

Inverted Opal Luminescent Ce-Doped Silica Glasses

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Inverted opal Ce-doped silica glasses (Ce : Si molar ratio $1 \cdot 10^{-3}$) were prepared by a sol-gel method using opals of latex microspheres as templates. The rare earth is homogeneously dispersed in silica host matrix, as evidenced by the absence of segregated CeO₂, instead present in monolithic Ce-doped SG with the same cerium content. This suggests that the nanometric dimensions of bridges and junctions of the host matrix in the inverted opal structures favor the RE distribution avoiding the possible segregation of CeO₂.

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1. INTRODUCTION

Luminescent rare-earth (RE)-doped silica glass (SG) materials are employed in many applications for optical devices. In particular, Ce³⁺-doped SG is a promising material to be used as a scintillator for the detection of X-rays, γ -rays, or neutrons [1, 2] and tunable solid state lasers operating in the near-UV, violet, and blue regions [3, 4]. Notable properties of luminescent Ce³⁺ ions are the fast decay time and the high efficiency of the allowed 5d-4f transition in the UV-visible region.

SG hosts for luminescent centers are alternative to crystalline systems, owing to their attractive characteristics as low cost, flexible shape, and possible employment in fiber technology. A possible drawback is the presence of point defects and OH groups in the matrix, which cause an increased non-radiative deactivation rate through the creation of multiple vibrational quanta of the OH stretching vibration, lowering the energy transfer efficiency from the host glass to the emission centers [5]. In order to synthesize high-purity glasses, embedding controlled amounts of RE activator ions, the sol-gel technique can be used instead of conventional quenching of oxide melts [6–8]. In fact, according to this method, the precursor reactions and the thermal processes for glass densification occur at lower temperatures, in principle avoiding or lowering the probability of point defects in the glass.

A second drawback of RE-doped SG, which unfavorably affects the luminescence yield, is the ions aggregation due to the poor solubility of RE cations in the glass matrix. When the RE concentration increases, the interionic distance

becomes comparable to the critical distance, at which the radiative decay probability equals the energy transfer rate, leading to nonradiative processes [9]. Besides, in the case of Ce³⁺ doping, also the oxidation to nonluminescent Ce⁴⁺ can lead to the segregation of nanocrystalline CeO₂ in the glass matrix, causing significant luminescence quenching [8, 10].

In order to embed Ce³⁺ ions into the glass matrix, avoiding ion aggregation and CeO₂ segregation, codoping of SG with different heteroatoms was demonstrated to be a good tool to produce highly efficient optical materials [11, 12], creating a different solvation structure [13] and a preferential coordination of the codopant around RE ions. Our recent study on Ce-doped boro-(BSG), phospho-(PSG), and borophosphosilicate (BPSG) glasses demonstrated that the Ce³⁺ emission yield was enhanced in PSG and BPSG with respect to SG and BSG, because of the coordination of P=O groups. These are located in phosphoryl [O=PO_{3/2}], metaphosphate [O=PO_{2/2}O]⁻, and pyrophosphate [O=PO_{1/2}O₂]²⁻ units, linked to the silica network, and preferentially interact with Ce³⁺ ions, very probably hindering both CeO₂ segregation and the oxidation of isolated Ce³⁺ ions to Ce⁴⁺ [12].

In the frame of the research on new luminescent materials with novel and tunable optical properties, intensively pursued by industry and university laboratories, many efforts have been made in the field of the synthesis of porous materials [14–19] with different pore sizes and ordered nanoscale architectures, where RE luminescent centers are embedded into the matrix or grafted onto the pore walls. In this paper, we focused our attention on the porous and nanosized

host structures of SG inverted opals; a material built by nano-sized bridges and junctions around a regular and compact arrangement of air spheres. Many glasses and ceramics have been prepared as opal and inverted opals [20], in particular for their properties of photonic crystals with a luminescent probe inside the pore, or embedded in the matrix [18, 19].

