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# Novel Er-doped $SiC/SiO_2$ nanocomposites: Synthesis via polymer pyrolysis and their optical characterization

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**Abstract**

Erbium activated $SiC/SiO_2$ nanocomposites doped with $Er^{3+}$ concentrations ranging from 1 to 4 mol% were prepared by pyrolysis of sol–gel derived precursors. The gels were obtained from modified silicon alkoxides containing Si–$CH_3$ and Si–H groups. Thin discs obtained from the monolithic xerogels were pyrolyzed in an alumina tubular furnace in flowing Ar (100 ml/min) at 800, 1000, 1200 and 1300 °C. The samples were investigated by absorption and photoluminescence spectroscopies. Emission in the C-telecommunication band was observed at room temperature for all the samples upon continuous-wave excitation at 980 or 514.5 nm. The shape of the emission band corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is found to be independent both on Erbium content and excitation wavelength, with a Full Width Half Maximum (FWHM) of 48 nm. By increasing the pyrolysis temperature the intensity of the luminescence increases and the electronic bandgap energy decreases.


*Keywords:* FWHM; $^4I_{13/2}$; Emission band

## 1. Introduction

Novel, nanostructured multicomponent refractory ceramics of the general system Si–C–N–B–O can be easily produced by pyrolysis of suitable preceramic precursors.[1] According to this route, a cross-linked preceramic network is pyrolyzed in inert atmosphere at temperature as low as 800–1000 °C and an amorphous ceramic is obtained.[2] By increasing the pyrolysis temperature, nanocrystalline carbides and nitrides are formed in the amorphous matrix at temperatures that can be as low as 1200 °C (SiCO system)[3] or as high as 1700 °C (SiBCN system).[4] Excess C is also usually present leading to black, not transparent materials. These polymer-derived ceramics (PDCs) show exceptional mechanical, thermal, and chemical properties.[5–7]

PDCs belonging to the ternary SiCO system, and often referred as silicon oxycarbide glasses, can be easily prepared from sol–gel derived siloxane networks containing different Si–R, R = H, $CH_3$, $CH_2CH_3$, $C_6H_5$ . . . groups.[8] The sol–gel process allows to precisely tailoring the composition of the siloxane network by the appropriate choice of the starting silicon alkoxides. This, *in turn*, allows a very good control of the composition of the resulting SiCO ceramics. Accordingly, we have shown that stoichiometric SiCO glasses, which at 1200 °C leads to a nanostructured $SiC/SiO_2$ ceramics with negligible amount of free C, can be produced.[9] This result has been achieved using modified silicon alkoxides containing both Si–H and Si–$CH_3$ moieties.[10]

Silicon carbide is a wide bandgap (2.2 eV) optoelectronic material, is transparent over a wide range of wavelengths (0.54–2.0 μm) and exhibits high refractive index (2.57).[11] Thus, composites formed by a dispersion of SiC nanocrystals into a dielectric $SiO_2$ matrix, could find application as a multifunctional optoelectronic materials also working in

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harsh environment. Tailoring of intrinsic luminescence has been already demonstrated for $SiC/SiO_2$ nanostructured systems.[12,13] In particular, the possibility to obtain transparent glass ceramics, based on the $Er^{3+}$-activated $SiC/SiO_2$ glasses, could get a significant improvement to broad band optical amplifier fabrication.[14,15] Among different techniques, the sol–gel technique is playing an increasing role in the development of silica-based glasses activated by $Er^{3+}$ ions.[16–18] On the other hand, processing of $SiC/SiO_2$ nanocomposites by loading a sol–gel solution with silicon carbide powders is very difficult due to the very limited dimension required for of the SiC nanocrystals.

In this work we will show that it is possible, starting from a suitable, sol–gel derived preceramic precursor, to synthesize $SiC(Er)/SiO_2$ nanocomposites which display interesting photoluminescence behaviour.

