Dynamical processes of Ln$^{3+}$ ions doped in LaF$_3$ nanocrystals embedded in transparent oxyfluoride glass

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Abstract

The transverse and longitudinal relaxations from the excited electronic levels of rare earth ions (Ln$^{3+}$) in nanocrystals are reviewed. Employing the frequency up-converted emission, we have studied the ion–ion interactions and the distribution of the ions within Pr$^{3+}$:LaF$_3$ nanocrystals embedded in oxyfluoride glass. The phonon-assisted energy transfer between Pr$^{3+}$ ions is discussed and the relation between the energy transfer rate and the buildup of the up-converted emission is established. The results suggest that the Pr$^{3+}$ concentration inside the nanocrystals is 5–10 times that of the average concentration. A jump in the energy transfer rate is observed as the concentration increases, and the possible processes behind it are discussed.

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1. Introduction

Transparent oxyfluoride glass ceramics containing LaF$_3$ nanocrystals combines the optical advantages of a fluoride crystal host with the mechanical advantages of oxide glass. In these materials, LaF$_3$ nanocrystals doped with Ln$^{3+}$ ions are formed through nucleation and their size is controlled by the post-heat-treatment after the initial formation of the glass [1,2]. The energy level structure of Ln$^{3+}$ ions, determined by their local environment, remains nearly the same for the ions doped in nanocrystals and in the bulk crystals, except for an increased inhomogeneous broadening seen in the nanocrystals. The optical dynamics of Ln$^{3+}$ ions partitioned into the crystal
phase is greatly affected by the surrounding glass matrix and the confinement due to their size-restricted nature [3–6]. For isolated Eu2O3 nanoparticles and Eu-doped Y2O3 nanoparticles in 5–30 nm diameter range, the spectral hole burning (SHB) line width increases as the particle size decreases. The temperature dependence of the line width approximately follows a $T^3$ behavior that results from the confinement effect on the vibrational modes of nanoparticles [4]. The size-restricted nature of nanoparticles produces a discrete spectrum of acoustic modes with a minimum cutoff frequency which replaces the continuous modes that describes bulk crystals, leading to a $T^3$ temperature dependence for isolated nanocrystals. When the nanocrystals are embedded in a glass matrix, a non-zero value extrapolated to zero temperature and a nearly linear temperature dependence in the low-temperature region (generally below 4–5 K) is observed, and a strong temperature dependence above 5 K is detected for both Pr$^{3+}$- and Tm$^{3+}$-doped samples [7,8]. Two-pulse photon echo (time domain) experiments that access the optical dephasing on a much shorter time scale (ns) than the SHB technique (microseconds to seconds) have been performed and the photon echo signals have been obtained from the transition of $^3H_4\rightarrow^3P_0$ in Pr$^{3+}$:LaF$_3$ nanocrystals embedded in oxyfluoride glass. The dephasing time $T_2$ ($T_2 = 1/\pi\Gamma_{\text{hom}}$) is found to be 30–50 ns, which is 50–100 times shorter than that from the corresponding bulk crystal (2.4 $\mu$s) [7,8]. A similar quasi-linear temperature dependence is obtained, but no evidence of the strong temperature dependence above 5 K is detected as seen in the SHB. The results from both the SHB and the two-pulse photon echo indicate that spectral diffusion occurs on the time scale of the SHB experiment, which is possibly due to a few local modes associated with the boundary between each nanocrystal and the glass whose resonances are activated exponentially with temperature. It is the interaction of Ln$^{3+}$ ions with the two-level system (TLS) of the glass that dominates the dephasing of optical transitions at low temperatures [5,7,9].

The homogeneous line width and dephasing time reveal the transverse relaxation of the excited Ln$^{3+}$ ions, while the fluorescence decay gives information on the longitudinal relaxation. For Ln$^{3+}$-doped nanocrystals embedded in an amorphous matrix, the size of the nanocrystals, the effective index of refraction, and the effect of distortions of the Ln$^{3+}$ sites associated with the homogeneous broadening affect the radiative relaxation rate. The competition between the site distortion and the effective refractive index determines the shift of the fluorescence lifetime [6], and the decrease of the nanocrystal size results in a shorter fluorescence lifetime. For example, the fluorescence lifetime of Pr$^{3+}$:LaF$_3$ nanocrystals embedded in oxyfluoride is found to be greater than that of LaF$_3$ bulk crystals, as expected when the effective refractive index dominates the phenomenon. In the case of Ho$^{3+}$:LaF$_3$ nanocrystals, the effect of distortions becomes important and the fluorescence lifetime becomes shorter than that in the bulk crystal. As the size of the nanocrystal increases, the fluorescence lifetime gets closer to that in the bulk crystal.

