



Structural and spectroscopic characterization of poly(styrene sulfonate) films doped with neodymium ions

Marcelo C. Silva^a, A.S.S. de Camargo^b, L.A.O. Nunes^b, R.A. Silva^c, Alexandre Marletta^{c,*}

^aDepartamento de Ciências da Natureza, Universidade Federal do Acre, 69915-900 Rio Branco, AC, Brazil

^bInstituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13660-970 São Carlos, SP, Brazil

^cInstituto de Física, Universidade Federal de Uberlândia, 38400-902 Uberlândia, MG, Brazil

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ABSTRACT

This work reports the structural and spectroscopy characterization of poly(styrene sulfonate) (PSS) films doped with neodymium (Nd) ions. Nd–PSS films were processed using the acid of poly(styrene sulfonate) – H–PSS and neodymium nitrate – Nd(NO₃)₃; the maximum incorporation of Nd ions in the polymeric matrix was equal 19.3%. The absorption in the UV–Vis–NIR spectral region presents typical electronic transitions of Nd³⁺ ions, with well resolved peaks. The infrared spectra present the transition bands of PSS with characteristic line shape broadening, and the presence of vibrational modes of N–O groups in the range of 1400–720 cm⁻¹, prove the permanence of Nd(NO₃)_x, with x = 1, 2 and/or 3, in the H–PSS matrix. UV–Vis site selective photoluminescence data indicate that the incorporation of Nd³⁺ introduces a blue shift in PSS emission (325–800 nm), decreasing the interaction between adjacent PSS lateral groups (aromatic rings). Nd³⁺ reabsorption and energy transfer effects between the PSS matrix and Nd³⁺ were also observed. The IR emission of Nd–PSS films at 1076 nm (⁴F_{3/2} → ⁴I_{11/2}) present constant efficiency, independent on Nd³⁺ concentration. The Judd–Ofelt theory was employed to analyze radiative properties. The excitation spectra prove the energy transfer between the polymeric matrix and Nd³⁺. Complex impedance data was used to probe relaxation processes during the charge transport within the polymeric matrix.

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1. Introduction

In order to meet the challenges of the constantly growing optical technology market, increasing attention has been devoted to the development of novel materials with applications in a variety of photonic devices [1–7]. Among them, rare-earth ion doped polymeric matrixes are very attractive candidates due to their flexible and low cost synthesis and processing. These features make them ideally suitable for applications in electroluminescent devices [4], integrated waveguides [5], color displays [6], and polymeric optical fibers [7]. However, one limitation normally encountered in the preparation of such materials, lies in the difficulty found in dissolving the rare-earth ions in commercial polymer matrixes. Hence, various synthesis routes have been proposed [2,8–10], to contour this drawback. Recently we have been working on the development of a successful, simplified synthesis route, for the obtainment of neodymium (Nd³⁺) doped poly(styrene sulfonate) (PSS) films [11]. One large advantage of this method is that it allows a significant increase in the concentration range of doping ions, in the precursor solution. Thus, this new proposition opens up the

perspective of using other rare-earth doped polyelectrolyte films, with increased efficiency, as materials for photonic device applications.

The interest in doping these materials with rare-earth ions lies in the fact that they present intraconfigurational f–f electronic transitions with high absorption and emission cross sections. The 4f shell, to which some of the most important ions (Nd³⁺, Er³⁺, Yb³⁺) belong, is shielded by the outer 5s and 5d shells and as a consequence, the spectroscopic properties of these ions are not drastically influenced by the ligand field [12]. Even so, they can play the role of structural probes very effectively. The trivalent neodymium is by far the most studied ion, because of its highly efficient near-infrared laser emission around 1060 nm (⁴F_{3/2} → ⁴I_{13/2} transition), with applications in several areas from spectroscopy to medicine. One remarkable advantage of this emission is that it can be efficiently pumped by high power and low cost 808 nm diode lasers, at the high absorption cross section levels ²H_{9/2} and ⁴F_{5/2}. Since these levels are close in energy to the emitting ⁴F_{3/2} (~1200 cm⁻¹) excitation of the latter is achieved by relaxation. From these premises, it becomes evident that to characterize the potential of Nd³⁺ doped materials, it is indispensable to carry out a detailed spectroscopic investigation. In that respect, the rare-earth concentration, distribution in the matrix, and ligand field

* Corresponding author. Tel.: +55 34 32394190; fax: +55 34 32294106.
E-mail address: marletta@ufu.br (A. Marletta).

are important parameters to be investigated, because they influence radiative and non-radiative properties, including the probabilities of ion–ion and ion–matrix energy transfers.

In this work, we report the new synthesis route to obtain poly(styrene sulfonate) (PSS) films doped with Nd^{3+} ions, and their detailed structural characterization. The results are discussed in terms of the advantages of the proposed experimental procedure to yield polymeric films with very interesting radiative properties (also analyzed by the well known Judd–Ofelt theory) [13], that are promising candidates for photonic applications.