In the present work, inverted opals of Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) were synthesized by a sol-gel method, using latex opals as templates. The aim was to study the influence of the ordered porosity and the nanoscale dimensions of the glass matrix on the stabilization and dispersion of the RE luminescent centers, aiming to improve the Ce^{3+} dispersion in the host glass matrix and to lower the oxidative CeO_2 segregation observed in SG [10, 11].

The structure of the inverted opal architecture and the possible occurrence of crystalline CeO_2 phase were investigated by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Electron paramagnetic resonance (EPR) was used to get information about the environment of paramagnetic Ce^{3+} ions embedded in glass. Finally, the luminescence properties were verified by measuring the emission decay curve of the Ce^{3+} 4d-5f transition.

2. EXPERIMENTAL

The colloidal suspension of polystyrene latex microspheres (350 nm diameter) in water (2.5 wt%) was from Alfa Aesar. Polystyrene opal was first prepared by centrifugation (3 h, 2000 rpm) of the colloidal microsphere aqueous suspensions. After removal of the surfactant solvent, the opal was dried at 308 K for 24 h, then placed in a vial and further dried in vacuum (10^{-1} torr) at room temperature for 30–60 min.

Inverted opal Ce-doped SiO_2 was obtained by drop-wise impregnation of the polystyrene template under a dry N_2 atmosphere with the minimum amount of the solution of tetraethylortosilicate, TEOS, (99.999% Aldrich); acetic acid, CH_3COOH (99.99%, Aldrich); and millQ water containing the suitable amount of $Ce(NO_3)_3 \cdot 6H_2O$. TEOS : CH_3COOH : H_2O molar ratio was 1 : 4 : 5; Ce : Si molar ratio was $1 \cdot 10^{-3}$. After impregnation, samples were kept in a thermostatic chamber at 308 K for 24 h in order to complete the sol-gel transition and, finally, they were heated ($10^\circ C/h$) at 1073 K for 4 h in flowing O_2 ($30 \text{ cm}^3/\text{min}$).

The sample morphology was analyzed by SEM, using a Vega TS5136 XM Tescan microscope in a high-vacuum configuration. The electron beam excitation was 30 kV at a beam current of 25 pA and the working distance was 12 nm. In this configuration the beam spot was 38 nm. Previous to the SEM analysis, samples were gold-sputtered.

HRTEM analysis was performed at 300 kV using a Jeol 3010 apparatus with a high-resolution pole piece (0.17 nm point-to-point resolution), equipped with a Gatan slowscan 794 CCD camera. Elemental composition was determined by an Oxford Instruments EDS microanalysis detector (Mod. 6636). Glass samples were ground in an agate mortar and the resulting fine powder suspended in isopropanol. A $5 \mu\text{L}$ drop of this suspension was deposited on a holey carbon film supported on 3 mm copper grid for TEM investigation.

Ce^{3+} EPR spectra were recorded at 4.2 K on inverted opal samples by a conventional Bruker EMX spectrometer operating at the X band frequency, equipped with an Oxford cryostat operating in the $4.2 \div 373$ K temperature range. The g values were measured by using diphenylpicrylhydrazyl (DPPH) as standard.

The luminescence decay curves in the UV region were measured at room temperature exciting at 290 nm with the second harmonic of a dye laser (using Rhodamine 6G as the dye) pumped with the second harmonic (532 nm) of a pulsed Nd-YAG laser. A fiber optic probe was employed to collect the emission. The signal was analyzed by a half-meter monochromator equipped with a 150 lines/mm grating. A GaAs photomultiplier and a digital oscilloscope were used to measure the emission decay curves. The decay times were obtained from the emission decay curves using a deconvolution procedure which takes into account the shape and the duration of the excitation pulse.

