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Short communication

Defect-induced luminescence in sol–gel silica samples doped with Co(II) at different concentrations

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Abstract

The defect-induced luminescence properties of silica samples prepared by the sol–gel method and doped with Co(II) are reported. Silica monoliths doped with different concentrations of Co(II) were laser irradiated (He–Ne 632.8 nm) producing fluorescence. However, this fluorescence is exponentially reduced with the irradiation time, to practically disappear. The rate the fluorescence decays can be well modeled with a double exponential function of the irradiation time, containing two different relaxation times; a baseline is also required to take into account some residual fluorescence. The characteristic times involved in this luminescence quenching process are in the range of seconds. This luminescence suppression can be associated to the local heating produced by the laser irradiation when focused in a small area (2 μm in diameter) on the sample. This heating process reduces physical (grain boundaries, surface states) and chemical (oxygen vacancies produced by the dopant) defects in the sample.

Keywords: Fluorescence; Luminescence quenching; Silica; Cobalt; Dopant; Sol–gel process

1. Introduction

The sol–gel technology has allowed to design inorganic materials with specific morphologies by controlling the chemistry and structure [1–5]; additionally, this technique allows doping materials with a large list of organic and inorganic compounds, thus increasing substantially the range of applications in many fields of science and technology, from catalytic supports, to doped thin films of high purity [6–9] for specific applications.

It is well known that the sol–gel method produces highly porous materials, i.e. materials with large internal and external surfaces. This high surface area is partially responsible for the presence of a large number of surface states that affects the optical response of these materials [10–12]. Additionally, the presence of dopants in sol–gel materials produces oxygen vacancies and concomitantly, internal shear deformations in the oxygen sub-lattice due to the difference in oxidation states between the cations in the matrix and the dopant [13,14]. It is also known that the presence of dopants allows obtaining high temperature phases at relative lower temperatures [15]. It is generally accepted that the mechanism associated with this phase stabilization is the generation of metastable states in the system due to the presence of these oxygen vacancies. Oxygen atoms in doped sol–gel materials become quite mobile when the temperature is increased, hoping through the vacant sites and displaying substantial ionic conductivity. This characteristic is technologically important due to its wide number of applications: oxygen sensors, electrochemical oxygen pumps, etc. [16–18].

The oldest, and possibly the most important, type of sol–gel material prepared is silica, where the silicon atom coordinates four oxygens producing tetrahedrons; then, an amorphous silica material is a continuous three-dimensional network of corner-sharing SiO_4 tetrahedral units [19]. As mentioned, this material has been doped with a large list of compounds, including cobalt [20,21]. All properties of the cobalt-doped silica system depends on the spatial distribution of the cobalt atoms into the silica matrix; it can be uniformly distributed into the matrix forming a solid solution, or can segregate in clusters to produce a composite or nano-composite depending on the clusters size [22,23]. The formation of a solid solution depends on several conditions: (a) the ratio of the ionic radii of both cations should not be larger than 1.15. In this particular case the ratio of the ionic radii is

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1.8, which is significantly larger than the limiting value; this means that the distortion produced by the cobalt atoms into the lattice is considerably high, reducing the possibility to obtain a solid solution. (b) The similarity between crystalline structures for silica is hexagonal, for quartz, monoclinic for tridymite and a zincblende-like structure for crystobalite, while CoO has a FCC structure; the difference between crystalline structures represents also a problem to produce a solid solution. (c) The coordination sphere of the cations Si has only a coordination of 4, while Co has coordination of 4, 5, 6 and 8; in this sense the coordination may not be a problem for the formation of a solid solution. (d) The electronegativity of the cations should be similar to each other; in this case the electronegativities are similar: 1.90 for Si and 1.88 for Co [24,25]. As can be seen, some conditions are fulfilled while others are not, meaning that the formation of a solid solution is not straightforward and can be compromised when some external parameters (like temperature) are changed. It is known that in the CoO case, a fraction of the Co^{2+} divalent cations (around 1%) are oxidized to the trivalent state Co^{3+}, resulting in a cation deficiency and consequently in a change in the oxygen deficiency [26].

In this work, the luminescence properties of SiO$_2$ samples doped with different amounts of Co(II) are reported. When the samples are continuously irradiated with the laser light, the fluorescence signal decreases until it reaches a minimum value (residual luminescence) that depends on the cobalt concentration [27]. The light source for the irradiation was a He–Ne laser with energy of 1.96 eV; this value is well below the SiO$_2$ bandgap (around 9 eV for amorphous SiO$_2$). The presence of cobalt atoms into the silica lattice has several contributions to the fluorescent response of the material: as mentioned, it can favor the phase transition from amorphous to quartz, tridymite or crystobalite induced by the energy absorption during the laser irradiation; it is known that cobalt atoms are excellent light absorbers, producing an increment in the local temperature of the sample [28]. Additionally, the solubility properties of Co into the silica matrix are concentration and temperature dependent. The presence of cobalt atoms produces also defects (surface states) that modify the optical response of the material [29].