## 2. Experimental

The Si alkoxides were purchased from ABCR and used as-received. Gel samples were obtained by co-hydrolysis of triethoxysilane ($HSi(OCH_2CH_3)_3$, $T^H$) and methyldiethoxysilane ($HCH_3Si(OCH_2CH_3)_2$, $D^H$), using THF as solvent. A $HNO_3$ solution with a pH 2 was used for the hydrolysis. The molar ratio of $T^H/D^H$ was 2. This particular composition was chosen because it leads, after pyrolysis, to the formation of a pure silicon oxycarbide glass with negligible amount of free C.[10] An acidic aqueous solution 1 mol% of $ErCl_3{\cdot}6H_2O$ was prepared by dissolving the salt into an $HNO_3$ solution at pH 2. In a typical preparation, the alkoxides were mixed in THF using an ice bath. Then the acidic water was added drop by drop under vigorous stirring. Finally, the $ErCl_3$ solution was added in order to achieve the desired Er content (Er/Si = 1%) and to adjust a total $H_2O/O(CH_2CH_3)$ = 1 ratio. This solution was stirred for additional 20 min and then cast into small plastic tubes and sealed with plastic film. Gelation occurred within 2 h at room temperature. Gels were then slowly dried at room temperature for 3 weeks and then at 80 °C for an additional week. Monolithic, cylindrical samples 6 mm × 30 mm were accordingly obtained. From these samples thin gel discs, 0.5–1 mm thick were subsequently obtained by sectioning the original monolithic gels. Pyrolysis was performed in an alumina tubular furnace in flowing Ar (100 ml/min) at 800, 1000, 1200 and 1300 °C. Heating was performed at 5 °C/min and the samples were held for 1 h at the highest temperature. Crack-free, monolithic and transparent yellowish samples have been obtained.

## 3. Characterization techniques

Structural characterization of the SiCO glasses obtained from $T^H/D^H$ 2 gel precursor in the 800–1400 °C range has been the subject of several studies already reported in the literature.[9,19] In particular, the major weight loss associated with the pyrolysis process ends around 800 °C, from 800 to 1200 °C only minor amounts (less than 1 wt.%) of gases ($H_2$, $CH_4$) are released and from 1200 up to 1400 °C the weight of the SiCO sample is stable. From 1200 to 1400 °C β-SiC nanocrystals with dimensions in the range 1.5–3 nm precipitate in a $SiO_2$-based matrix. In the present study only selected samples were analyzed by X-ray diffraction to ensure that the actual samples follow the same, known evolution. Indeed, XRD patterns recorded on a SiCO sample doped with 1% Er and pyrolyzed at 1200 °C shows the presence of three broad peaks at $2\Theta \approx 35°$, 60° and 72° suggesting the presence of β-SiC-nc. The average crystallite size, as estimated by the Scherrer equation, is 1.5 nm (±10%).

Optical absorption spectra in the visible and near infrared (VIS-NIR) regions were measured at room temperature by a double beam spectrometer Cary 5000 Varian.

Photoluminescence measurements in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of $Er^{3+}$ ions (1400–1700 nm) were performed using a diode laser operating at 980 nm as the excitation sources and dispersing the luminescence light with a 320 mm single-grating monochromator with a resolution of 2 nm. The light was detected using or an InGaAs photodiode and lock-in technique.

## 4. Results and discussion

Luminescence of the $Er^{3+}$ ions present in the SiCO glasses were investigated as a function of the pyrolysis temperature.

Fig. 1 shows room-temperature photoluminescence spectra for the 1 mol% $Er^{3+}$ doped SiOC at different temperature. Luminescence from the excited $^4I_{13/2}$ state is observed in all the samples with a main emission peak at 1533 nm. The shape

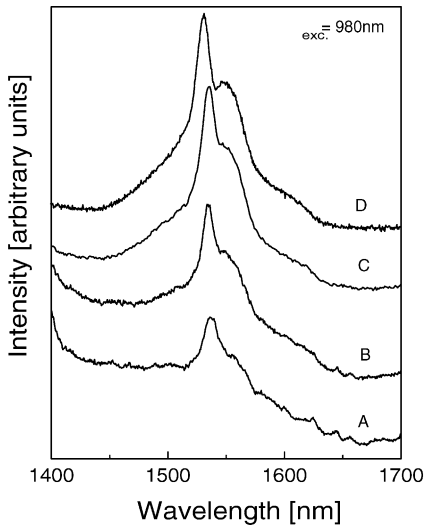


Fig. 1. Photoluminescence spectra relative to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the $Er^{3+}$ ions for the 1 mol% $Er^{3+}$ doped SiOC glass pyrolyzed at: (A) 800 °C, (B) 1000 °C, (C) 1200 °C and (D) 1300 °C for 1 h. The emission spectra were obtained using a diode laser operating at 980 nm as a pump beam.

