Studies of the spectroscopic properties of Pr$^{3+}$ doped LaF$_3$ nanocrystals/glass

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Abstract

Emission and excitation spectra are presented for praseodymium (Pr$^{3+}$, 0.01 at%) doped oxyfluoride glass host containing LaF$_3$ nanocrystals. Two types of Pr$^{3+}$ ions, those in LaF$_3$ nanocrystals and those in the glass host, are characterized by spectroscopic and dynamical studies. Pr$^{3+}$ ions in the glass are selectively excited by pumping the 4f5d band and UV emission is observed. For Pr$^{3+}$ ions in the glass, the relaxation of $^3P_0$ is dominated by multi-phonon processes to $^1D_2$.

Keywords: Rare earth spectroscopy; Glasses; Nanocrystals; Praseodymium

1. Introduction

Oxyfluoride glass ceramics offer low phonon energies enabling emission from the rare-earth (RE) energy levels that may be quenched in high-phonon energy glasses [1]. Trivalent praseodymium-doped oxyfluoride glasses are of great interest for their optical and fluorescence properties and have potential use in fiber amplifiers, up-conversion lasers, and displays. When the ceramics are annealed, LaF$_3$ nanocrystals containing active RE ions form with optical properties nearly identical to those of bulk sample crystals. The RE solubility and thermal and environmental stability have been greatly improved [2] in fluoride nanocrystals-based oxyfluoride glass ceramics since they were first reported in 1993 [3].

In this paper, a detailed spectroscopic study of praseodymium (Pr$^{3+}$, 0.01 at%) doped LaF$_3$ nanocrystals embedded in glass is presented. Two types of Pr$^{3+}$ ions, one type contained in the LaF$_3$ nanocrystals and the other in the glass host, are distinguished by their spectroscopic and dynamical properties. The lowest 4f5d state of Pr$^{3+}$ ions in glass lies below 4f$^2$ $^1S_0$, allowing efficiently selective excitation of the Pr$^{3+}$ ions in glass and yielding UV emission. The relaxation of $^3P_0$ is dominated by multi-phonon processes to $^1D_2$ acting on the Pr$^{3+}$ ions in the glass.

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2. Experimental

Transparent oxyfluoride glass samples were prepared by Corning, Inc, by melting the appropriate batch materials [2]. Pr-doped nanocrystals are formed within the glass with a size of ~20 nm, and the size can be controlled by the annealing temperature. While the average concentration of Pr$^{3+}$ in the glass is 0.01%, in the annealing process, RE ions partition into the LaF$_3$ crystals, causing the concentration of Pr$^{3+}$ in the nanocrystals to be several times higher than the average of the glass ceramic. The fluorescence measurements were taken with a SPEX 500M spectrometer equipped with a SpectrAco photon counting system. A Spectra Physics/Quanta Ray Nd: YAG pumped LAS LDL 20505 dye laser was used as a pulsed excitation source. UV excitation was performed with a Jobin Yvon-Spex FluroMax III spectrofluorimeter. The fluorescence decay was recorded using a Tektronix 460A digital oscilloscope. Low temperature measurements were made with either a RMC Helium Closed-Cycle Cryosystem or a liquid nitrogen cryostat.

