

Silver as a sensitizer for erbium

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The photoluminescence of Er^{3+} in borosilicate glass is strongly enhanced by the presence of silver. Samples prepared by a combination of erbium ion implantation and $\text{Na}^+ \leftrightarrow \text{Ag}^+$ ion exchange show an increase of the Er^{3+} excitation efficiency of up to a factor 70 when excited at 488 nm. Excitation of Er^{3+} is possible over a broad wavelength range in the near ultraviolet and visible. Our data suggest that absorption of light occurs at a silver ion/atom pair or similar defect, followed by energy transfer to Er^{3+} . We can exclude that silver nanocrystals are part of the dominant excitation mechanism, neither via local field enhancement effects due to their surface plasmon resonance nor via absorption and subsequent energy transfer to Er^{3+} . © 2002 American Institute of Physics. [DOI: 10.1063/1.1499509]

The small absorption cross sections of rare earth ions such as erbium or neodymium 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 ion in question. In the specific case of erbium, codoping with ytterbium (although itself a rare earth ion, it has a reasonably high absorption cross section at 980 nm) has found its way into application in lasers and optical amplifiers for 1540 nm light,^{1,2} and broadband sensitization in the visible via organic complexes³ and silicon nanocrystals⁴ has been demonstrated.

We have turned our attention to photoluminescence enhancement effects that silver might have on Er^{3+} in oxide glass. Silver can be introduced easily to concentrations of several atomic percent into glasses via an ion exchange process,⁵ interchanging network modifiers of the glass like sodium or potassium and silver ions. This is a standard process to fabricate waveguides for integrated optics. Several absorption and emission bands in the visible and near-ultraviolet related to silver have been observed in glasses,^{6,7} opening the possibility of energy transfer towards Er^{3+} .

Doping glasses with silver however gains an additional dimension from the fact that nanometer-sized crystals can be precipitated. Besides other interesting optical properties, such glass/metal nanocrystal composites exhibit large optical nonlinearities caused by enhanced local electric fields around the nanocrystals.⁸ Some evidence for the effect of this local field on the emission of Eu^{3+} ions has been reported.⁹

We present investigations of borosilicate glass doped with erbium by ion implantation and with silver by ion exchange. By adjusting the doping procedure we are able to fabricate samples with a high concentration of dissolved silver and little to no silver nanocrystals, and samples where a considerable amount of the silver aggregates into crystallites. We observe a broad excitation band of the photoluminescence of Er^{3+} in the visible and near-ultraviolet, with luminescence enhancements up to a factor of 70 at a pump wavelength of 488 nm. We conclude that the excitation efficiency of Er^{3+} is increased by energy transfer from Ag^+ related

centers rather than under the influence of silver nanocrystals.

The borosilicate glass substrates were 1 mm thick Schott BK7 wafers. Silver was introduced by a $\text{Na}^+ \leftrightarrow \text{Ag}^+$ ion exchange in a salt melt containing 5 mol % AgNO_3 and 95 mol % NaNO_3 . The samples were left in the melt for 7 min at 310 °C. Erbium was implanted at an energy of 925 keV to a fluence of $3.1 \times 10^{15} \text{ cm}^{-2}$ into the glass substrate at liquid nitrogen temperature. Two samples were prepared combining these two doping techniques. One was first implanted with erbium and subsequently ion exchanged, while the other underwent the ion exchange first, and the resulting Ag^+ doped glass was then implanted with erbium. The bombardment of Ag^+ doped glass with heavy ions, as in the latter case, has been shown to lead to the formation of silver nanocrystals.¹⁰ For reference purposes, another glass sample was implanted with erbium under the same conditions, but did not undergo ion exchange. All samples were annealed in vacuum for 30 min at 350 °C.

