New lanthanide doped amorphous materials containing small metallic particles

Gilberto F. de Sá

Departamento de Química Fundamental, Departamento de
Física, CCEN, UFPE, Cidade Universitária,
50739, Recife, PE, Brazil

Abstract – Amorphous materials doped with lanthanide ions and
containing small metallic particles may be useful and
interesting media for the study of linear and non linear
optical processes. In this study the characterization of these
particles in a given medium (concentration, structure, size
and shape distributions) is of crucial importance. In this
work we present and discuss recent results on the luminescence
and characterization of these composite materials with
emphasis directed toward the electron microscopy and EXAFS
techniques.

INTRODUCTION

Inorganic amorphous materials have shown to be very useful as host media in
which small metallic particles can be grown. The optical properties of these
systems have been of interest since the beginning of the century when Maxwell-
Garnett (ref.1) and Mie (ref.2) provided the first theoretical framework
to explain the resonant absorption which characterizes such sytems.In addition
the optical properties of colloidal metal particles in different media (mostly
glasses (ref.3) or ionic crystals (ref.4,5) have been studied because of their
potential technological importance as efficient photothermal solar-energy
converters (ref.5), etc.

The nucleation and growth of small silver particles in the bulk of isotropic
media have, recently, gained a new interest which is the study of the effect
of these small particles on the absorption and emission processes in molecules
or ions diluted in glasses and/or glass ceramics (ref.6,7). 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 (ref.8,9).

The enhancement of the emission of lanthanide ions due to plasmons localized
in silver particles has firstly been observed in the case of a rough silver
surface coated with a Eu^{3+} complex (ref.8). In the case of a volumetric
distribution of silver 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, there 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 weght). 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.

In a recent series of experiments these amorphous materials have been studied
in our laboratory (ref.10-12). In these studies, a basic point is the
characterization of the silver particles in the medium (size and shape
distributions concentrations and structure). This is usually done by an
Electron Microscopy Analysis. However we have recently also made an energy
dispersive analysis of X-rays (EDAX) and used the technique of Extended X-ray
Absorption Fine Structure (EXAFS) in order to get more information on the

structure and composition of these particles.In this work we wish to describe preliminary results obtained from this structural analysis and to emphasize the correlation with fluorescence enhancement data.

EXPERIMENTAL PROCEDURE

The samples were prepared in essentially the same way as already described elsewhere (ref.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 purpose. The high stability of the samples permits the realization of subsequent annealing without destroying the basic sample characteristics.

Host composition was such that the weight of glass forming B_2O_3 and CaF_2 was $(CaF_2 + B_2O_3)/CaF_2 = 1.43$ and the doping concentrations, by weight, were x Eu_2O_3 (with x = 0.0 (with x = 0.0 and 3.0%), y Ag (with y = 0.0 and 3.0%), z Sb_2O_3 (with z = 0.0, and 1.5% and z' CeO_2 (with z' = 0.0 and 0.2%).The glass samples were optically polished plates and their absorption spectra were recorded with a Beckman Acta CV double beam 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 100μm. 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. For the electron microscopy analysis the glass samples were used in powder form, mixed with ethanol and dropped on a copper grid covered with a thin double layer of collodion and amorphous carbon.

The selected area diffraction analysis was carried out with a model JEOL CX 200 scanning transmission electron microscopy (STEM),at 100 KV where the probe diameter was <50°Å Thus, it was possible to obtain diffraction information from areas of the order of 100 Å in diameter. The X-ray detector was a typical Sili detector. When using the STEM mode, the specimens were also analyzed with an energy dispersive analysis of X-rays (EDAX) attachment to determine the chemical composition.

To determine the size distribution of silver particles, TEM photomicrographs were enlarged for data acquisition with a Carl Zeiss Videoplan image analyzer (ref.11).

The X-ray absorption data of these samples have been carried out at LURE (Orsay),using synchrotron radiation, emitted by the DCI storage ring operating at 1.85 GeV with a 300 mA starting current. The EXAFS spectra have been analyzed within a classical procedure as reported in (ref.13).