of the emission spectra is characteristic of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ ions in amorphous environment. We can observe an enhancement of the intensity of the Er emission with the pyrolysis temperature. This evidence must be related to the reduction of the Si–H, C–H and O–H moieties with thermal treatment. Indeed, it is well known that the presence of Si–H, Si–C and C–H vibrational modes in the silica matrix results into a quenching of the luminescence by multiphonon mechanism. The spectrum of Fig. 1D, which corresponds to the sample treated at 1300 °C, exhibits a more defined Stark structure associated to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ ions. The thermal treatment leads to an enhancement of the luminescence associated to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of $Er^{3+}$ ions, that could partially depend on the role played by SiC nanocrystals. Infact, the thermal treatments above 1200 °C lead to the precipitation of nanosized β-SiC embedded into an amorphous $SiO_2$ matrix. Further measurements, such as excitation and fluorescence line narrowing spectra, are necessary to assess the role of SiC nanocrystals as Erbium luminescence sensitizer.

Fig. 2 reports the luminescence spectra of SiC/$SiO_2$ nanocomposites glasses doped with different Erbium content, ranging from 1 to 4 mol%, and annealed at 1200 °C. Luminescence from the excited $^4I_{13/2}$ state is observed in all the samples with a main emission peak at 1533 nm. A spectral bandwidth of 48 nm, measured at 3 dB from the maximum of the intensity, were observed for all the samples. The shape of the emission spectra and the spectral bandwidth do not change with Erbium concentration, showing that constant site-to-site inhomogeneities are present in the amorphous matrix, at least

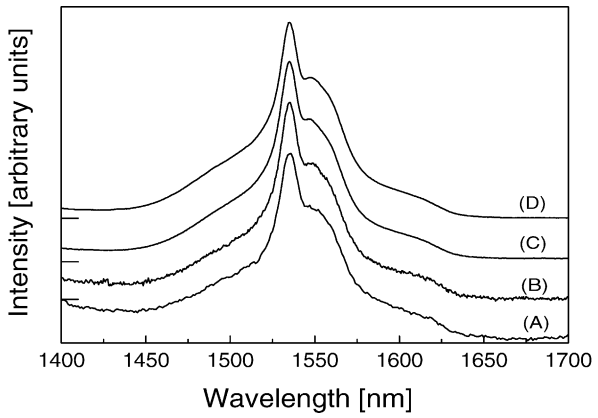


Fig. 2. Photoluminescence spectra relative to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the $Er^{3+}$ ions for the $Er^{3+}$ activated SiC/$SiO_2$ nanocomposite pyrolyzed at 1200 °C for 1 h and doped with: (A) 1 mol%, (B) 2 mol%, (C) 3 mol% and (D) 4 mol% $Er^{3+}$. The emission spectra were obtained using a diode laser operating at 980 nm as a pump beam.

for Er concentration up to 4 mol%. This effect suggests a flexibility of the SiCO network, which may accommodate $Er^{3+}$ contents without appreciable matrix strains.[20]

The spectral bandwidth of 48 nm of the emission bands is due to inhomogeneous and homogeneous broadening plus additional Stark splitting of the excited and ground states.[21] It is large enough for application in wavelength division multiplexed (WDM) signal amplifiers.[22] The luminescence spectra do not show evidence of crystalline environment for the $Er^{3+}$ ion, suggesting that, at least the majority of Erbium ions are accommodated in the glass.[23] No further