The main difference between the samples prepared by ion exchange and ion implantation is the presence or absence of silver in ionic or metallic form. From Rutherford backscattering spectrometry we obtain a silver concentration of 2.2 at. % in the sample first ion-exchanged then erbium implanted, and around 3 at. % for the sample implanted with erbium before the ion exchange. These values are approximately constant up to a depth of around 600 nm. For comparison, the erbium range for our implantations amounts to 250 nm. We attribute the difference in Ag concentration between the two samples to variations in the diffusivity of Ag^+ ions caused by damage from the ion irradiation in the glass. While silver is present predominantly as Ag^+ ions in the sample implanted with erbium before ion exchange, irradiation with heavy ions after ion exchange leads to the agglomeration of a considerable amount of the silver ions in metallic nanocrystals.¹⁰ Figure 1 compares the absorbance induced by the preparation of the two samples doped with silver and erbium. The distinctive band peaking at 420 nm observed for the sample ion-implanted after ion exchange is caused by the surface plasmon resonance of the silver nanocrystals. The fraction of silver agglomerated in nanocrystals, as estimated from the strength of the absorption, is around 30%. The

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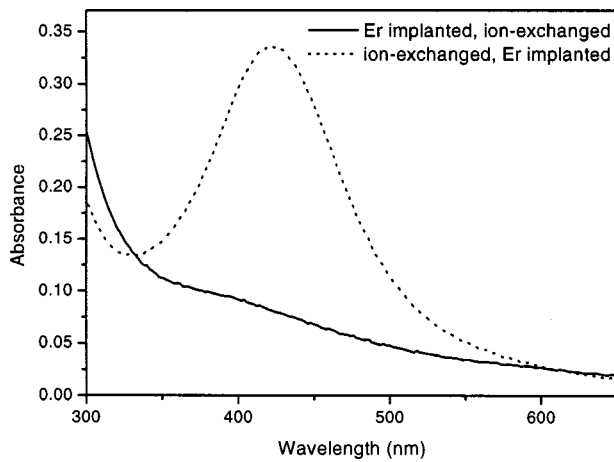


FIG. 1. Absorbance of the samples doped with erbium and silver. The band around 420 nm is caused by the plasmon resonance of silver nanocrystals formed during erbium implantation into silver-containing glass. The data were measured relative to an untreated reference glass slide.

sample that was ion exchanged after erbium implantation shows an increased absorbance, rising towards shorter wavelengths, whose origin might be related to the ion exchange. A similarly shaped, yet slightly lower, structure underlies the surface plasmon band.

Figure 2 plots the emission spectra of the three samples (including the reference sample containing no Ag) between 1400 and 1700 nm. The emission line is caused by transitions between the first excited state and the ground state of Er^{3+} . It is identical for the three samples. While the luminescence of the sample without silver has been excited with 488 nm radiation into the ${}^4F_{7/2}$ state of Er^{3+} , the samples containing silver show strong photoluminescence even when excited with 476 nm light, a wavelength at which Er^{3+} does not absorb. This is illustrated by the excitation spectrum for the sample doped with only erbium in Fig. 3(a), measured using the lines from the Ar^+ laser. Only when excited at 515, 488 and 360 nm, significant emission from Er^{3+} around 1540 nm is observed. In contrast, Er^{3+} can be excited over a wide spectral range in both samples containing silver, extending from the near ultraviolet to the red, as evident from Fig. 3(b) measured using a Xe lamp as the excitation source in combination with a monochromator with 20 nm spectral resolution for wavelength selection. Note the difference in the intensity scale between Figs. 3(a) and 3(b), calibrated by photoluminescence intensity measurements excited with the 488 nm line of the Ar^+ laser. The photoluminescence decay rate measured at 1538 nm is 400 s^{-1} for the sample doped only with erbium, and 1000 s^{-1} for the samples doped with erbium and silver. This increased decay rate on doping with silver is mainly caused by increased nonradiative de-excitation of the first excited state of Er^{3+} . This is put into evidence by the fact that Ag doping reduces the emission intensity at 1538 nm by more than a factor of two when excitation takes place into the $\text{Er}^{3+} {}^4I_{11/2}$ level at 980 nm. At this wavelength, the sensitizing effect of silver on the emission from erbium is negligible, and the emitted intensity is determined exclusively by the ratio of radiative decay rate to total decay rate of the $\text{Er}^{3+} {}^4I_{13/2}$ level.