3. RESULTS AND DISCUSSION

The micro-structural characterization of inverted opal Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) was performed by SEM and HRTEM. Figure 1 shows representative SEM and HRTEM micrographs obtained for opals of 350 nm latex microspheres. The figure clearly shows the structure of bridges and junctions of amorphous silica surrounding a regular array of circa 280 nm diameter hollow spheres, about 20% smaller than that of the template spheres, due to the shrinkage of the glass matrix. The SEM pictures show the large extension and homogeneity of the sample architecture (Figure 1(a)). HRTEM analysis demonstrates that, at the conditions of the preparation procedure, the silica matrix is amorphous and no undesired segregation of nanocrystalline CeO_2 occurred in inverted opal Ce-doped SG samples (Figure 1(b)). The latter behavior is different from that of monolithic Ce-doped SG prepared by sol-gel method with the same RE content [10, 11], even if it cannot be excluded that CeO_2 particles too small to be detected are present. As the elemental analyses demonstrated that no cerium was lost during sample preparation, it appears that the tendency of CeO_2 to segregate in the nanosized bridges and junctions of the inverted opal SG matrix is inhibited, favoring RE dispersion.

The EPR analysis of the paramagnetic Ce^{3+} centers was performed at 4.2 K. In fact, no resonance lines were detected above 20 K, due to the rapid relaxation time T_1 which broadens the line width (line width $\propto T_1^{-1}$), according to the behavior of most lanthanides [21] with the exception of S-state ions with a half-filled subshell 4f [7]. EPR spectra of inverted opal Ce-doped SG showed a complex signal spanning about 10^4 G and consisting of several overlapped broad resonances (Figure 2(a)).

The assignment of particular sets of lines to well-defined Ce^{3+} centers is not easy, as the wave function of the $^2F_{5/2}$ ground state results, for a specific crystal field symmetry, from the linear combination of the $|M_j = \pm 1/2\rangle$, $|M_j = \pm 3/2\rangle$, and $|M_j = \pm 5/2\rangle$ eigenfunctions [22]. Thus the

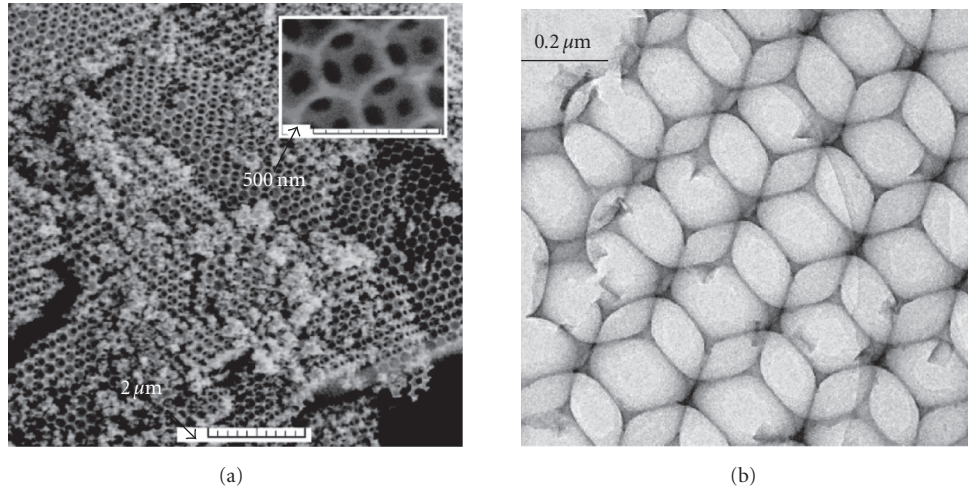


FIGURE 1: (a) SEM and (b) HRTEM micrographs of Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) inverted opals.

