

Rare earth doped silicate glasses have gained much attention due to their potential application in optical memory [1], solid state laser [2], phosphors and medical imaging [3]. The small absorption cross sections of rare earth ions, such as erbium, have spawned numerous attempts to increase these ions excitation efficiency. Most concepts rely on energy transfer from a species with a large absorption cross section to the rare earth ions.

We have turned our attention to photoluminescence modification and enhancement that silver might have on Er^{3+} in oxide glasses. It has been suggested that silver nanoclusters incorporated in rare earth doped glasses remarkably influence the fluorescence of the rare earths ions due to the surface plasma oscillation of metal particle [4-5]. However, recently, C. Strohhöfer and A. Polman suggest that the excitation efficiency of Er^{3+} ions, in Ag-Er co-doped silicate glasses, is increased by defects related to Ag pairs rather from silver nanocrystals [6]. Actually, the mechanism that controls the excitation efficiency of the rare-earth ions is still under debate, and quantitative investigations that correlate the local environment of erbium and silver atoms to the photoluminescence properties are lacking.

To investigate this subject, we prepared a set of samples co-doped with Er and Ag with a combined sol-gel and ion-exchange route. To understand the possible role of the silver states as a sensitizer inducing the PL enhancement at $1.54 \mu\text{m}$, the state of silver was selected in the forms of atoms dispersed in the matrix and/or aggregated in Ag multimers or nanoclusters. In this framework, silver ion exchange doping procedure plays a fundamental role. In fact, it gives the possibility to introduce dispersed Ag^+ ions in the glass matrix over the limit of solubility [7], and, subsequently, to control the aggregation of silver in multimers or cluster structure by performing suitable treatments (reducing thermal annealing and/or light ion irradiation). The obtained samples have different photoluminescence (PL) response.

X-ray absorption spectroscopy was performed, at liquid nitrogen temperature, at Er L_{III} -edge (8357 eV) and Ag K-edge (25514 eV) for characterizing the local environment of erbium and silver in the co-doped glasses. The quantitative analysis of the first two coordination shells of atoms surrounding the absorber, has given the possibility to estimate the site of erbium and, in the case of silver, the presence of oxidizing phase, multimer or cluster formation. In this way it was possible to correlate the local environment of the species involved in the fluorescence process to the photoluminescence spectra. These findings have contribute to shed light in the phenomena regarding Er^{3+} -Ag interactions that are responsible for the luminescence properties of these systems [8].

From EXAFS investigation we have correlate Er ions environment to the feature of PL spectrum, that exhibits different shape (in terms of peak position and band). For this study, EXAFS is an elective technique for its sensitivity to local order, and so to detect local environment of dopant species.

But the most interesting result involves the study of Ag local environment. In fact, it was possible to correlate PL characteristic emission at $1.54 \mu\text{m}$ to the state of silver incorporated into the matrix. In particular, it was found that the enhancement of a factor 7 of the PL emission at $1.54 \mu\text{m}$ was achieved by introducing in the film silver in forms of multimer structure, formation detected by an EXAFS investigation and not achievable with other techniques. PL emission was detected also for non-resonant Er excitation, indicating that Ag multimers play the role of sensitizing elements for Er^{3+} ions, as they absorb pumping radiation and transfer it to the rare-earth ions, that emit at $1.54 \mu\text{m}$. The process is very efficient as the measured cross section values, ranging from 1.2 to $1.6 \cdot 10^{-17} \text{cm}^2$, are much higher than those for the direct absorption of Er^{3+} ions, which is of the order of 10^{-21}cm^2 in glass.