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Site-selective spectroscopy of Nd^{3+} in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser crystal

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Abstract- Laser excited site-selection spectroscopy of Nd^{3+} ion in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ laser garnet crystal has been investigated for the transitions $^2Z(I_{3/2}^{12}) \rightarrow ^4D(^4G_{5/2})$ and $^4F_{3/2} \rightarrow ^4I_{9/2}$ in order to understand the nature of the different Nd centers in terms of the possible charge compensating defects. Lifetime data of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition obtained as a function of Nd concentration have allowed to distinguish the Nd^{3+} ions compensated by Ga^{3+} ions ($\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Ga}^{3+}(\text{Ge}^{4+})$) from other kind of Nd^{3+} ions, which can be presumably associated with $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Nd}^{3+}(\text{Ge}^{4+})$ pairs.

1. INTRODUCTION

Recently, the attention on the identification of the non-equivalent crystal field sites of rare-earth ions in garnet crystals has increased, since it is essential for a complete understanding of the laser properties of the material (1,2).

At the present, new laser garnet crystals such as $\text{Ca}(\text{Nb,Ga})_2\text{Ga}_2\text{O}_{12}$ (3) and $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (4,5) activated with Nd^{3+} ions have been investigated. In the case of the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet (CGG), the compensation of the excess charge of Nd^{3+} ions substituting Ca^{2+} dodecahedral c-lattice ions can be performed by Ga^{3+} ions entering Ge^{4+} tetrahedral d-lattice ions (4). Recently, it has been proposed that other possible compensating defects can be $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Nd}^{3+}(\text{Ge}^{4+})$ pairs, in which the excess charge compensation can be achieved by other Nd^{3+} ion entering Ge^{4+} tetrahedral site (5). Thus, the formation of different types of $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Ga}^{3+}(\text{Ge}^{4+})$ and $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Nd}^{3+}(\text{Ge}^{4+})$ associations gives place to different non-equivalent Nd centers. In fact, six different Nd centers in the CGG garnet have been observed using site-selective spectroscopy. The most predominant centers, assigned as I, II and IV, have been associated with Nd^{3+} ions forming different $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Ga}^{3+}(\text{Ge}^{4+})$ configurations, while that centers V and VI have been tentatively correlated to Nd^{3+} ions forming $\text{Nd}^{3+}(\text{Ca}^{2+})\text{-Nd}^{3+}(\text{Ge}^{4+})$ pairs (5).

We continue our site-selective fluorescence studies of the Nd-doped CGG garnet crystal since the different Nd centers play an important role in the spectroscopic properties of the garnet.

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2. EXPERIMENTAL

The Nd-doped CGG crystals employed in this work were grown from the melt by the Czochralski technique. Absorption, site-selection fluorescence and lifetime measurements at 10 K were obtained with the same experimental equipment as described elsewhere (5,6).

3. RESULTS

Figure 1 shows the 10 K absorption spectra of the $Z(^4I_{9/2}) \rightarrow D(^4G_{5/2})$ transition for CGG crystals doped with Nd concentrations ranging from 0.5 to 8 at.%. Only the absorption bands corresponding to Nd centers I, II, IV and VI are clearly resolved. These bands are broader and less resolved as the Nd concentration is higher indicating, therefore, that the crystal becomes more inhomogeneous and disordered as the Nd concentration increases.

Figure 1. 10 K absorption spectra corresponding to the $Z(^4I_{9/2}) \rightarrow D(^4G_{5/2})$ transition of Nd in CGG doped with a) 0.5, b) 2, c) 4 and d) 8 at.% of Nd.

Excitation either into the $^4G_{5/2}$ or $^4F_{3/2}$ excited levels produces the same emission spectrum, due to radiationless relaxation from the $^4G_{5/2}$ level down to the $^4F_{3/2}$ lower level, from which emission takes place. Figure 2 shows the 10 K emission spectra, corresponding to each Nd center (I, II, IV and VI), for the sample of CGG doped with 2 at.% of Nd. These spectra, corresponding to the transition $^4F_{3/2} \rightarrow ^4I_{9/2}$, were obtained exciting selectively into the corresponding absorption band (displayed in fig. 1b). Each emission spectrum consists of five lines in agreement with the expected number of Stark components at low temperature.

