

Mechanisms of Ag to Er energy transfer in silicate glasses: A photoluminescence studyM. Mattarelli,^{1,*} M. Montagna,¹ K. Vishnubhatla,^{1,2} A. Chiasera,³ M. Ferrari,³ and G. C. Righini^{4,5}¹*Dipartimento di Fisica, CSMFO Group, Università di Trento, Via Sommarive 14, 38050 Trento, Italy*²*School of Physics, University of Hyderabad, Hyderabad 500046, India*³*IFN-CNR, Istituto di Fotonica e Nanotecnologie, CSMFO Group, Via Sommarive 14, 38050 Trento, Italy*⁴*Department of Materials and Devices, CNR, Via dei Taurini 19, 00185 Roma, Italy*⁵*Photonic Materials and Devices Laboratory, IFAC CNR, 50019 Sesto Fiorentino, Italy*

(Received 31 October 2006; revised manuscript received 12 January 2007; published 2 March 2007)

The photoluminescence properties of a silicate glass coactivated with silver and erbium ions were studied. Absorption and photoluminescence spectra allowed to distinguish in the glasses several active species related to the silver, whose ratio depends on heat treatment and silver concentration. The broad emission of silver related species in the visible region of the spectrum has been studied in correlation with the nonresonant excitation of the erbium ions. The comparison of the excitation spectra of silver and erbium shows that the erbium ions are excited through radiative and nonradiative energy transfer from small silver aggregates.

DOI: [10.1103/PhysRevB.75.125102](https://doi.org/10.1103/PhysRevB.75.125102)

PACS number(s): 81.40.Tv, 78.40.-q, 78.55.-m, 42.70.Ce

I. INTRODUCTION

The study of the interactions between rare earths (RE) and metals received enormous interest in recent years¹ because it connects the scientific interest of understanding the effect of changing the photonic mode density (PMD) on the fluorescence properties of the ions with the technological appeal of increasing both pumping efficiency and radiative decay rate by suitably enhancing the electric field near the ions. As a matter of fact, several studies showed that the presence of metal surfaces or nanoparticles modifies the PMD, which can be regarded as vacuum fluctuations or as supported electromagnetic modes. In turn, by virtue of the well-known Einstein relation,² the PMD is proportional to the probability of spontaneously emitted radiation, which therefore is affected both in the decay rate and in the spatial distribution. This happens for any inhomogeneity in ϵ_r ; a remarkable effect is in photonic band-gap materials where certain k transitions may be completely inhibited.³ Also, for metals, the closeness between active centers and metals can induce an important nonradiative decay through the coupling of the excited energy levels of the RE to the surface-plasmon polaritons.⁴ These properties might be exploited in the design of devices activated with RE; in fact, the technologically interesting $4f$ transitions of these ions have weak oscillation strengths, prohibited by the Laporte rule, and the possibility to increase the electric field near them could allow (1) to diminish the pumping energy density required to invert population and (2) to favor the radiative decay with respect to the nonradiative decay in order to increase the quantum efficiency.

These motivations stimulated in 1985 Malta *et al.* to investigate the effect of the nucleation of silver nanocrystals on the spectroscopic properties of a europium-doped borosilicate glass.⁵ They found that the visible luminescence of europium increased after the introduction of silver in the matrix. In analogy to surface-enhanced Raman scattering,⁶ they attributed the result to the increase of the electric field in proximity of the metal nanoparticles. Their results were confirmed by Hayakawa and co-workers,^{7,8} but recently⁹⁻¹² it was shown that the excitation occurs also out of resonance,

which led us to think that energy transfer is responsible for the increased luminescence.