The shape of the excitation spectrum is identical for both the sample that was ion exchanged after erbium implantation

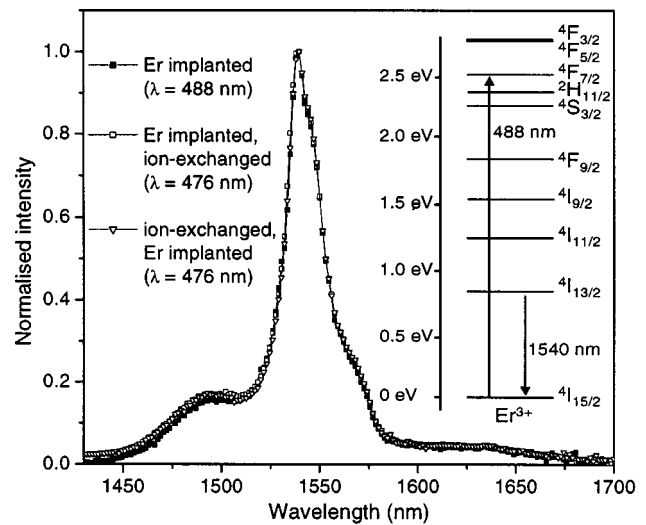


FIG. 2. Spectra of Er^{3+} emission in borosilicate glass doped with silver by an ion exchange process (open symbols). Note that the photoluminescence was excited at a wavelength which cannot be absorbed directly by Er^{3+} . The emission spectra are identical to the one obtained for Er^{3+} in glass without silver when excited to its ${}^4F_{7/2}$ state (solid squares). The inset shows the energy level scheme of Er^{3+} .

and the sample implanted with erbium after ion exchange. The intensity of the Er^{3+} emission is however higher for the sample that underwent the ion exchange after implantation of erbium. This is the sample with both a higher silver concentration and more silver dispersed in ionic form in the glass matrix, i.e., not aggregated to form silver nanocrystals. Since the nanocrystals form predominantly in the region of the glass around the range of the implanted erbium ions, the concentration of silver ions in the vicinity of erbium is reduced by their precipitation. The emission intensity at 1540 nm is enhanced by a factor of 20 and 70 for the samples ion exchanged before and after implantation of erbium, respectively, when excited with 488 nm radiation. At 360 nm, the emission intensity increases even by factors of 220 and 55, respectively.

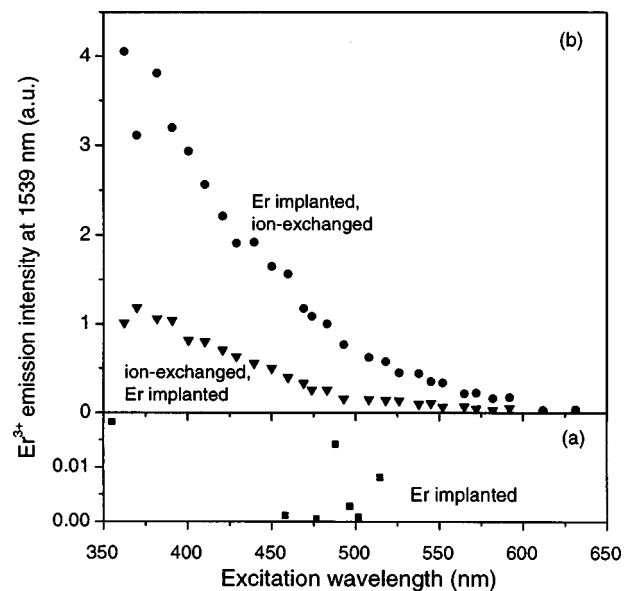


FIG. 3. Photoluminescence intensity at 1539 nm as a function of excitation wavelength for three different samples: (a) borosilicate glass doped with erbium only; (b) erbium and silver doped borosilicate glass.

