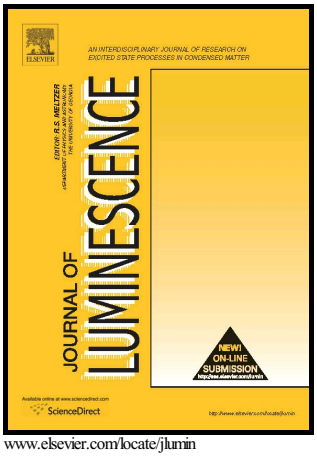

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PII: S0022-2313(17)32078-1
DOI: https://doi.org/10.1016/j.jlumin.2018.05.009
Reference: LUMIN15591

To appear in: *Journal of Luminescence*

Received date: 1 December 2017
Revised date: 19 March 2018
Accepted date: 4 May 2018

Cite this article as: G.A.S. Flizikowski, V.S. Zanuto, A. Novatski, L.A.O. Nunes, L.C. Malacarne, M.L. Baesso and N.G.C. Astrath, Upconversion luminescence and hypersensitive transitions of Pr3+–doped calcium aluminosilicate glasses, *Journal of Luminescence,* https://doi.org/10.1016/j.jlumin.2018.05.009

Upconversion luminescence and hypersensitive transitions of Pr^{3+}–doped calcium aluminosilicate glasses

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Abstract

We present a detailed spectroscopic study of photoluminescence in calcium aluminosilicate glasses doped with different concentrations of Pr^{3+} (0.2, 0.5, 1.0 and 2.0 wt.%). Optical transitions for the levels $^3H_4 \rightarrow {}^3P_{0,\,1,\,2}$; $^1I_6$; $^1D_2$; $^1G_4$; $^3F_{2,\,3,\,4}$ and $^3H_6$ have been observed using UV–Vis–NIR spectroscopy at room temperature. Emissions from levels $^3P_0$ and $^1D_2$ were detected and curves deviate from exponential behavior. Upconversion to UV was also observed when the samples were excited in the ^3P_j level, populating 4f5d upper level — via energy transfer upconversion and/or excited state absorption — which decays emitting UV light. In addition, the unusual variation of the peak intensities of transitions $^3P_0 \rightarrow {}^3F_2$ and $^3P_0 \rightarrow {}^3F_4$ suggests they are hypersensitive, although the $^3P_0 \rightarrow {}^3F_4$ electronic transition does not entirely obey all the classic selection rules.

Keywords: Upconversion, Praseodymium, Hypersensitive, Aluminosilicate, Non-exponential decay

1. Introduction

Calcium aluminosilicate glasses (CAS) have been extensively studied considering a number of applications for presenting appropriate physical properties such as high thermal conductivity, good mechanical strength and elevated transition temperature, besides transparency extending up to about 5 μm [1]. Several investigations have reported the effects of the composition of the glass on the physical properties [2, 3], as well as spectroscopic features when CAS is doped with rare-earth ions. As rare-earth host, CAS glasses are potential candidates for application in optical devices such as tunable white light system [4, 5] and solid state lasers [3, 6, 7].

Among rare-earth ions, trivalent praseodymium ion (Pr^{3+}) has been widely used for doping optical materials due to a broad infrared emission, which makes it interesting for telecommunication applications. Besides the infrared emission, Pr^{3+}–doped glasses exhibit a large visible emission spectrum, which comprises blue, green and orange-red emissions, depending on the host matrices [8]. As red emitting devices, these materials present great potential for applications in medical therapies due to the optical skin transmittance in this spectral range [9]. Alongside the variety of possible emissions, Pr^{3+} ions can also emit in the UV range when excited in the 4f5d level directly or via upconversion mechanisms.

Upconversion processes have been extensively studied for applications such as converting low-energy laser radiation into high-energy radiation by exchanging two or more low energy photons to one higher energy photon. This process has increased the response of solar cells in particular wavelengths [10–14] and, recently, studies showed the possibility to diagnose the Ebola virus using upconverting nanoparticles [15]. For Pr^{3+} ions, upconversion to UV has been studied, for instance, in ceramics [16] and crystals [17–19] and its origin could be due to energy transfer upconversion and/or simultaneous absorption of photons.

Despite the shielding of the 4f–4f transitions that makes rare-earth elements unique, some transitions are very sensitives to the dopant environment, causing unusual alteration in the emission intensity — known as hypersensitive transitions. Reports showed hypersensitive transitions are affected by the dopant coordination, site symmetry, and ligand covalency [20, 21]. These transitions, specifically, can be used in optical fiber amplifiers and lasers [20].

This work reports a spectroscopic study of Pr^{3+}–doped CAS glasses. The optical absorption spectra were obtained for the UV–Vis–NIR range and the photoluminescence spectra for the UV–Vis range. Luminescence decay measurements were also carried out to understand the energy processes involving Pr^{3+} ions in this particular glass matrix.

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