These contrasting conclusions are perhaps induced by the fact that silver ions in glasses are very mobile and have a strong tendency to aggregation. This prevents a simple analysis of the effects of silver doping, because single ions, cluster of few atoms (dimers, trimers, etc.), and nanoparticles of various sizes can coexist. In fact, the heat treatments are scarcely selective because they have the primary effect of increasing the mobility of the silver ions and atoms, producing, first, the formation of dimers and, successively, of cluster of increasing size. In addition, it is difficult to obtain the distribution of size and the state of aggregation because different probes are sensitive to different silver related species. For instance, transmission electron microscopy and x-ray diffraction detect only formed particles, whereas only ions or small clusters luminesce. Even when the probes are sensitive to all the species, as in optical absorption¹³ or x-ray photoelectron spectroscopy,¹⁴ the signals are often partially superimposed, thus precluding a reliable quantitative analysis. Moreover, the increase in size of the nanoparticles changes not only the intensity but also the frequency position of the surface-plasmon absorption band.¹⁵ Silver ions, dimers, and small clusters present very broad absorption and Stokes shifted fluorescence bands, which are due to transitions of $4d$ electrons.¹⁶⁻¹⁹ As the d electrons are not shielded, unlike the $4f$ electrons of RE ions,² this results in a stronger coupling with the static crystal field and with the lattice vibrations that in turn induces a broadening of the energy levels and a large dependence of the spectroscopic features on the matrix.

In this work, we investigate the energy-transfer processes involving silver and erbium electronic excited states. In order to discriminate between the different excitation mechanisms, different doping concentrations and heat treatments have been used to change the relative concentration of the silver related species in an erbium doped soda-lime glass and to try to connect the visible fluorescence of these species with the erbium excitation. Apart from the technological interest, erbium has a practical advantage over europium as the efficient radiative emission at $1.5\ \mu\text{m}$ is completely separated from

the silver luminescence, which is centered in the visible region.

II. EXPERIMENT

The composition of the rare-earth-doped silicate glass is (mol %) 71.5 SiO₂, 15 Na₂O, 10.4 CaO, 1.2 Al₂O₃, 0.4 P₂O₅, 0.6 K₂O, 0.3 Er₂O₃, and 0.6 Yb₂O₃. From this glass, four plates were cut, thinned down to 200 μ m, and optically polished. One of these plates was kept as reference (labeled as Ref) while the others were ion exchanged by keeping them for 67 h at 390 °C in a molten salt bath of NaNO₃ and a variable molar concentration (0.5%, 1.5%, and 5%) of AgNO₃. These ion-exchanged plates will be referred to as AgEr5, AgEr15, and AgEr50, respectively. The exchanged depth was estimated to be around 100 μ m from each side of the glass plate, so that silver ions should be present along their whole thickness.

Optical absorption spectra were obtained in the near-ultraviolet, visible, and near-infrared regions (0.2–3.2 μ m) using a double-beam spectrometer with a resolution of 1 nm. Excitation spectra were recorded using a Xe lamp coupled to a single-grating monochromator as excitation source, in a spectral range extending from 320 to 750 nm. The resolution of the exciting light was set to 5 nm. The signal was collected at several wavelengths, both in visible and IR ranges. The setup for the detection of the infrared signal consisted in a 320 mm single-grating monochromator with a resolution of 2 nm connected to an InGaAs photodiode, while for the visible range, it consisted in a double monochromator with a resolution of 10 cm⁻¹ connected to a photon counting system. The excitation spectra were corrected by dividing by the spectral output of the source collected by a calibrated photodiode. Photoluminescence (PL) measurements in the visible and infrared regions (in particular, around the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the Er³⁺ ions) were obtained on several excitation wavelengths. Time-resolved photoluminescence measurements were carried on in the visible range, exciting the samples by the third harmonic (355 nm) of a *Q*-switched Nd:YAG laser with a pulse width of 6 ns and a repetition rate of 10 Hz. The luminescence decay was collected at several wave numbers with the setup previously described and recorded by a multichannel analyzer. Further information was obtained by polarization spectroscopy. The polarized beam of an Ar⁺ laser, operating at 488 nm, was used for the excitation and the luminescence with parallel (VV) or with perpendicular (VH) polarization was detected. A scrambler was inserted between the polarizer and the spectrometer for equalizing the setup response. All measurements were taken at room temperature.