2. Experimental

The casting films of neodymium–poly(styrene sulfonate) (Nd–PSS) were processed using aqueous solutions of acid poly(styrene sulfonate) (H–PSS). Fig. 1(a) displays the chemical exchange reaction of the commercial polymer sodium poly(styrene sulfonate) (Aldrich – $M_w = 70000$) and Amberlite IR-120. Nd–PSS films were obtained by mixing H–PSS and $\text{Nd}(\text{NO}_3)_3$ (neodymium nitrate) aqueous solutions in a constant volume ratio of 6:1. The concentrations of $\text{Nd}(\text{NO}_3)_3$ were 0.25, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5 and 2.0 mol/L and the concentration of H–PSS was 0.15 mol/L. Fig. 1(b) presents the chemical scheme of 3H^+ and Nd^{3+} ionic ex-

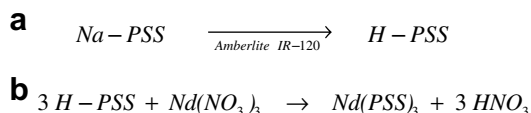


Fig. 1. Synthesis route of (a) polystyrene acid H–PSS and (b) Nd–PSS film.

change. After letting the precursor solution of H–PSS and $\text{Nd}(\text{NO}_3)_3$ rest overnight at 5 °C, the liquid phase was removed and the films were dried in vacuum. The samples labels are presented in Table 1. Using 1.5 ml of H–PSS and 0.9 ml of $\text{Nd}(\text{NO}_3)_3$, the films thickness is approximately 200 μm using a micrometer. Similar procedure was adopted in Ref. [11].

Absorption measurements in the UV–Vis–NIR spectral range were performed using a DT-Mini light source and a USB2000 spectrometer as detector. In the infrared, a NEXUS 470 FTIR spectrophotometer was used in reflectance mode. The UV–Vis photoluminescence measurements were carried out exciting the samples at 457.8 and 514.5 nm with an Ar^+ laser and detecting with a USB2000 spectrometer. Temperature effects were investigated using a Janis cryostat in a closed He circuit at 10 and 300 K. Near-infrared emissions were measured at 300 K using as excitation source a diode laser at 800 nm, a simple monochromator (0.3 m), an InGaAs detector, and a lock-in amplifier. Impedance spectroscopy was carried out using a Solartron – Impedance/Gain Phase Analyser; the frequency-dependent dielectric properties were measured from 10 Hz to 10 MHz. The samples were placed in the planar and parallel geometry with aluminum electrodes.

3. Results

In order to verify the changes in the absorption line shapes and spectral peak positions of neodymium 4f–4f transitions, as function of the salt composition, we measured the spectra presented in Fig. 2(a). The curves of Nd07 film, NdCl_3 (0.02 mol/L) and $\text{Nd}(\text{NO}_3)_3$ (0.02 mol/L) were normalized to unit at 795 nm. For comparison, the spectrum of H–PSS (0.003 mol/L) is also presented. In this case, it can be seen that above 300 nm the H–PSS solution is totally transparent for Nd^{3+} electronic transitions and the band at

Table 1
Samples labels

Label	H–PSS	Nd025	Nd03	Nd05	Nd07	Nd09	Nd11	Nd13	Nd15	Nd20
$\text{Nd}(\text{NO}_3)_3$ (mol/L)	–	0.25	0.3	0.5	0.7	0.9	1.1	1.3	1.5	2.0

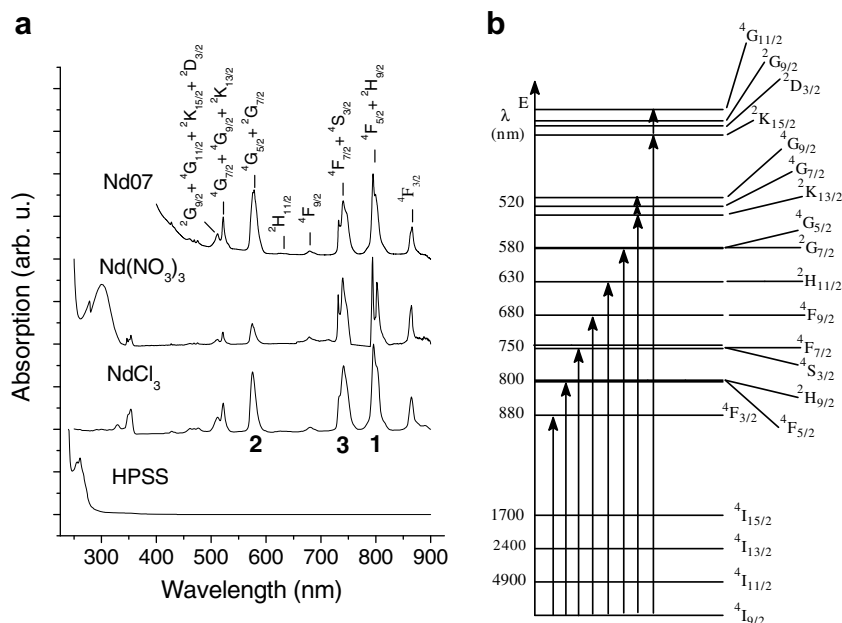


Fig. 2. (a) Absorption spectra of aqueous solutions of H–PSS (0.003 mol/L), NdCl_3 (0.02 mol/L), $\text{Nd}(\text{NO}_3)_3$ (0.02 mol/L); and the Nd07 film. (b) Transitions energy diagram for Nd^{3+} .

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