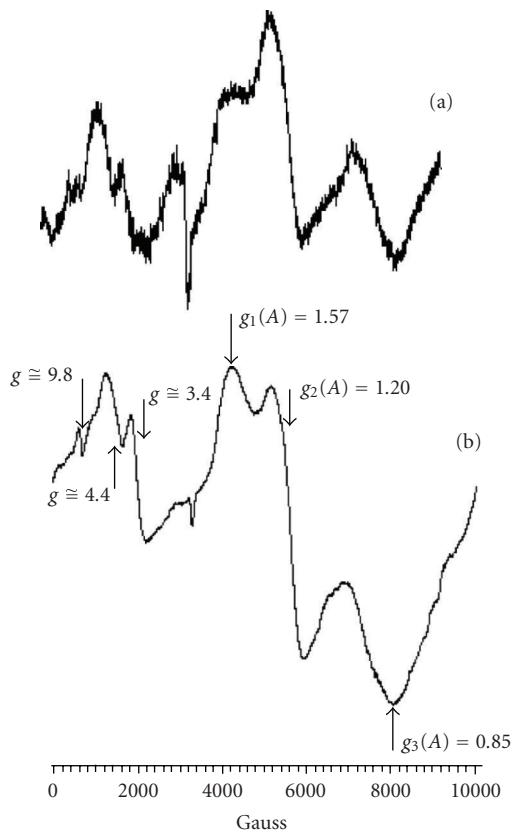


FIGURE 2: EPR spectra recorded at 4.2 K of (a) Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) inverted opals and (b) monolithic Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) prepared by sol-gel method [11].

experimental g -tensors values for Ce^{3+} can vary in a wide range of values [23–26], in particular in amorphous hosts where the paramagnetic centers experience several and differently distorted symmetry fields. In a previous paper [11]

on monolithic Ce-doped SG prepared by sol-gel method, we suggested that the resonances at $g_1 = 1.57$, $g_2 = 1.20$, $g_3 = 0.85$ could be attributed to a single species in orthorhombic symmetry (species A in Figure 2), as g values are very similar to those reported by Yamaga et al. [23] for a Ce-doped LiCaAlF_6 single crystal. Besides, the weaker overlapped lines at low magnetic field, ranging from $g \sim 10.5$ to $g \sim 3$, were due to different Ce^{3+} species [11] and in particular the values $g \sim 3.4$ and $g \sim 4.4$ are reminiscent of the g_{zz} components reported by Misra et al. [24, 25] for Ce^{3+} ions in the orthorhombic crystal field of $\text{CeBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{CeBa}_2\text{Cu}_4\text{O}_8$, the related g_{xx} and g_{yy} being covered by the stronger lines of signal A. It is interesting to note that the EPR signal due to Ce^{3+} ions in inverted opal SG is the same as that in monolithic SG, indicating the same environment of RE in the glass matrix.

The luminescence properties of the inverted opal Ce-doped SG (Ce : Si = $1 \cdot 10^{-3}$ molar ratio) were studied by measuring the emission decay curve at room temperature of the Ce^{3+} allowed 4d-5f transition ($\lambda_{\text{exc}} = 290 \text{ nm}$; $\lambda_{\text{em}} = 415 \text{ nm}$). The emission decay time (τ) obtained from the emission decay curve, shown in the semilog plot of Figure 3, using a deconvolution procedure, is $47 \pm 2 \text{ ns}$. This value was very similar to that reported for Ce^{3+} in silica glass [27] and that found for monolithic Ce-doped SG prepared by sol-gel method [11]. This confirms that the observed luminescence is really due to Ce^{3+} centers and indicates that the environment of Ce^{3+} ions is similar in both inverted opal and monolithic host matrices, as suggested by EPR investigation.

4. CONCLUDING REMARKS

Inverted opal Ce-doped SG (Ce : Si molar ratio $1 \cdot 10^{-3}$) was prepared by a sol-gel method using a latex opal as template, which allowed a single-step introduction of the rare earth in the silica matrix.

Morphological and structural characterizations showed the absence of undesired segregation of CeO_2 , which affected

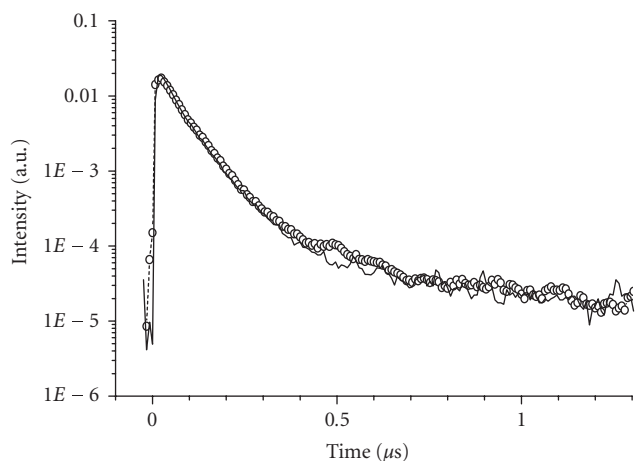


FIGURE 3: Experimental (solid line) and simulated (circles) emission decay curves at RT of Ce-doped SG (Ce : Si = $1 \cdot 10^{-3}$ molar ratio) inverted opals ($\lambda_{\text{exc}} = 290$ nm; $\lambda_{\text{em}} = 415$ nm).