III. RESULTS

Figure 1 shows the absorption spectra of the silicate samples. The sharp weak peaks are due to Er³⁺ absorption. They should be common to all samples, but in fact it seems that their intensity decreases after the ion exchange. This process exchanges Na⁺ ions with Ag⁺ ions, but probably also some Er³⁺ ions diffuse to the solution and are lost from the

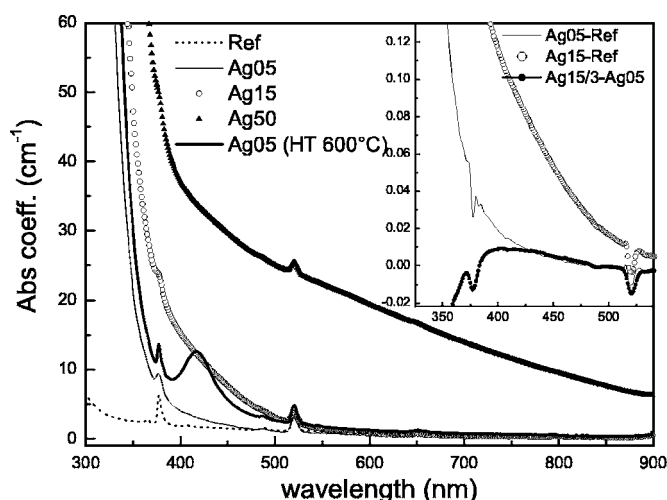


FIG. 1. Room-temperature absorption coefficient of the silicate samples. Inset: Differential spectra which highlight the silver species absorption.

glass. The plasmon band at 420 nm, typical of the spheroidal silver nanoparticles, is well observable in the sample Ag05 heated at 600 °C in air, but does not appear for annealings at $T < 400$ °C. The other silver species are not easily discernible in the absorption spectra.^{13,19} The differential absorption measurements in the inset of Fig. 1, where the absorption of the reference sample is subtracted, can help in the detection of the contribution of different silver aggregates. Neglecting the sharp dips due to the Er³⁺ absorption, the spectra look different in the blue and UV ranges, where the absorption becomes strong. We attribute this absorption to Ag⁺ ions, whose absorption is centered at about 250 nm.¹⁹ As expected, the absorption is higher in the Ag15 than in the Ag05 sample. Unfortunately, the measurement in Ag50 is not significant, since the metallic silver on the surface greatly reduces the transmission in all the visible range. Apart from the intensity, also the shapes of the absorption profile in Ag5 and Ag15 seem to be different, the latter presenting a shoulder at about 400 nm. If the exchange process would simply replace Na⁺ with Ag⁺ ions without the formation of any silver aggregate, the absorption spectra of all as-exchanged samples should have the same shape, with an intensity proportional to the Ag⁺ concentration. The difference spectrum, $\alpha(\text{Ag15})/3 - \alpha(\text{Ag5})$, shows that this is not the case and that silver tends to aggregate already during the exchange process. This is reflected in a reduction of the absorption at low wavelengths and in the presence of the now clearly observable band, at about 400 nm, attributed to silver dimers or larger aggregates.¹⁹

Figure 2 shows the excitation spectra of the exchanged silicate glasses collecting the signal at 1532 nm, i.e., from the maximum of Er³⁺ $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission. It is important to note that no luminescence, other than that of erbium, is detected at around 1.5 μ m after excitation in the visible. As shown in the inset for an excitation at 420 nm, the luminescence intensity goes to zero on the two sides of the Er band. The excitation spectra were normalized to the intensity of the line at 650 nm, which corresponds to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ of the Er³⁺ ions. This allows to compare more reliably the excita-