RESULTS AND DISCUSSION

(a) Fluorescence enhancement

The nature of the absorption bands shown in Fig.1 can be clarified according to the following arguments. The electron microscope results showed that the particle size distribution is peaked at two different radii (see next section). Thus we may think in terms up two types of particle distribution inside the material, each distribution being responsible for a plasmon absorption band shown in Fig.1. While the lower energy band (at ~450 nm) may be unambigously attributed to the bigger particles (see ref.14), the higher energy one needs to be analysed more carefully.

This latter band is possibly a superposition of three contributions: the 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.

The excitation spectra of the samples with and without silver, for 1.5% Sb_2O_3 concentrations, are shown in Fig.2. It may be noticed that depending on the excitation wavelength a considerable fluorescence enhancement is observed. In this case, an enhancement factor of ~ 6 is gained at 365 nm (Hg lamp).
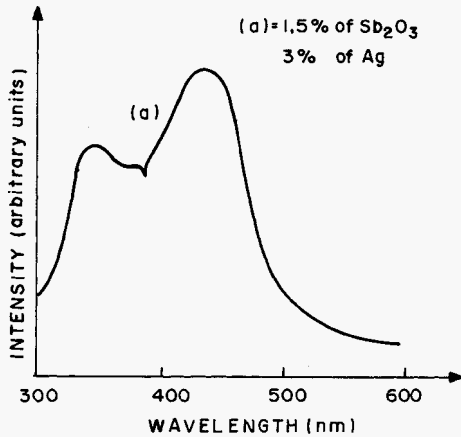
Fig.1. Absorption spectrum of $B_2O_3-CaF_2$, 3% Eu_2O_3, 3% Ag and 1.5% Sb_2O_3 glass using the sample without silver as the reference.
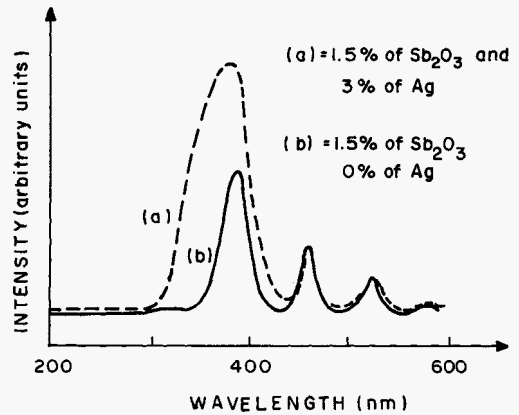

Fig.2. Excitation spectra of the luminescence of Eu^{3+} (at 6120 Å) in B_2O_3-CaF glass. The dotted line corresponds to the sample containing silver and the solid correspond to the reference sample (0% Ag).

An analysis based on these results together with the energy level distribution of the Eu^{3+} ion can be made in order to rationalize this effect which represents a compromise between the enhancement of absorption and emission rates and quenching by the localized plasmons (ref.11). In fact, the fluorescence yield enhancement shown in Fig.2 has been satisfactorily interpreted in terms of the electromagnetic model as developped in reference 7. It is important to notice that in this model energy transfer between the Eu^{3+} ions and the silver particles must be taken into account.