The transverse and longitudinal relaxations, in the review described above, are one part of the dynamical process of optically excited states. Interactions among the Ln$^{3+}$ ions resulting in the energy transfer are another important topic in the study of the dynamic process [10]. Among Ln$^{3+}$ ions, trivalent praseodymium (Pr$^{3+}$) is an attractive optical activator ion since there exist several metastable states in its energy level spectrum, such as $^1G_4$, $^1D_2$, and $^3P_0$ manifolds, which may produce stimulated emissions from infra-red to blue [11–13]. The states with lower decay rates, e.g., $^1D_2$, also enhance the possibility of sequential two-photon absorption using these states as intermediate levels. The anti-Stokes blue emissions from $^3P_0$ state have been observed upon excitation of the $^1D_2$ manifolds in both bulk crystals [11,14,15] and glass hosts [16,17]. Two dominant up-conversion mechanisms have been proposed for the Pr$^{3+}$-doped crystals: (1) cooperative energy transfer involving a pair of Pr$^{3+}$ ions, which has been observed in Pr$^{3+}$:LaF$_3$ [11,15], Pr$^{3+}$:K Pb$_2$Cl$_5$, and some Pr$^{3+}$-doped glasses [18], and (2) sequential two-photon absorption or excited-state absorption involving a single Pr$^{3+}$ center, which has also been observed in both
the crystal host (Pr\(^{3+}\):La\(_2\)Ti\(_2\)O\(_7\)) and glass hosts [19–21].

In this paper, we want to explore energy transfer between Ln\(^{3+}\)-ions-doped nanocrystals, and the possible effects resulting from size confinement of the nanocrystals and effects associated with coupling to the surrounding matrix. Since the energy transfer rate is very sensitive to the distribution of the Ln\(^{3+}\) ions [10], the study of up-conversion induced from the energy transfer could be a very effective way to explore the ion distributions inside the nanocrystals. In this paper, the ion–ion interactions within nanocrystals which lead to the transfer of optical excitation are studied by the frequency up-converted emission in Pr\(^{3+}\):LaF\(_3\) nanocrystals embedded in oxyfluoride glass. An enhancement in the buildup and decay processes has been observed, and the actual concentration of Ln\(^{3+}\) ions inside the LaF\(_3\) nanocrystals is estimated. Useful information on the distribution of Pr\(^{3+}\) ions inside the nanocrystals is obtained by establishing the relation between the buildup time and the energy transfer rate. In the temperature range of 10–80 K, the rise and decay times of the up-converted emission show a weak temperature dependence.

2. Experiment and results

The transparent oxyfluoride glass ceramic samples have been prepared by Corning Inc., by melting appropriate batch materials [1,2]. In the current study, Ln\(^{3+}\):LaF\(_3\) nanocrystals are formed within the glass with a size of 20–30 nm after annealing the ceramic glasses to 750 or 775 °C for 4 h in air. The Pr\(^{3+}\) concentrations of the starting materials are from 0.01% to 0.5%. During the post-heat-treatment, Pr\(^{3+}\) ions partition into the LaF\(_3\) crystals. The resulting concentration of Pr\(^{3+}\) in the nanocrystals is several times that of the average value (which is further proved to be about 10 times from this work). A Spectra Physics/Quanta Ray Nd:YAG (DCR-1) pumped PDL pulsed dye laser is employed as the light source. The output wavelength of the dye laser is tuned to the center of the absorption from the \(^3\)H\(_4\) (0) to \(^1\)D\(_2\) (10 cm\(^{-1}\)) states in the crystalline phase. The spectroscopic measurements are carried out with a 0.75 m SPEX 1702 spectrometer equipped with a SR 400 gated photon counter. The fluorescence decay is recorded using a Tektronix TDS 460A digital oscilloscope. Low-temperature measurements are made with either a liquid helium cryostat or a RMC Helium Closed-Cycle Cryosystem.

The up-converted emission from \(^3\)P\(_0\) is measured in the time domain by exciting the \(^1\)D\(_2\) electronic level. Fig. 1 depicts the time evolution of the overall emission for a series of Pr\(^{3+}\) concentrations. The starting time (\(t = 0\) s) corresponds to the moment immediately after the excitation pulse. It shows that the buildup of the population of the \(^3\)P\(_0\) level starts from zero, which is a proof that the mechanism of up-conversion is energy transfer between the Pr\(^{3+}\) pair. The buildup time \(\tau_r\) and decay time \(\tau_d\) decreases as the Pr\(^{3+}\) concentration increases. At the bottom of Fig. 1, we have added the result measured from 0.5% Pr\(^{3+}\):LaF\(_3\) bulk crystal. Comparing the results obtained from the bulk crystal and the ceramic samples, one can see that the Pr\(^{3+}\) concentration inside the LaF\(_3\) nanocrystals should be 5–10 times higher than the average concentration, which is consistent with the observations by Macfarlane and Dejneka [24].