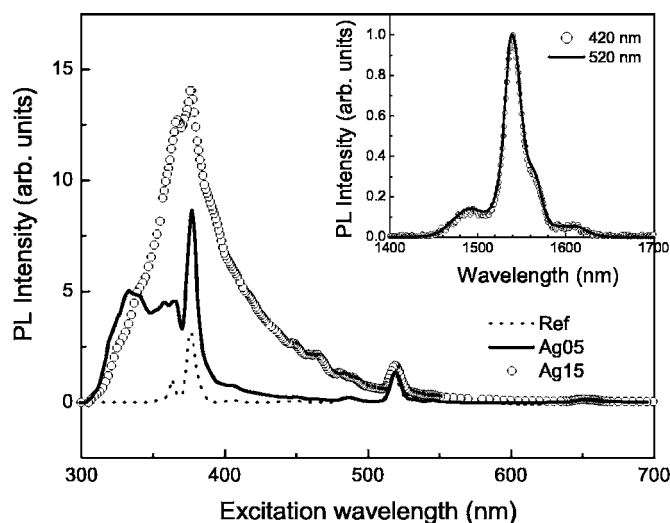


FIG. 2. PL excitation spectra collected at 1532 nm from Er^{3+} $^4I_{13/2} \rightarrow ^4I_{15/2}$. Inset: Normalized PL spectrum of Ag05 upon excitation resonant (520 nm) and nonresonant (420 nm) with erbium energy levels.

tion spectra of different samples in the presence of some unavoidable changes in the experimental conditions. In fact, the samples have different refractive indices and different surface roughness, induced by the deep ion exchange. The excitation spectrum of the Ref sample shows only the sharp lines due to the direct excitation of the inhomogeneously broadened erbium levels. In the exchanged samples, also a broadband contribution appears. It is remarkable that not only the intensity but also the shape of this continuous contribution change as the silver content is increased. As already observed,^{9–12} the excitation out of the electronic energy levels of the erbium ions is a clear indication of the presence of an energy-transfer process. In comparing the shapes of the excitation spectra of different samples, we have to consider not only the presence of different energy-transfer mechanisms through which the erbium ions are excited but also the fact that the samples are thick and the absorption is strong at low wavelength. Therefore, the excited volume is sample and wavelength dependent, causing a nonlinearity of the excitation response.

Some centers that absorb the light and transfer the excitation to the erbium ions also produce their proper luminescence. Their spectroscopy and their activity in the transfer process can be studied by a detailed comparison of the excitation spectra taken at different emission frequencies and of the luminescence spectra obtained by exciting at different frequencies, possibly in time-resolved experiments. Figure 3 shows the PL spectra of the Ag15 sample excited at different wavelengths between 410 and 595 nm. All spectra show a very broad band, whose maximum shifts with the excitation frequency. A positive contribution to the PL from the erbium ions in this scale is visible only for the excitation at 520 nm, which is resonant with the $^4I_{15/2} \rightarrow ^2H_{11/2}$. For the other excitations, not resonant with erbium transitions, a dip in the broad band appears always at 520 nm. This dip is attributed to reabsorption by the Er ions of the luminescence from silver aggregates.

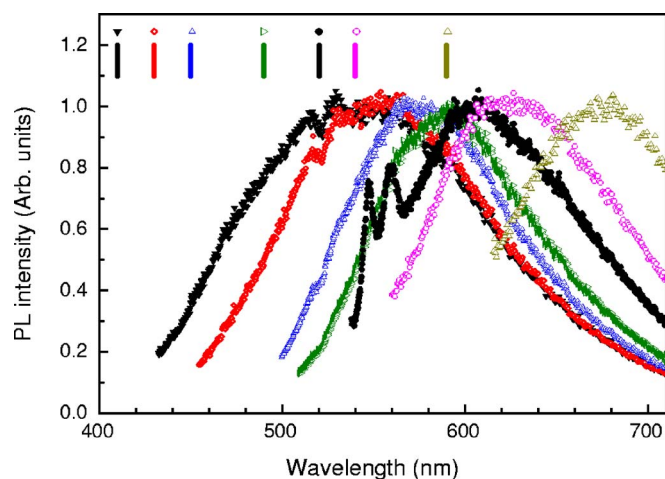


FIG. 3. (Color online) Normalized PL spectra of Ag15 sample upon excitation by a Xe lamp at several wavelengths (indicated in figure).