monolithic Ce-doped SG with the same RE content, indicating a homogeneous dispersion of RE in the matrix. This suggests that the nanometric dimensions of the bridges and junctions, which constitute the architecture of the inverted opal host matrix, favor the RE distribution avoiding the possible aggregation of CeO_2 .

The silica matrix environment of the luminescent Ce^{3+} centers does not significantly change in the inverted opal structure with respect to monolithic samples.

REFERENCES

- [1] M. Nikl, K. Nitsch, E. Mihokova, et al., "Efficient radioluminescence of the Ce^{3+} -doped Na-Gd phosphate glasses," *Applied Physics Letters*, vol. 77, no. 14, pp. 2159–2161, 2000.
- [2] S. Baccaro, R. Dall'Igna, P. Fabeni, et al., " Ce^{3+} or Tb^{3+} -doped phosphate and silicate scintillating glasses," *Journal of Luminescence*, vol. 87, pp. 673–675, 2000.
- [3] T. Murata, M. Sato, H. Yoshida, and K. Morinaga, "Compositional dependence of ultraviolet fluorescence intensity of Ce^{3+} in silicate, borate, and phosphate glasses," *Journal of Non-Crystalline Solids*, vol. 351, no. 4, pp. 312–316, 2005.
- [4] M. Laroche, S. Girard, R. Moncorgé, M. Bettinelli, R. Abdulsabirov, and V. Semashko, "Beneficial effect of Lu^{3+} and Yb^{3+} ions in UV laser materials," *Optical Materials*, vol. 22, no. 2, pp. 147–154, 2003.
- [5] E. Auffray, D. Bouttet, I. Dafinei, et al., "Cerium doped heavy metal fluoride glasses, a possible alternative for electromagnetic calorimetry," *Nuclear Instruments and Methods in Physics Research, Section A*, vol. 380, no. 3, pp. 524–536, 1996.
- [6] G. E. Malashkevich, I. M. Melnichenko, E. N. Poddenezhny, and A. A. Boiko, "New optical centers of triply charged cerium ions in silica gel-glasses saturated with hydrogen," *Journal of Non-Crystalline Solids*, vol. 260, no. 1-2, pp. 141–146, 1999.
- [7] K. Itoh, N. Kamata, T. Shimazu, C. Satoh, K. Tonooka, and K. Yamada, "Improved emission characteristics of Tb^{3+} -doped sol-gel glasses by utilizing high solubility of terbium nitrate," *Journal of Luminescence*, vol. 87–89, pp. 676–678, 2000.
- [8] A. Vedda, A. Baraldi, C. Canevali, et al., "Optical properties of Ce^{3+} -doped sol-gel silicate glasses," *Nuclear Instruments and Methods in Physics Research, Section A*, vol. 486, no. 1-2, pp. 259–263, 2002.
- [9] G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer, Berlin, Germany, 1994.
- [10] D. Di Martino, A. Vedda, G. Angella, et al., "Evidences of rare earth ion aggregates in a sol-gel silica matrix: the case of cerium and gadolinium," *Chemistry of Materials*, vol. 16, no. 17, pp. 3352–3356, 2004.
- [11] C. Canevali, M. Mattoni, F. Morazzoni, et al., "Stability of luminescent trivalent cerium in silica host glasses modified by boron and phosphorus," *Journal of the American Chemical Society*, vol. 127, no. 42, pp. 14681–14691, 2005.
- [12] A. Saitoh, S. Matsuishi, M. Oto, T. Miura, M. Hirano, and H. Hosono, "Elucidation of coordination structure around Ce^{3+} in doped SiO_2 glasses using pulsed electron paramagnetic resonance: effect of phosphorus, boron, and phosphorus-boron codoping," *Physical Review B*, vol. 72, no. 21, Article ID 212101, 2005.