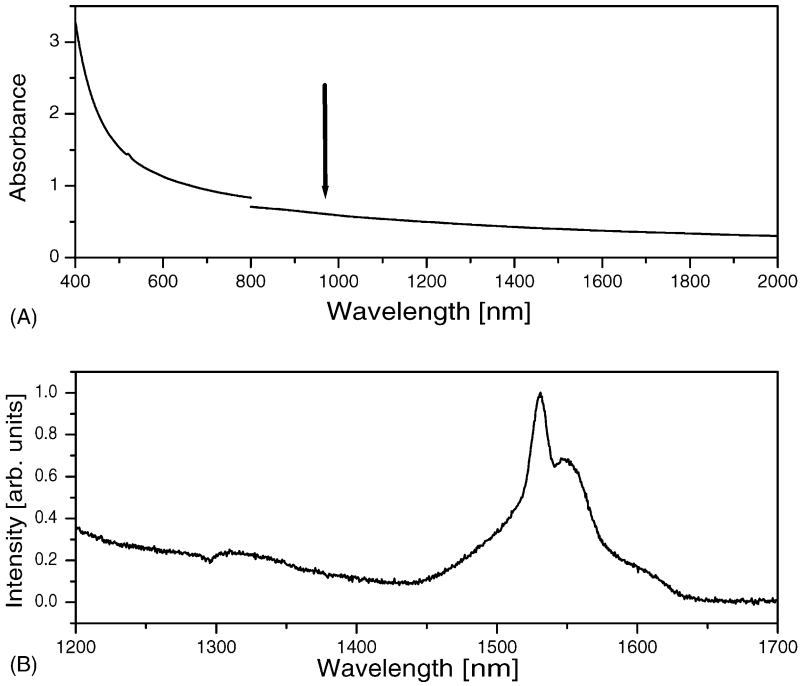


Fig. 3. (A) Optical absorption and (B) photoluminescence spectra for the $Er^{3+}$ activated SiC/$SiO_2$ nanocomposite doped with 1 mol% and submitted to thermal treatment at 1200 °C. The emission spectra were obtained using a diode laser operating at 980 nm as a pump beam.

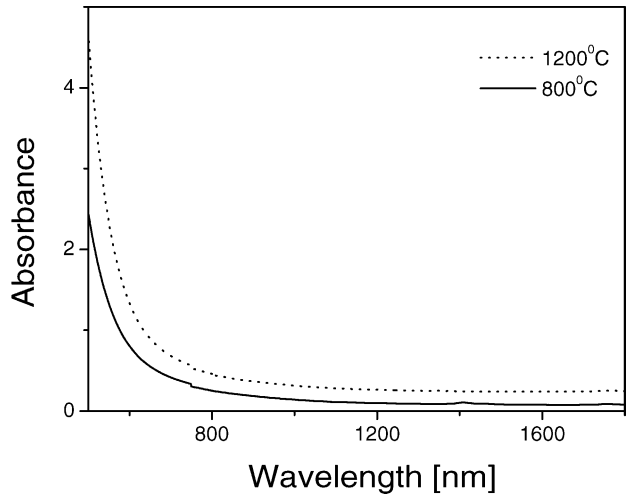


Fig. 4. Optical absorption spectra for the 1% $Er^{3+}$ activated $SiC/SiO_2$ nanocomposite submitted to thermal treatment at (A) 800 °C and (B) 1200 °C.

information is available, at this stage of the research on the $Er^{3+}$ ion repartition in possible different local environments. Further experiments, such as time-resolved size selection spectroscopy measurements, are necessary to obtain more information about the local symmetry around Erbium by a crystal field analysis.[14,20]

Fig. 3 shows (i) the optical absorption spectrum in the visible and near infrared regions and (ii) photoluminescence spectrum in the near infrared region, for the 1 mol% Er–$SiC/SiO_2$ nanocomposite, submitted to thermal treatment at 1200 °C. The arrow shows the excitation wavelength (980 nm) used to obtain the luminescence spectra shown in Figs. 1 and 2. It is seen that the UV edge shifts to longer wavelengths, in respect to pure silica glasses. The absorption spectrum is dominated by the matrix contribution with a long tail extending down to the NIR region. For this reason, the peaks attributed to the 4f intra-configurational transitions of the Erbium ions are not visible, except for a shoulder at abut 521 nm due to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition which is characterized by an high value of the absorption cross-section.[21] The UV edge shifts to longer wavelengths as increase the temperature at which the nanocomposites are submitted, resulting in a corresponding decrease in the electronic bandgap energy (Fig. 4).

## 5. Conclusions

Erbium activated $SiC/SiO_2$ nanocomposites doped with $Er^{3+}$ concentrations ranging from 1 to 4 mol% were prepared by pyrolysis of sol–gel precursors. Crack free, monolithic and transparent SiCO glass discs were obtained after pyrolysis at temperature in the range 800–1300 °C. Emission in the C-telecommunication band was observed at room temperature for all the samples upon continuous-wave excitation at 980 nm. A spectral bandwidth of 48 nm, enough large for WDM application, was observed for all the samples. The shape of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ luminescence band appears to be independent on the Erbium content, at least for $Er^{3+}$ concentration up to 4 mol%. This effect suggests that the SiCO network if flexible enough to accommodate $Er^{3+}$ without appreciable matrix strains. The luminescence spectra do not show evidence of crystalline environment for the $Er^{3+}$ ion, suggesting that, at least the majority of Erbium ions are accommodated in the glass.

The UV edge shifts to longer wavelengths as increase the annealing temperature resulting in a corresponding decrease in the electronic bandgap energy.

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