Time-resolved spectroscopy upon 355 nm pulsed excitation shows that different centers contribute to the broadband luminescence. Figure 4 shows an attempt to separate three contributions with lifetimes in the ranges of about 10, 50 μs , and higher than 100 μs . The procedure used to obtain Fig. 4 is described in the following. The decay curve of the luminescence has been measured at some wavelengths. The inset shows the curve of decay taken at 455 nm, together with a fit by three exponentials, whose parameters are reported in Table I. The three decay times needed for the best fit slightly change with the detection frequency, but remain in ranges around the values of Table I. Delayed spectra in different time windows were measured and the integrated luminescence was attributed to three contributions with the decay times of Table I. The result has to be taken as purely indicative, since it is evident that a continuous distribution of lifetimes is actually present and the shapes of the bands depend

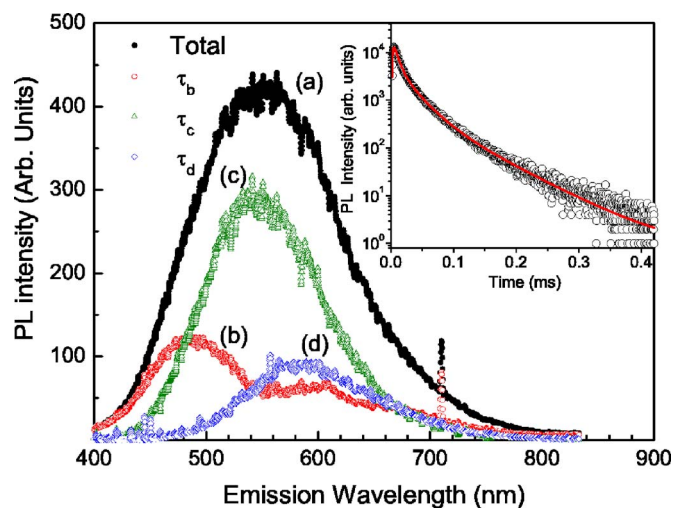


FIG. 4. (Color online) (a) PL spectrum of sample Ag05 upon pulsed excitation at 355 nm; [(b)–(d)] decomposition of spectrum (a) in components with different decay times. Inset: Decay curve collected at 455 nm.

TABLE I. Lifetimes (μs) of the bands (see Fig. 4), which constitute the visible luminescence of the silver species, collected upon 355 nm pulsed excitation.

Sample	τ_b	τ_c	τ_d	Rise $\tau(b,d)$	Rise $\tau(c)$
Ag05	10	50	100	1	6
Ag15	5	30	80	1	4
Ag50	3	10	50	1	2

on the choice of the three characteristic lifetimes.

In any case, the shape of the band (4d) with the longer decay time is similar to that observed in Refs. 19 and 20 and attributed to small Ag^0 clusters. A band in the blue, similar in form of the blue component of Fig. 4(b) with fast decay time, was attributed to Ag_3^{2+} species.¹⁶ Other centers with silver ions bound to silver atoms in dimers or trimers are expected to be present and they could explain the presence of the low-frequency band of Fig. 4(b) and of the band of Fig. 4(c).¹⁹ In particular, Paje *et al.*²¹ provided evidence that in soda-lime glasses Ag^+-Ag^+ dimers have a broad luminescence centered at about 525 nm, i.e., practically coinciding with band 4c, while mixed species of Ag^0 and Ag^+ in dimers or trimers should emit at longer wavelength.

