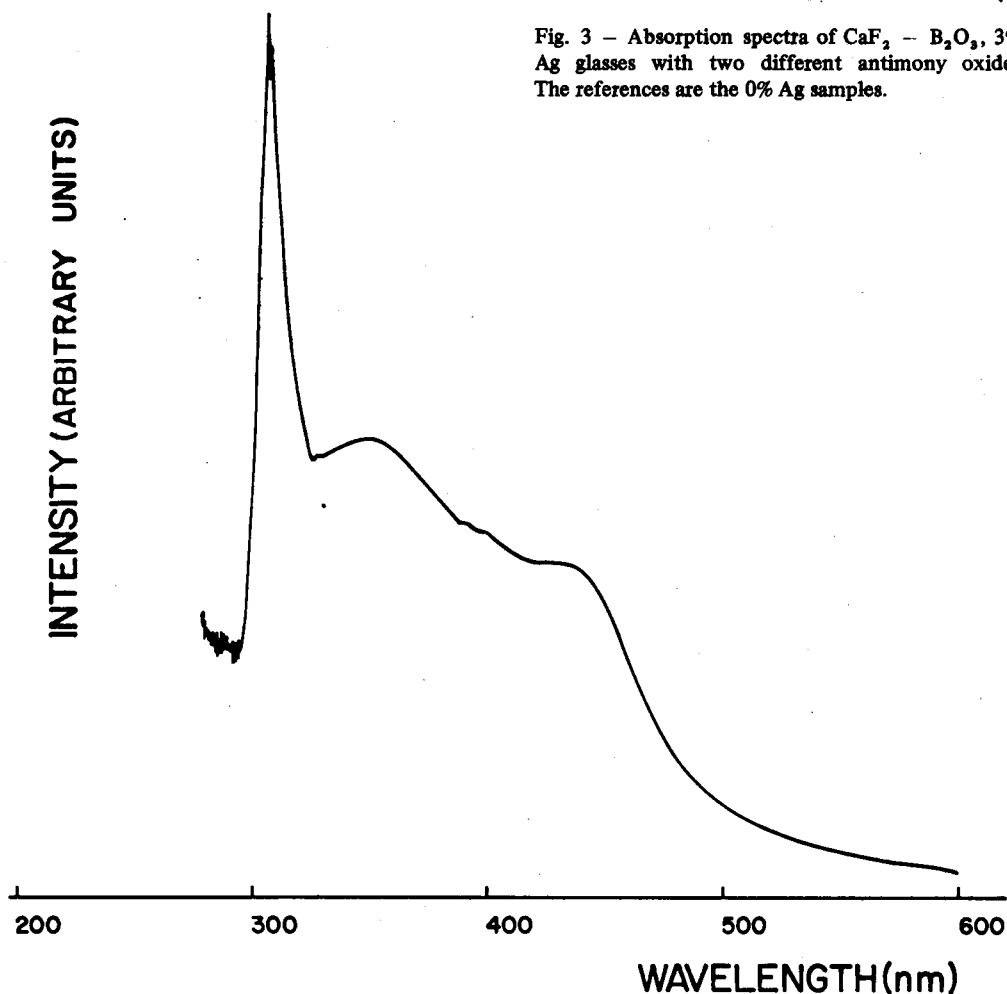


Fig. 4 - Absorption spectrum of the 3% Sb_2O_3 , 3% Ag sample after 24h of annealing at 500°C.

The excitation spectra of the samples with and without silver, for both concentrations of Sb_2O_3 , are shown in figure 5. We notice that depending on the excitation wavelength a considerable fluorescence enhancement is observed. The enhancement is much more pronounced for the 1.5% Sb_2O_3 sample. In this case, an enhancement factor of ~ 6 is gained at 3650Å (Hg lamp).