3. Results and discussion

Fig. 1 shows the emission spectrum at 11.0 K excited at 478.7 nm with light resonant with the $^3$H$_4$$\rightarrow$$^3$P$_0$ transition of Pr$^{3+}$ in the nanocrystals. Sharp and well-defined emission peaks ($^3$P$_0$$\rightarrow$$^3$H$_5$, $^3$P$_0$$\rightarrow$$^3$H$_6$, and $^3$P$_0$$\rightarrow$$^3$F$_2$ manifolds) are from Pr$^{3+}$ ions inside the nanocrystals. There are no significant differences observed for the sharp line emissions of Pr$^{3+}$ in the nanocrystals from that of Pr$^{3+}$ in bulk LaF$_3$ single crystals except for some inhomogeneous broadening occurring in the glass ceramic sample. The strong absorption of 478.7 nm is due to the first excited sublevel of $^3$H$_4$ at 57 cm$^{-1}$ that is populated, as seen in the excitation spectrum (inset in Fig. 1), when 600.1 nm ($^3$P$_0$$\rightarrow$$^3$H$_6$) emission is monitored. Another weak absorption at 136 cm$^{-1}$ ($^3$H$_4$(III)) above the ground state is also observed, indicating the local temperature at the excitation is higher than 11 K because of the focused laser beam and the low conductivity of the glass. Broad features observed around 544 and 596 nm (lying underneath the sharp features) are the emissions from the Pr$^{3+}$ ions situated in the glass. Fig. 2 shows a similar spectrum to that of Fig. 1 at 11.0 K but excited at 483.0 nm (non-resonant with the nanocrystals) that is absorbed mostly by the Pr$^{3+}$ ions in the glass, resulting in two main broad features. Emission around 600 nm may be attributed to two possible transitions that overlap, $^3$P$_0$$\rightarrow$$^3$H$_6$ and $^1$D$_2$$\rightarrow$$^3$H$_4$ [4]. Studies of the emission decay processes clearly indicate the existence of both of these transitions for Pr$^{3+}$ ions in the glass. Fig. 3 depicts the fluorescence decays with $^3$P$_0$ excitation at 483.0 nm. As seen in Fig. 3(a), when the short wavelength spectral edge at 599 nm (just below 600 nm; see Fig. 2) is monitored, an initial rise time and longer decay are observed, indicating that the fluorescence originates from the $^1$D$_2$ state that is populated by the relaxation from the $^3$P$_0$ state. When monitoring the spectral positions at longer wavelength (607 nm) that results from $^3$P$_0$ emission, no rise time is observed (Fig. 3(b)) since the $^3$P$_0$ state is directly excited by the laser. The decay time of the fast component (Fig. 3(b)) of the $^3$P$_0$ state of Pr$^{3+}$ ions in the glass matches the rise time of $^1$D$_2$ (Fig. 3(a)). All the sharp peaks around 600 nm in Fig. 1 result from $^3$P$_0$ state emission since they show no rise time (decay time is 56 µs), suggesting that multi-phonon relaxation to $^1$D$_2$ is not important for Pr$^{3+}$ ions in the nanocrystals.

Fig. 4 shows two excitation spectra monitoring the $^3$P$_0$ emission at 600 nm (nanocrystals) and 624 nm (glass). In addition to the sharp features around 450 nm due to absorption from the ground state to $^3$P$_{0,1,2}$ and $^1$I$_6$, both spectra show a broad feature in the UV range that is due to absorption of the 4f5d states of the Pr$^{3+}$ ions in the glass. The UV absorption is relatively strong when monitoring at 624 nm. It is known that the 4f5d band of Pr$^{3+}$ ions in LaF$_3$ crystals is well above 4f$^2$ 1S$_0$ [5], however, the excitation peak around 230 nm indicates that lowest 4f5d state of the ions in the glass lies below that of the 4f$^2$ 1S$_0$, which has also been observed in other Pr$^{3+}$-doped glasses with strong crystal fields [6]. This makes selective excitation of Pr$^{3+}$ ions in the glass very efficient.
excitation of the 4f5d band. The $^3P_0 \rightarrow ^3H_4$ emission is much weaker and the $^1D_2 \rightarrow ^3H_4$ emission is relatively strong in Fig. 5(c), compared to the spectrum in Fig. 5(a) under resonant excitation (442 nm) of Pr$^{3+}$ ions in the nanocrystals. Similar results are recorded (Fig. 5(b)) with off-resonant (430 nm) excitation that mainly excites Pr$^{3+}$ ions in the glass. This supports the suggestion that $^3P_0 \rightarrow ^1D_2$ non-radiative decay dominates the relaxation of $^3P_0$ for ions in the glass. This is consistent with the observation reported in other Pr doped hosts with low concentrations [7]. Concentration quenching of the $^1D_2 \rightarrow ^3H_4$ transition has often been observed due to the cross
relaxation between the Pr$^{3+}$ ions [8,9]. The broad feature around 520 nm in Fig. 5(c) is attributed to transitions of the lowest 4f5d state to $^3P_{0,1,2}$ and $^1I_6$. UV emission is also observed under 230 nm excitation as shown in the inset of Fig. 5, where the arrow marks the 4f5d $\rightarrow ^3H_4$ transition.

In summary, we have characterized the Pr$^{3+}$ ions in LaF$_3$ nanocrystals and in glass by
spectroscopic and dynamical studies. UV emission is observed from Pr$^{3+}$ ions in the glass upon selective excitation of the 4f5d band. The broad $^1D_2 \rightarrow ^3H_4$ feature is observed and is dominated by Pr$^{3+}$ ions in the glass as a result of strong non-radiative relaxation processes of the $^3P_0$ state for Pr$^{3+}$ ions in the glass.

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