By increasing the silver content, in Ag15 and Ag50 samples, the fast decay components become stronger in comparison with the others and all lifetimes become shorter. On the contrary, the shapes of the bands of Fig. 3 do not change very much. These results could indicate that energy transfer between different active centers is present and becomes more and more important with increasing silver content. This hypothesis is supported also by the behavior of the rise time of the luminescence, which is different at different wavelengths (1 μs at 445 and 625 nm, 6 μs at 555 nm for Ag05). This seems to indicate that at 355 nm we do not excite directly the emitting centers and that different channels are active in the excitation of the other centers. Furthermore, the rise time of the emission at 555 nm is close to the fast decay time of the luminescence at 445 nm. This could indicate that centers that produce luminescence at 445 nm also can transfer the excitation to other centers that have luminescence at 555 nm. In polarized measurements, the visible luminescence band of the Ag05 sample shows a ratio of intensity $I_{\text{VH}}/I_{\text{VV}} \sim 1/3$. This low value is distinctive of centers with an oriented dipole, which can absorb and emit light only polarized along the axis.²² This property is typical of dimers,¹⁷ but other small clusters with a preferential axis cannot be excluded.

Figure 5 shows the excitation spectra of the Ag05 and Ag15 samples collected at 515 nm from the broad luminescence band of the silver centers. (Compare Fig. 3 and note that, as there are several emitting centers, the excitation spectra from the silver aggregates acquired at different wavelengths may substantially differ.) At this frequency, we are sure that there is no luminescence from excited states of Er^{3+} ions. The shapes of the excitation bands of Fig. 5 are practically coincident with those of the broadband contribution observed in the excitation spectra of the Er^{3+} luminescence, detected at 1.5 μm . This result indicates that the channel through which the erbium ions are excited is the silver ag-

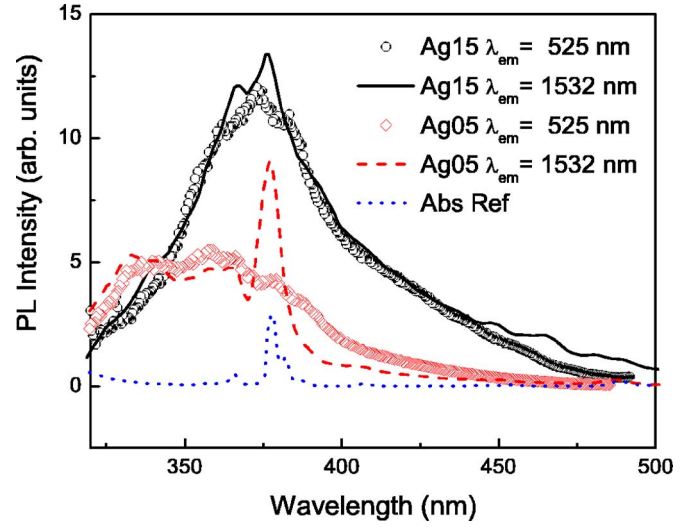


FIG. 5. (Color online) Comparison of the excitation spectra of samples Ag05 and Ag15 collected at 525 nm (Ag species luminescence) and 1532 nm (erbium luminescence). The absorption spectrum of sample Ref is reported to locate the absorption lines of erbium.

gregate that emits at about 515 nm. The sharp lines of the Er^{3+} absorption do not appear in the excitation spectra of the silver aggregate, indicating that energy transfer from Er to silver is negligible. Therefore, the transfer from silver to erbium appears to be unidirectional.