The origin of the increase in emission intensity may be inferred from the excitation spectra and the absorbance induced by the processing of the different samples, Figs. 3 and 1. Several conclusions can be drawn from these plots: in contrast to the work by Hayakawa and co-workers,⁹ who investigated the luminescence enhancement of Eu^{3+} in glasses containing silver nanoparticles, we can exclude field enhancement effects due to the surface plasmon resonance of silver nanoparticles as the dominant mechanism responsible for the increased luminescence from our samples. Such a process does not change the position of the energy levels of Er^{3+} , and therefore the shape of the excitation spectrum, in clear contrast to the observations presented in Fig. 3. Furthermore, we can also exclude energy transfer from silver nanoparticles to erbium ions. The excitation spectrum does not overlay the surface plasmon absorption, which therefore cannot be the initial step in the excitation of Er^{3+} . Also the fact that the sample containing silver nanocrystals exhibits a lower Er^{3+} luminescence intensity than the one containing no nanocrystals, points into the direction that nanocrystals do not lead to enhanced emission from Er^{3+} .

The spectral shape of the excitation spectra of the samples doped with silver does not match the spectrum of the absorption we believe to be induced by the ion exchange shown in Fig. 1. The absorbance spectrum does not approach zero at 600 nm, as is clear from Fig. 1, while Er^{3+} can hardly be excited at that wavelength (cf. Fig. 3). However, it can be argued that a much weaker absorption than the one observed in the sample ion exchanged after erbium implantation is sufficient to obtain the photoluminescence enhancement seen for that sample. From considerations of the detection efficiency of the photoluminescence measurement system, an absorbance lower by five orders of magnitude would explain the results reported in Fig. 3 for a conversion efficiency from absorbed pump photon to emitted photoluminescence photon of 1. It therefore seems likely that the absorption that constitutes the initial step in the excitation of Er^{3+} is completely hidden in Fig. 1 by a second, stronger absorption not linked to Er^{3+} excitation.

The shape of the silver-related band from where energy transfer towards Er^{3+} originates, can in our experiments only be deduced from the excitation spectra. Several authors^{6,11} have observed an absorption band in the spectral region between 300 and 450 nm in glasses containing high concentrations of silver, and attributed it to pairs of silver ions/atoms. Similar centers might be at the origin of the energy transfer to Er^{3+} . Assuming a concentration of ion pairs of 0.1 at. % We estimate the absorption cross section of the pairs to have a value between 10^{-19} and 10^{-16} cm^2 , depending on the quantum efficiency assumed. Although in the absence of data on the energy transfer efficiency, this estimate is very inaccurate, its range spans three orders of magnitudes of absorption cross sections usually measured for metal ions in dielectrics. With suitable diligence, it can therefore be seen as further indication that metal ions are at the origin of the light absorption.

The absorption of Ag^+ ions in glasses is generally found at wavelengths much shorter than the range covered by our measurements, and Ag^+ is therefore unlikely to take part in the excitation mechanism of Er^{3+} reported here. Unlikely for similar reasons is that the excitation takes place via the glass band edge, shifted to longer wavelengths owing to the introduction of Ag^+ into the glass. This displacement is usually small for silver concentrations comparable to the ones in our samples.⁶

Finally, let us mention that sensitizing of Er^{3+} emission by codoping with silver is not restricted to doping by ion exchange. Samples into which silver was introduced by ion implantation also showed the broad excitation band for the photoluminescence of Er^{3+} .

To summarize, the photoluminescence from Er^{3+} around 1540 nm is strongly enhanced in borosilicate glass codoped with silver. An excitation efficiency as high as 70 times the one of Er^{3+} in the same glass without silver has been obtained under excitation at 488 nm. For excitation at 360 nm the increase even amounts to 220. The excitation spectrum in the visible is broadband and does not reproduce the erbium intra- $4f$ absorption lines. There are indications that the excitation takes place via absorption at a defect related to a pair of silver ions/atoms and energy transfer towards Er^{3+} . Furthermore we can conclude that silver nanocrystals do not play a role in the enhancement of the Er^{3+} photoluminescence in our samples, neither as origin of an enhanced local field nor as absorption centers for a subsequent energy transfer.

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