2. Experimental

Samples of silica doped with different concentrations of Co^{2+} (0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol%) were prepared by the acid hydrolysis of tetraethylorthosilicate (TEOS) (Aldrich, USA) using acetic acid as a catalyst. One mole of TEOS was mixed with 2 mol of glacial acetic acid (Baker Co.) and with 4 mol of 2-propanol (Baker Co.) in an ice bath; then the mixture was heated to room temperature. The hydrolysis reaction was carried out by adding 2 mol of water mixed with 4 mol of 2-propanol and the corresponding amount of cobalt nitrate (Baker Co.) according to the desired concentration. The gelation process takes place in a few hours producing monoliths. The samples were dried by heating them at 80 °C in air for 48 h and stored at room conditions for two months. A pure silica sample was also prepared as reference.

X-ray diffractograms were obtained using a Rigaku D/max-2100 diffractometer with Cu Kα1 radiation and a thin film attachment; the 2θ angle was varied from 10° to 80°. The Raman spectra, showing the photoluminescence (PL) signal, were obtained at room temperature using a Dilor system model Labram; the Raman shift was measured from 200 to 3000 cm^{-1} with respect to the He–Ne laser ($\lambda = 632.8$ nm) utilized to excite the samples. A 50× microscope objective was used in the measurements producing a *ca.* 2 μm diameter laser spot on the sample. A series of Raman spectra were obtained as a function of time during 30 min of continuous irradiation: every 15 s during the first min; every 30 s during the next 2 min; every min for the next min; every 2 min for the next 6 min and every 5 min during 20 min. After this irradiation time, the laser was blocked because the PL signals remain practically constant (the residual luminescence). From these spectra, the fluorescence was analyzed

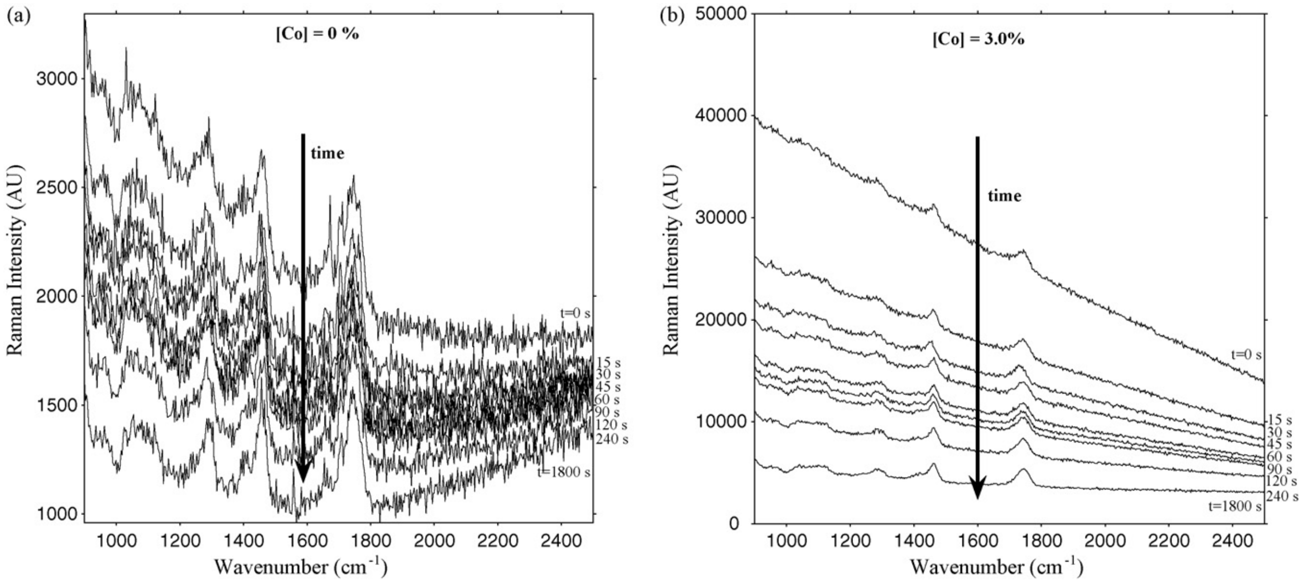

Fig. 1. Set of micro-Raman spectra taken at different irradiation times for: (a) pure silica and (b) silica doped with 3.0% of Co.