IV. DISCUSSION

The luminescence and excitation spectra indicate that silver aggregates, showing absorption in the blue and a green luminescence, can transfer the excitation to erbium ions. The energy-transfer mechanism is still to be discussed. The transfer probability is proportional to the superposition integral of the two spectral shapes of the cross sections in the emission of donors (Ag aggregates) and in the absorption of acceptors^{23,24} (Er^{3+} ions):

$$P^{\text{Ag-Er}} = C \int \sigma(\nu)_{\text{abs}}^{\text{Er}} \sigma(\nu)_{\text{em}}^{\text{Ag}} d\nu. \quad (1)$$

Equation (1) describes both the radiative and nonradiative resonant energy transfers, i.e., with the exchange of real or virtual photons. In the latter case, C is a constant, which measures the strength of the coupling and depends on the physical mechanism, as dipole-dipole, dipole-quadrupole, exchange coupling, and on the actual space distributions of donors and acceptors. Phonon-assisted energy-transfer processes are expected to be less probable. As the erbium absorption spectrum has a very intense transition, the hypersensitive $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition centered at about 520 nm, which contribute to about 90% of the whole visible absorption, $P^{\text{Ag-Er}}$ is practically proportional to $\sigma(\nu)_{\text{abs}}^{\text{Er}}$ evaluated at the frequency transition. Equation (1) can also explain why the transfer from erbium to silver is inhibited: there is no strong absorption of silver aggregates at the wavelengths at which the erbium emits.

In a phosphate glass, we found that the radiative transfer, i.e., reabsorption, dominates the very weak nonradiative transfer. In fact, energy transfer was observed only in thick samples,^{11,25} where reabsorption can be more effective. In silicate, on the contrary, energy transfer was observed not only in our 200 μm plates but also in thin films.^{9,12} The radiative mechanism of transfer from silver to erbium is, for sure, active, as it is testified by the dip in the luminescence spectrum of Fig. 3, in correspondence with the $^2H_{11/2} \rightarrow ^4I_{15/2}$ transition. However, the radiative mechanism is not very effective, given the poor erbium cross section, and probably it is dominant only in phosphate glasses,²⁵ where the glass structure allows a very effective separation of the active centers,²⁶ with small nonradiative transfer rate. On the contrary, the structure of silicate, which allows tighter packing of the erbium and silver ions, should favor the nonradiative energy transfer.

Our spectroscopic study shows that several emitting centers coexist and can absorb the visible light and transfer the excitation to erbium ions. However, since the erbium ions can efficiently accept excitation only in a narrow range around 520 nm, only the centers that emit at this wavelength can efficiently transfer their excitation to erbium. In particular, according to the spectrum in Fig. 4, the centers with the strongest emission in this region are the silver dimers, which are therefore expected to be the favored channel for the erbium excitation. On the other hand, the transfer to erbium may involve also levels other than the $^2H_{11/2}$, even if less effectively. This may explain the shape of the excitation band of erbium, which is a weighted sum of different absorption bands of silver aggregates.

Looking only at the IR excitation spectra, it appears that, as often stated, the introduction of silver has beneficial effects on the erbium luminescence, which in the silver-doped samples is always higher than in the undoped sample with an enhancement factor ranging between 1 and over 100, in the regions where the erbium does not absorb. However, it seems more meaningful to consider what is the actual efficiency of the pumping mediated by silver. A rough estimation may be obtained by comparing the absorption and IR excitation spectra. From the ratio between the continuous background and the erbium absorption peak, in the excitation spectrum of sample Ag15, we see in Fig. 2 that, by pumping at 520 nm, the erbium luminescence due to transfer from Ag species is about 1/2 of that due to direct erbium excitation. At the same wavelength, 520 nm, the absorption of silver is about two times that of erbium. Therefore, about 1/4 of the silver species transfers the excitation to erbium. This transfer efficiency slightly increases by lowering the excitation wavelength, and it reaches a maximum of about 50% at 370 nm because the silver centers that absorb at this wavelength have the maximum of $\sigma(\nu)_{\text{Ag}}^{\text{Ag}}$ at 520 nm in correspondence with the maximum of $\sigma(\nu)_{\text{Er}}^{\text{Er}}$. Similar results are obtained for Ag05, the transfer efficiency being slightly smaller. Note that the donor lifetime (10-100 μs) is quite larger than that of acceptors [$\sim 1 \mu\text{s}$ (Ref. 27)] in the level $^2H_{11/2}$. This forbids detrimental back transfer effects.