(b) Electron microscopy and X-ray structural investigation

In order to confirm the presence of the particles of silver in our samples, we have performed and electron microscopy analysis. Care was taken in order to avoid the possible formation of silver clusters due to the action of the electron beam. To determine the size distribution of Ag particles, measurements were taken for at least ten different spots for each sample. The TEM micrographs (Fig.3) show typical images of particle dispersion. In the selected photos the external contour of the silver particles were drawn by a videoplan.
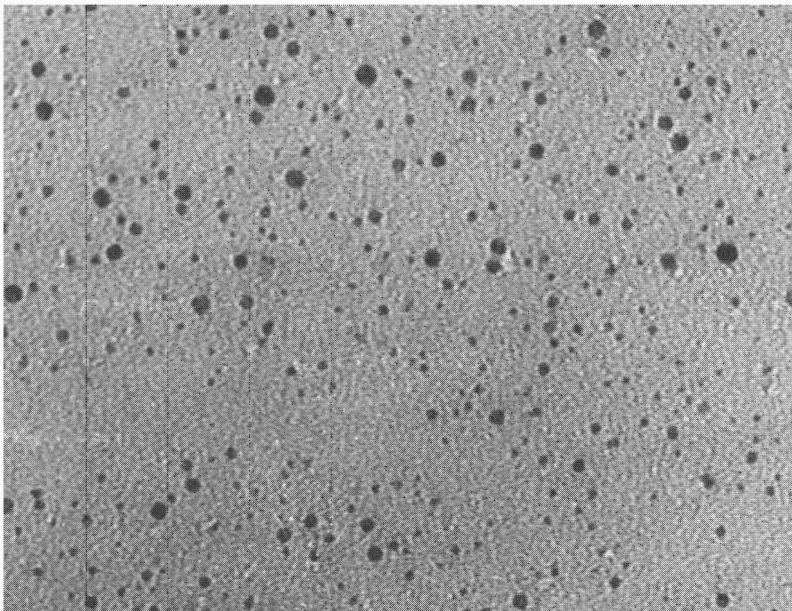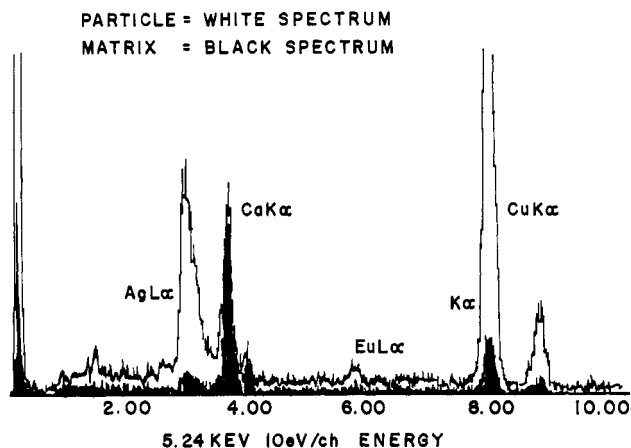

Fig.3
A TEM micrograph of silver particles in the sample with 1.5% of Sb_3O_3 and 3% of Ag.

PARTICLE = WHITE SPECTRUM
MATRIX = BLACK SPECTRUM

Fig.4 A STEM-EDAX chemical analysis in the sample with 1.5% of Sb_2O_3 and 3% of Ag. The analysis is done on a large silver particle (white spectrum) and among silver particles (black spectrum). The cooper signal comes sample holder.

These results show that the particles are nearly spherical and that they are rather uniformly distributed inside the sample (Fig.3). In addition,a detailed analysis reveals that the particle size is highly inhomogeneous. The average radius of particles in these samples is about 60Å, however, a lot of very small contrasted spots are visible, meaning that, besides this first size population, a second family of particles, with average radius of 15Å, is also formed during the annealing process. The biggest particles (50 to 100Å) are well crystalized as shown by the microdiffraction patterns.

The results of the STEM EDAX analysis for a typical sample are shown in Fig.4 where the signal coming from the matrix is in black. The calcium K_α emission is used to normalise this signal with the spectrum issued from one particle (white spectrum). Two main points can be note: i) The silver amount present in the pure matrix is quite low. ii)The Eu^{3+} ions seems to be uniformly dispersed as the L_α intensity is detected from the B_2O_3-CaF_2 matrix and from the particle. This doping element may therefore be considered as in a real solid solution.