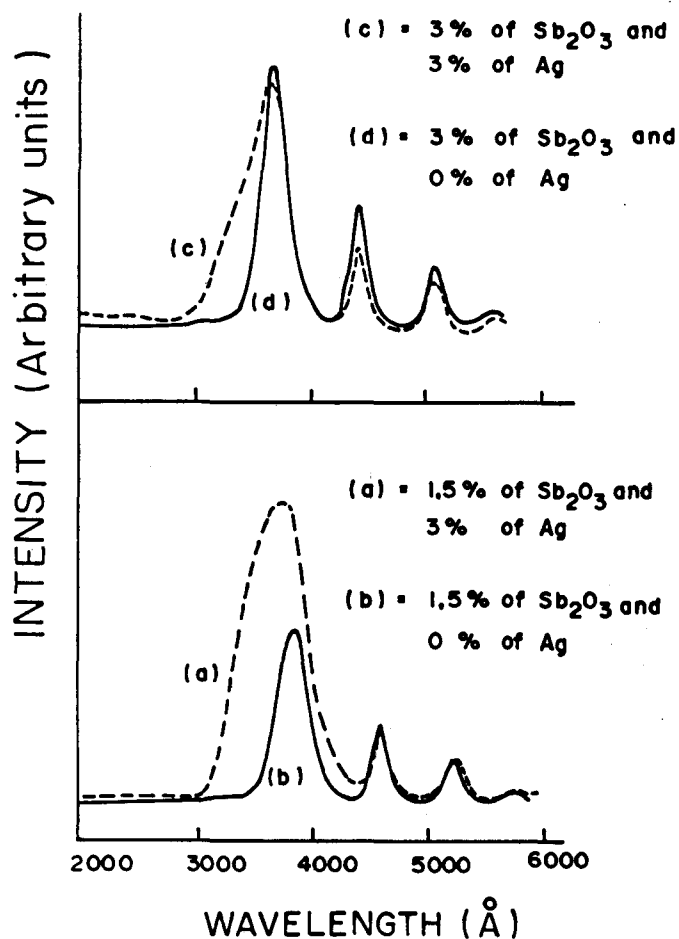


Fig. 5 - Excitation spectra of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission line (6120Å) of the Eu^{3+} ion. The dotted line corresponds to the samples containing silver and the solid line corresponds to the reference samples (0% Ag).

The fluorescence spectrum of the sample with 1.5% of Sb_2O_3 and 3% of Ag is shown in figure 6. We notice that besides the Eu^{3+} fluorescence lines, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2}$, a rather weak emission band is also observed which we assign to the luminescence of Ag atoms in the glass [11]. This assignment is based on the fact that this band is absent in the samples without silver.

3. BRIEF THEORETICAL CONSIDERATIONS

The fluorescence yield is the result of a balance between absorption and emission rates. It is increased if, for example, the transition rates corresponding to populating channels are increased. Thus, a study of the fluorescence yield enhancement requires a knowledge of



Fig. 6 - Fluorescence spectrum of the 1.5% Sb_2O_3 , 3% Ag sample at room temperature.

the energy levels of the fluorescent species and, what is more important, their relative positions with respect to energy levels due to the surrounding medium.

In the electromagnetic model the effects of small metallic particles on the absorption and emission processes in molecules or ions, diluted in an isotropic medium of dielectric constant ϵ_0 , can be described by a macroscopic Lorentz type correction to the external incident field, and a distance dependent correction due to high field gradients nearby the particles [1, 3].

The former correction is essentially given by the complex dielectric constant of the composite medium.

$$\epsilon(\omega) = \epsilon_1 - i\epsilon_2 \quad (1)$$

where

$$\epsilon_1 = \epsilon_0 + \frac{q \omega_p^2 (\omega_R^2 - \omega^2)}{(\omega_R^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (2)$$

and

$$\epsilon_2 = \frac{q \omega_p^2 \gamma \omega}{(\omega_R^2 - \omega^2)^2 + \gamma^2 \omega^2} \quad (3)$$

In these equations, the resonance or Mie frequency ω_R is given by

$$\omega_R^2 = \frac{(1-q)}{3\epsilon_0} \omega_p^2 \quad (4)$$

where ω_p is the plasmon frequency of the metallic particles. The factor γ is the width, at half intensity, of the plasmon absorption band. The effective electric field amplitude inside the medium is given by

$$E = \left(\frac{\epsilon_0 + 2}{3}\right) \left[1 + \frac{q \omega_p^2}{3\epsilon_0 (\omega_R^2 - \omega^2 + i\gamma\omega)}\right] E_0 \quad (5)$$

where E_0 is the electric field amplitude of the external radiation.

The distance dependent correction, to which we have referred above, is mainly due to oscillating dipoles induced in the metallic particles by the effective radiation field. These oscillating dipoles produce a new radiation with high field gradients, nearby the particles, having a maximum at $\omega = \omega_R$. The total field nearby a particle is then given by

$$\vec{E}'(\vec{x}) = \vec{E} + \vec{E}(\vec{x}) \quad (6)$$

where \vec{x} is the position with respect to the center of the particle. Transition rates are then reevaluated by using the total distance dependent effective field given by eq. (6) [1].

Another aspect, which must be taken into account in the fluorescence yield enhancement problem, is the energy transfer between the particles and the fluorescent ions. It has been shown [12] that the non-radiative energy transfer rate, W_{NR} , for this case may be expressed in the

$$W_{NR} = \frac{k}{R^6} \quad (7)$$

form where R is the distance between donor and acceptor and k is a quantity particularly sensitive to the energy mismatch conditions. Thus, if there are resonances between the plasmon absorption band and emission bands of the fluorescent ions, a quenching effect may be present.