By the light of the conclusions presented, it seems significant to rediscuss the results^{5,7} which led us to attribute to silver nanoparticles the Eu luminescence enhancement, in

order to evaluate if our explanation, which does not consider the influence of the plasmon band, may apply also there.

In the work of Malta *et al.*,⁵ we notice that the differential absorption spectrum shows a peak at 320 nm that is due not only to silver colloids (it should be centered at longer wavelength) but also to ions or multimers that are known to absorb at these wavelengths and whose influence cannot therefore be excluded. Also in the works of Hayakawa and co-workers,^{7,8} the luminescence enhancement could be related to the presence of these small silver clusters. In fact, for short delay times they find a broad visible luminescence, which moreover presents dips in correspondence with the europium absorption bands.⁸ Additionally, they do not find the decrease of the europium decay time to be connected with the increase of the oscillation strength of the transition, and this suggests that the PL intensity increase is due to a greater efficiency of the pumping.

The works of Strohhofer and Polman, Portales *et al.*, and Mazzoldi *et al.* all agreed that the main mechanisms of the RE excitation had to be energy transfer, even if the donor's nature was not surely determined. However, in Refs. 9 and 12, the sensitizing effect of the silver appears stronger and for excitation at lower wavelengths with respect to Ref. 11. Two reasons may be given for this: the first one resides in the different format, planar waveguides and bulk, of the samples. As a matter of fact, when lowering the excitation wavelength toward the Urbach edge, the absorption coefficient increases and, in bulk systems, only the first layer is excited, reducing the final excitation of the erbium. On the contrary, the extinction of the exciting beam is very weak in films and the spatial distribution of excitation does not depend on the wavelength. Moreover, in bulk system, especially if prepared by melt-quenching technique, the silver content cannot be as high as in films. The second reason regards the solubility of the RE and silver in the various hosts. The capability to have a good separation between the active dopant ions, which makes phosphate glasses preferable to silicon oxide or borosilicate as matrix for highly doped devices,²⁸ makes them unfit to promote the closeness between lanthanide ions and silver luminescent centers that is required to have an effective energy transfer. From this point of view, soda-lime glasses appear to have intermediate properties.

We can conclude that, in our case, the enhancement of the erbium luminescence is not due to an increase in the absorption or in the emission cross section, but to an electric dipole induced energy transfer. As a matter of fact, the distance between luminescent centers and metallic surfaces has to be controlled in order to obtain significant changes on the radiative decay rate, because the PMD oscillates around the value obtained without metal with the distance from the metal surface.^{1,29} Instead, in the case of random space distributed metal nanoparticles in the rare-earth-doped matrix, as obtained by heat treatment of the samples, there is no average increase of the electric field near the active ions.

V. CONCLUSION

The modification of the PMD is a really attractive topic and randomly distributed metal particles in a dielectric host

may be a suitable system to study light localization; however, given the difficulties in controlling the fabrication of the samples at this length scale, it is important to discriminate when the effects observed are due to a different, coexistent process. In particular, the enhancement of the erbium luminescence in a silver-doped glass is due to an energy-transfer process from silver species, especially dimers. The mechanism of transfer operates in the visible through the excitation of the high-energy levels of the erbium. The infrared erbium luminescence upon visible excitation increases because of the high absorption cross section of the silver

species which, moreover, may transfer the excitation with an efficiency of up to 50%. Hosts where the doping ions are easily segregated allow to have stronger coupling between silver species and rare earths with increased nonradiative transfer efficiency.

ACKNOWLEDGMENTS

We wish to acknowledge the financial support of MIUR-FIRB RBNE012N3X, ITPAR, and MIUR PRIN projects.

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