- [13] K. Arai, H. Namikawa, Y. Ishii, H. Imai, H. Hosono, and Y. Abe, "Nature of doping into pure silica glass by plasma torch CVD," *Journal of Non-Crystalline Solids*, vol. 95–96, pp. 609–616, 1987.
- [14] T. Jüstel, H. Nikol, and C. Ronda, "New developments in the field of luminescent materials for lighting and displays," *Angewandte Chemie - International Edition*, vol. 37, no. 22, pp. 3084–3103, 1998.
- [15] J. Rocha and L. D. Carlos, "Microporous materials containing lanthanide metals," *Current Opinion in Solid State and Materials Science*, vol. 7, no. 3, pp. 199–205, 2003.
- [16] B. J. Scott, G. Wirnsberger, and G. D. Stucky, "Mesoporous and mesostructured materials for optical applications," *Chemistry of Materials*, vol. 13, no. 10, pp. 3140–3150, 2001.
- [17] J. Sauer, F. Marlow, B. Spliethoff, and F. Schüth, "Rare earth oxide coating of the walls of SBA-15," *Chemistry of Materials*, vol. 14, no. 1, pp. 217–224, 2002.
- [18] M. J. A. de Dood, L. H. Slooff, A. Polman, A. Moroz, and A. van Blaaderen, "Modified spontaneous emission in erbium-doped SiO_2 spherical colloids," *Applied Physics Letters*, vol. 79, no. 22, pp. 3585–3587, 2001.
- [19] S. V. Gaponenko, V. N. Bogomolov, E. P. Petrov, et al., "Spontaneous emission of dye molecules, semiconductor nanocrystals, and rare-earth ions in opal-based photonic crystals," *Journal of Lightwave Technology*, vol. 17, no. 11, pp. 2128–2137, 1999.
- [20] Y. Xia, B. Gates, Y. Yin, and Y. Lu, "Monodispersed colloidal spheres: old materials with new applications," *Advanced Materials*, vol. 12, no. 10, pp. 693–713, 2000.
- [21] J. M. Baker, "EPR and ENDOR in the lanthanides," in *Electron Spin Resonance*, vol. 13B, chapter 3, The Royal Society of Chemistry, Cambridge, UK, 1993.
- [22] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Metal Ions*, Clarendon Press, Oxford, UK, 1970.
- [23] M. Yamaga, M. Honda, K. Shimamura, T. Fukuda, and T. Yosida, "Electron spin-resonance study on Ce^{3+} in BaLiF_3 ," *Journal of Physics Condensed Matter*, vol. 12, no. 27, pp. 5917–5928, 2000.
- [24] S. K. Misra and S. Isber, "EPR of the Kramers ions Er^{3+} , Nd^{3+} , Yb^{3+} and Ce^{3+} in $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ single crystals: study of hyperfine transitions," *Physica B*, vol. 253, no. 1-2, pp. 111–122, 1998.
- [25] S. K. Misra, Y. Chang, and J. Felsteiner, "A calculation of effective g-tensor values for R^{3+} ions in $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and

- $\text{RBa}_2\text{Cu}_4\text{O}_8$ (R = Rare Earth): low-temperature ordering of Rare-Earth moments," *Journal of Physics and Chemistry of Solids*, vol. 58, no. 1, pp. 1–11, 1997.
- [26] M. Yamaga, M. Honda, N. Kawamata, T. Fujita, K. Shimamura, and T. Fukuda, "Site symmetry and crystal field of Ce^{3+} luminescent centres in KMgF_3 ," *Journal of Physics Condensed Matter*, vol. 13, no. 14, pp. 3461–3473, 2001.
- [27] M. Nikl, K. Nitsch, E. Mihokova, et al., "Efficient radioluminescence of the Ce^{3+} -doped Na-Gd phosphate glasses," *Applied Physics Letters*, vol. 77, no. 14, pp. 2159–2161, 2000.

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