Fig. 2 shows the concentration dependence of \(\tau_r\) and \(\tau_d\), which are obtained by fitting the data of Fig. 1 to the function of \(A(\exp(-t/\tau_d)-\exp(-t/\tau_r))\). To make the concentration of the Pr\(^{3+}\) ions in the crystal phase close to the real distribution in nanocrystals, the concentration labeled for the nanocrystals is eight times that of the average sample concentration. Data reported for the bulk crystal [11] and for the glass [16] are also plotted in Fig. 2. Below 77 K, a weak temperature dependence of \(\tau_r\) and \(\tau_d\) were observed with Pr\(^{3+}\) concentrations of 0.01–0.5%, and the results are presented in Fig. 3. The fluorescence decay from \(^1\)D\(_2\) level is also studied and it is found to be non-exponential. The slower component of this fluorescence decay is recorded and plotted in Fig. 4 with the decay of the up-converted emission from \(^3\)P\(_0\) level. It suggests that the decay time of the up-converted emission from the \(^3\)P\(_0\) is about half of the \(^1\)D\(_2\) decay time.
3. Discussion

3.1. Mechanism of the up-converted emission

In Refs. [10,11,14,22], the up-conversion mechanisms have been discussed for Pr$^{3+}$-doped LaF$_3$ crystal. Figs. 1–3 suggest that the process in our study is the phonon-assisted energy transfer between two ions excited to the $^1D_2$ state. If the ions A (acceptor) and D (donor) are both pumped onto the $^1D_2(2)$ level, they will follow the transfer of

$$A(^1D_2(1)) + D(^1D_2(1)) \rightarrow A(^3P_2(5)) + D(^1G_4(9))$$

after a very quick relaxation to the $^1D_2(1)$ level. Here, the numbers 1, 5, and 9 next to the $^1D_2$, $^3P_0$, and $^1G_4$ indicate the sublevels of $^1D_2$, $^3P_0$, and $^1G_4$, respectively. The $^3P_0$ level will be populated after another quick relaxation from $^3P_2$, resulting in the up-converted emission from $^3P_0$. The energy transfer is not resonant, and a phonon with the energy of 427 cm$^{-1}$ has...
to be released [14,23]. Below 77 K, the population of thermal phonons of this energy is too small to affect the energy transfer process significantly. Thus, the weak temperature dependence shown in Fig. 3 is consistent with the above discussion. The confinement effect due to the finite size of nanocrystals does not likely influence the energy transfer [3,4], but it may affect the energy diffusion that occurs during the energy transfer.

To understand the concentration dependence of $\tau_t$ and $\tau_d$, and to explore the distribution of Pr$^{3+}$ ions inside the nanocrystals through the up-conversion, we start with the rate equations. Suppose that there are $N_0$ ions being excited to $^1D_2$ level at $t = 0$, $W_1$ and $W_3$ are the relaxation probabilities of $^1D_2$ and $^3P_0$ under direct excitation, respectively, and $W$ is the transfer rate between the ions A and D, then the equations for the population of the $^1D_2$ state ($N_D$) and $^3P_0$ state ($N_P$) read

$$\dot{N}_D(t) = -W_1 N_D(t) - WN_D^2(t), \quad (1)$$
$$\dot{N}_P(t) = -W_3 N_P(t) + WN_D^2(t). \quad (2)$$

The analytical solutions for Eqs (1) and (2) under the initial conditions of $N_D(t = 0) = N_0$ and $N_P(t = 0) = 0$ are

$$N_D(t) = \frac{W_1}{-W + (e^{W_1 t} - (W_1 + WN_0)/N_0)} \quad (3)$$
and

$$N_P(t) = \int_0^t \frac{W_3 e^{W_3 x}}{-W + (e^{W_1 x}(W_1 + WN_0)/N_0))} e^{-W_1 x} dx \quad (4)$$

Fig. 2. Concentration dependence of the buildup time ($\tau_t$) and decay time ($\tau_d$) of the up-converted emission from the $^3P_0$ when the $^1D_2$ level is excited. The data are obtained by fitting the curves represented in the Fig. 1 with the function of $A(exp(-t/\tau_d) - exp(-t/\tau_t))$. Note: the Pr$^{3+}$ concentration inside the nanocrystals for the glass ceramic samples is eight times that of the average Pr$^{3+}$ concentration.
In the case of $e^{w_1 x} > 1$, solution (4) can be simplified as

$$N_P(t) = \frac{W W_1^2 N_0^2}{(W_3 - 2 W_1)(W N_0 + W_1)^2} (e^{-2 W_1 t} - e^{-W_3 t}).$$