The balance of these effects on the absorption and decay rates gives the influence of the metallic particles on the fluorescence yield. Though at least for high particle concentrations, this influence may be considerable, other effects due to the chemical composition of the medium should be considered. The distribution of ions and/or atoms, participating in the formation of the metallic particles (Sb^{3+} , Sb^{5+} , Ag^+ and Ag^0 , in our case), and the external conditions of sample preparation may be such that not all of these ions and/or atoms enter in the particle growth process. These remaining species usually change the absorption edge of the medium towards longer wavelengths. Further, they can also present a rather localized absorption, typical of atomic impurities in a solid, which may be in resonance, or near resonance, with absorbing levels of the fluorescent ions (Eu^{3+} ions, in our case). Therefore, depending on the excitation frequency, the initial absorption of radiation by the sample turns out to be more efficient. As a consequence, by energy transfer, the excited states of the fluorescent ions become more populated increasing the fluorescence yield.

In the context of these theoretical considerations we wish now to make a qualitative discussion of the results presented in section 2.

4. DISCUSSION

The nature of the absorption bands shown in figure 3 can be clarified according to the following arguments. The electron microscope results showed that the particle size distribution is peaked at two different radii. Thus, we may think in terms of two types of particle distribution inside the material, each distribution being responsible for a plasmon absorption band shown in figure 3. While the lower energy band (at ~ 425 nm) may be unambiguously attributed to the bigger particles (see ref. [11] and references therein), the higher energy one needs to be analysed more carefully.

This latter band is possibly a superposition of three contributions: the intrinsic absorption edge of the glass, which has been modified by the inclusion of silver, plus atomic silver absorption and a broad absorption by very small silver particles. This is corroborated by the result from figure 4, where by increasing the annealing time and temperature, this band splits in two ones. We interpret this result assuming that, under these conditions, there is an increase in the reduction rate of Ag^+ ions with a subsequent increase in the rate of the reaction $nAg^+ \rightarrow (Ag^0)_n$. This will favor an increase in the specific volume of the smaller particles and a narrowing of their size distribution.

We discuss now the fluorescence enhancement results. To do this it is convenient to compare the energy level scheme of the Eu^{3+} ion with the absorption bands shown in figure 3. This is done in figure 7 below.

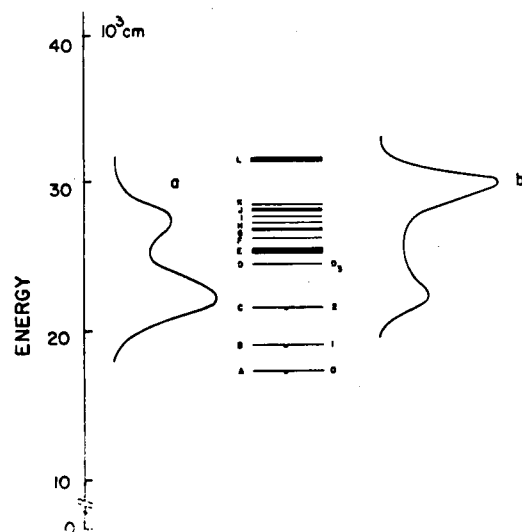


Fig. 7 - Energy level scheme of the excited states of the Eu^{3+} ion (from ref. [13]) including the absorption bands from figure 3.

Concerning the lower energy band, the absorption peak is the same in both cases, (a) and (b), and it is completely out of resonance with the fluorescing level 5D_0 . Therefore, no quenching of this level by the plasmon band should be expected. On the other hand, this band is in near resonance with the 5D_2 level. Since the experiment shows that excitation at ~ 425 nm produces no fluorescence enhancement (see figure 5), we are lead to conclude that, in this

case, an enhancement in the absorption by the 5D_2 level is being compensated by quenching of this level. It must be emphasized that quenching, due to energy transfer towards the plasmons, is particularly important for the lower 5D_j multiplets because of their much higher life-times as compared to those of the more excited Eu^{3+} absorbing levels.

In the case of the 1.5% Sb_2O_3 sample (a) we can clearly note a resonance between the higher energy absorption band and the group of Eu^{3+} absorbing levels in the range $24000 - 28000cm^{-1}$, while the absorption peak in case (b), i.e., 3% Sb_2O_3 , is completely out of resonance with these levels. This explains why the enhancement is more pronounced in the 1.5% Sb_2O_3 sample. In this case the enhancement is still observed when the excitation is made at 390nm, which is in the region of a considerable overlap between the plasmon bands and is in resonance with the highly absorbing level immediately above the 5D_3 multiplet of the Eu^{3+} ion. Since at this wavelength no absorption by the host and Ag atoms was observed, we conclude that, at least in this region, the enhancement is due to the presence of silver particles.

For higher excitation energies, at the present stage of our study, it is difficult to distinguish a possible contribution to the enhancement, due to the modified absorption

edge of the glass and atomic silver absorption. However, the result from figure 4 indicates that both these absorptions are situated at energies above $28000cm^{-1}$, suggesting an overwhelming contribution, due to the plasmons localized at the silver particles, to the observed fluorescence enhancement.

Though, for the moment, our intention is being mainly devoted to the fluorescence enhancement problem, it is worth to notice that other several interesting problems related to these new materials may be raised. We could mention, as examples, the kinetics of nucleation and growth of the metallic particles [11], their effect on non-linear optical processes and inelastic light scattering in these composite media.

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