To go further with these characterizations, we also undertook an X-ray absorption investigation to get a macroscopic view of the chemical and structural nature of the particles. Due to the low silver concentration and the high energy position of the silver K-edge, the spectra were added to get a good signal to noise ratio. EXAFS spectra were analyzed within a classical procedure (ref.13). The absorption due to the other components of the medium was firstly approximated by a Victoreen polynomial function, then normalized from the atomic-life? absorption by a second degree polynomial. The remaining long wavelength oscillations, if any, were removed by a multi-iteration curve smoothing procedure. The X(R) signal was Fourier transformed after a K^3 weighting. Fig.5 shows the modulus of this Fourier transform for samples A and B and that for the pure silver foil used as a reference compound. These pseudo radial distribution functions (they are uncorrected for phase shift, so that peaks are at lower distances than expected) can be considered as images of the silver environment, each contribution corresponding at least to one coordination shell.The complete analysis, after backtransforming the succesive isolated contributions, has not yet been done. These moduli are nevertheless clear enough compared to and compared to the first shell contribution of pure silver (12 atoms at 2.89 Å), the two probed samples present two features: i) Their intensities are very weak, a point in line with the fact that the average size of the corresponding particles is quite small (a few monometers), in agreement with the Electron Microscopy results. ii) As the Ag-O bond is 2.05Å in length, the first short distance contribution could be assigned to silver-oxygen bonds as it seems to peak around 2Å when the typical 0.3-0.4Å of phase shift is added. The silver oxyde phase could be more or less segregated from the core to the surface of the particle as the ratios between these first contributions and the second ones are very different from one phase to the other.
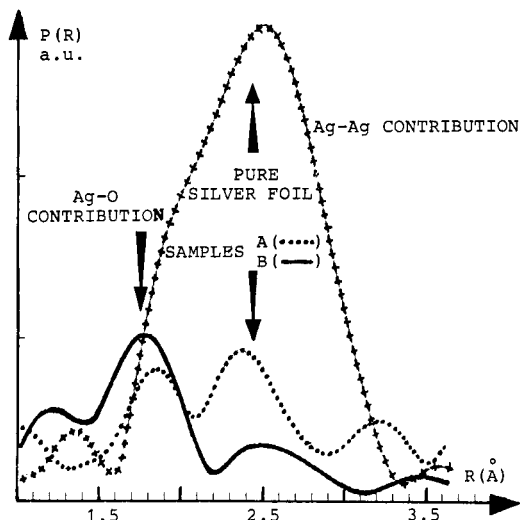
Fig.5 Modulus of the Fourier transforms of the $K^3 X(K)$ data at the (sample A) with 1.5% of Sb_2O_3, (sample B) with 0.0% of Sb_2O_3 and (pure silver foil) reference Ag-Ag (uncorrected for phase shifts).

These very preliminary results are obtained from first structural attempts. As the size, shape and concentration of the metallic particles are quite dependent on the preparation conditions, many different samples must be observed in order to draw stronger assumptions. These structural features has a direct influence on the fluorescence enhancement effect since the complex dielectric function of the composite medium depends directly on them.

Acknowledgements

REFERENCES

1. C. Maxwell-Garnett, Philos. Trans. R. Soc. Londo , 203 , 385 (1904).
2. G. Mie, Ann. Phys. , 25 , 377 (1908).
3. R.H. Doremus, J. Chem. Phys. , 40 , 2389 (1964).
4. A.E. Hughes and S.C. Jain, Adv. Phys. , 28 , 717 (1979).
5. J.S. Miller and A.J. Spstein, Prog. Inor. Chem. , 20 , 1 (1976).
6. A.J. Sievers, Solar Energy Conversion , p.5, Springer, Berlin, (1979).
7. O.L. Malta, P.A. Santa Cruz, G.F. de Sá and F. Auzel, J. Luminescence , 33 , 261 (1985).
8. O.L. Malta, P.A. Santa Cruz, G.F. de Sá and F. Auzel, Chem. Phys. Lett. , 116 , 396 (1985).
9. D.A. Weitz, S. Garoff, C.D. Hanson, T.J. Gramila and J.T. Gersten, J. Luminescence , 24 , 83 (1981).
10. G.F. de Sá, W.M. de Azevêdo and O.L. Malta, J. Luminescence , 40 , 133 (1988).
11. W.M. de Azevêdo, O.L. Malta, G.F. de Sá and I.P. Padovan, Q. Nova , 11 , 96 (1988).
12. G.F. de Sá, O.L. Malta, P.A. Santa Cruz and C.F. Portela, Inorganic Materials, 23 , 1716 (1987).
13. M.H. Tuiler, J. Dexpert-Ghys, H. Dexpert and P. Lagarde, J. Solid State Chem. , 69 , 153 (1987).
14. U. Kreibig, App. Phys. 10 , 255 (1976).