(5)

Therefore, the decay time of the up-converted emission from the $^3P_0$ level is either (a) half of the $^1D_2$ lifetime ($(2 w_1)^{-1}$) or (b) the $^3P_0$ lifetime ($W_3^{-1}$). Case (b) occurs when the excitation is off the center absorption and the energy transfer is induced by the super exchange between the very closely located ions in the wings of the absorption line [15,25]. When the center absorption line ($^3H_4^1D_2$) is excited, case (a) occurs, and the dipole-dipole interaction dominates the energy transfer. The transfer rate is proportional to $R^{-6}$ at a given temperature ($R$ is the distance between the interacting ions) [10]. Fig. 4 shows that the decay time of the up-converted emission is about half of the $^1D_2$ decay time, which excludes the possibility of the super exchange in our current study [25].

### 3.2. The distribution of Pr$^{3+}$ ions

Eq. (4) indicates that the dynamic process of $N_P(t)$ depends on the energy transfer rate $W$, but this dependence does not appear in Eq. (5), which means that the information on the energy transfer cannot be revealed by the decay time of the up-converted emission. In a small time region where the conditions of $e^{w_3 x} \approx 1 + W_3 x$ and $e^{w_1 x} \approx 1 + W_1 x$ are satisfied, Eq. (4) can be simplified by

$$N_P(t) = \frac{W N_0^2 e^{-W_1 t}}{W_1 + W N_0} \left\{1 + \frac{W_3}{W_1 + W N_0} \ln[1 + (W_1 + W N_0) t] - \frac{1 + W_3 t}{1 + (W_1 + W N_0) t}\right\}.$$
Therefore, the ion population $N_p(t)$ is related to the energy transfer rate $W$ through Eq. (6), i.e., the energy transfer can be studied through the buildup process of the up-converted emission. Taking the values of $W_1$ and $W_3$ from Ref. [26] and using Eq. (6) to fit the buildup of the curves plotted in Fig. 1, we find that the values of $W_N$ are 0.0062 $\mu$s$^{-1}$, 0.058 $\mu$s$^{-1}$, and 12.65 $\mu$s$^{-1}$, for 0.05%, 0.1%, and 0.5% ceramic samples (where the conditions of $e^{W_{3}x} \geq 1 + W_{3}x$ and $e^{W_{1}x} \geq 1 + W_{1}x$ are satisfied), respectively. Thus, $W_{N0}(0.05\%):W_{N0}(0.1\%):W_{N0}(0.5\%) = 1:9:201.6$, which results in a ratio of $W(0.05\%):W(0.1\%):W(0.5\%) = 1:4.5:201.6$. From the previous discussion on Fig. 1, we know that the interaction between the ions is dominated by the dipole–dipole interaction, and the energy transfer rate is proportional to $R^{-6}$ where $R$ is the distance between the interacting ions. It is reasonable to assume that the portion of the Pr$^{3+}$ ions partitioned into the nanocrystals are the same for the concentrations from 0.05% to 0.5% due to the concentration dependence represented in Fig. 2. If the Pr$^{3+}$ ions are uniformly distributed inside the nanocrystals, the energy transfer rate should give the ratio of $W_{tr}(0.05\%):W_{tr}(0.1\%):W_{tr}(0.5\%) = 1:4:100$. There are two possible reasons for the difference in the ratios of $W$ and $W_{tr}$ at high concentration: (1) higher multiple interactions, such as quadruple–dipole or quadruple–quadruple interactions, become important and cannot be neglected during the energy transfer; therefore, the distance dependence of the transfer rate could not be simply described by $R^{-6}$. (2) The interaction between the ions is still dominated by the dipole–dipole interaction, but the ions tend to gather together to form some kind of loose clusters resulting in a shorter distance (shorter than the average) at high concentrations. The decrease in $R$ would then explain the extra increase in the energy transfer rate at high concentration.
4. Conclusions

The ion-ion interactions and the distribution of the ions within Pr\(^{3+}\):LaF\(_3\) nanocrystals embedded in oxyfluoride glass are studied by the frequency up-converted emission. It is found that the Pr\(^{3+}\) concentration inside the nanocrystals is 5–10 times that of the average concentration. The dependencies of the buildup and decay time on concentration and on the transfer rate are investigated, and the experimental results are analyzed by solving the rate equations. The confinement effect may influence the diffusion process, but it does not likely influence the process of energy transfer. There is some evidence for clustering or non-uniform ion distributions within the nanocrystals at the higher concentrations.

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