The lifetimes corresponding to the transition from the $R(^4F_{3/2})$ fluorescence level to the $^4I_{9/2}$ ground state were obtained as a function of Nd concentration at temperature of 10 K. The 10 K decay scheme of Nd centers I, II and IV, in samples doped with 2 and 4 at.% of Nd, was found to consist of a single-exponential decay, with a time constant of about 200 μ s, while that center VI exhibits a non-exponential decay with a first exponential decay smaller ($\sim 130 \mu$ s). Fig. 3 displays the exponential decay exhibited by

Figure 2. 10 K emission spectra corresponding to the transition $R_1(^4F_{3/2}) \rightarrow ^4I_{9/2}$ of Nd^{3+} ions forming centers a) I, b) II, c) IV and d) VI in the CGG crystal containing 2 at.% of Nd.

Nd center I in the CGG:Nd(2 at.%) sample. For the sample doped with higher concentration of Nd (8 at.%), the fluorescence decay scheme is very similar for all centers (I, II, IV and VI), showing a non-exponential character with a first exponential decay still more reduced ($\sim 60 \mu s$). In addition, this lifetime behaviour is accompanied by a concentration quenching of luminescence.

4. DISCUSSION

From the absorption spectra of figure 1 and assuming the same absorption strength for all centers, it can be observed that the formation of center VI is stimulated as the Nd concentration increases in accordance with the results previously obtained (5). Thus, it has been proposed that center VI can be associated with Nd^{3+} ions forming $Nd^{3+}(Ca^{2+})-Nd^{3+}(Ge^{4+})$ pairs, while that centers I, II and IV have been attributed to $Nd^{3+}(Ca^{2+})$ ions forming different $Nd^{3+}(Ca^{2+})-Ga^{3+}(Ge^{4+})$ configurations.

The Nd^{3+} ions entering Ge^{4+} tetrahedral sites, indeed of Ca^{2+} dodecahedral sites, give place to a quite different crystal field. In

Figure 3. $R_1(^4F_{3/2}) \rightarrow Z(^4I_{9/2})$ emission decay of Nd^{3+} center I in the CGG:Nd(2 at.%) sample.

addition, the great difference between the radius of Nd^{3+} ions ($\sim 1 \text{ \AA}$) and substituted Ge^{4+} ions ($\sim 0.53 \text{ \AA}$) should involve a greater local distortion in these sites than that produced by $Nd^{3+}(Ca^{2+})$ ions, which have similar ionic radii ($r_{Nd} \approx r_{Ca} \sim 1 \text{ \AA}$). Under these circumstances, the $^4F_{3/2}$ splitting of $Nd(Ge)$ ions must be greater than that corresponding to $Nd(Ca)$ ions. Since center VI has associated a $^4F_{3/2}$ splitting (149 cm^{-1}) greater than that ($\sim 100 \text{ cm}^{-1}$) corresponding to centers I, II and IV (5), it is reasonable to think that center VI should be related to $Nd(Ge)$ ions of the pair. Moreover, the non-exponential luminescence decay of the $^4F_{3/2}$ level down the $^4I_{9/2}$ ground state exhibited by centers VI with a shorter first exponential decay reveals the presence of energy migration between Nd^{3+} ions. Thus, this fact supports the assignment of center VI to Nd^{3+} ions forming pairs. On the other hand, the $^4F_{3/2} \rightarrow ^4I_{9/2}$ fluorescence decay scheme of centers I, II and IV, consisting of a purely exponential decay at Nd concentrations no greater than 4 at.%, supports the fact that these centers should be associated with isolated $Nd^{3+}(Ca^{2+})$ ions, which can be compensated by $Ga^{3+}(Ge^{4+})$ ions.

Finally, it is important to note that when the Nd concentration is high (8 at.%), the garnet shows features of disorder. This is reflected in an inhomogeneous broadening of the luminescence and absorption bands, which causes a superposition of the different Nd centers. Thus, energy migration between distinct centers can occur. In fact, this phenomenon is evidenced by the non-exponential decay and concentration quenching of luminescence observed for all centers (I, II, IV and VI) of Nd in the higher concentration sample (8 at.%).

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