CHROMIUM-NEODYMIUM ENERGY TRANSFER IN YAP

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Abstract: Yttrium aluminum perovskite (YAP) co-doped with Cr\textsuperscript{3+} and Nd\textsuperscript{3+} is of interest in laser applications because the chromium-neodymium energy transfer is more efficient in YAP than in YAG. Investigation of the energy transfer from the chromium R lines and pair states in the wavelength range 720-740 nm to the Nd\textsuperscript{3+} upper laser level shows that neither individual Cr\textsuperscript{3+} ions nor Cr\textsuperscript{3+}-Cr\textsuperscript{3+} pairs are important energy donors in YAP. The results are consistent with a model of nonuniform distribution of donors.

Single crystals of YAlO\textsubscript{3}, also known as yttrium aluminum perovskite (YAP), or yttrium orthoaluminate, are of interest as a laser host for specialized applications. The orthorhombic symmetry of YAP\textsuperscript{\textdegree} causes anisotropy in the optical properties of substitutional, optically-active ions, and this anisotropy can be exploited in device design.\textsuperscript{2} For applications in which the lasing ion is a rare earth and the pump source is broad-band, it is desirable to co-dope the crystal to improve the spectral overlap between the pump emission and the activator ion. One common combination of rare earth activator ion and co-doped sensitizer is Nd\textsuperscript{3+} and Cr\textsuperscript{3+}.

Recent detailed spectroscopic investigations of a similar material, Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (yttrium aluminum garnet, or YAG),\textsuperscript{3,4} have shown that in this simpler cubic system both Cr\textsuperscript{3+} and Nd\textsuperscript{3+} occupy several inequivalent sites. This work has also demonstrated that in YAG the main Cr\textsuperscript{3+} site does not transfer energy to the main Nd\textsuperscript{3+} site, thus limiting the usefulness of co-doping in increasing the efficiency of Nd:YAG lasers. It is thus important to investigate similar materials to search for one in which energy transfers by a more efficient connection between the main sites of activator and sensitizer ions.

Previous studies\textsuperscript{5,6} have indicated that in YAP the energy transfer between Cr\textsuperscript{3+} and Nd\textsuperscript{3+} ions is more efficient than in YAG, and that the fluorescence dynamics of Nd\textsuperscript{3+} both alone and with Cr\textsuperscript{3+} may be unusually complex. In particular, multiple Cr\textsuperscript{3+} sites have been found in this host, and the Cr\textsuperscript{3+} fluorescence decay of co-doped Nd,Cr:YAP crystals cannot be explained by a model which assumes uniformly-distributed donors.\textsuperscript{7} Thus YAP is an interesting candidate material for more efficient Nd\textsuperscript{3+} lasers.

Since the distance between adjacent Cr\textsuperscript{3+} sites is relatively small in YAP (3.8 Å as compared to 5.2 Å in YAG),\textsuperscript{8} one possible source of the additional complexity of the fluorescence dynamics in co-doped Nd,Cr:YAP crystals is the existence of strong interactions between Nd\textsuperscript{3+} ions and Cr\textsuperscript{3+}-Cr\textsuperscript{3+} pairs. Thus, we have investigated the relationship between the lowest-lying Cr\textsuperscript{3+} single-ion and Cr\textsuperscript{3+}-Cr\textsuperscript{3+} pair states and emission from the Nd\textsuperscript{3+} \(4\text{F}_{3/2}\) level, which is the usual upper level in...
Nd³⁺ lasers.

Fig. 1. - Emission spectra for two Nd, Cr: YAP crystals containing approximately 0.15 at% Cr. The excitation wavelength is 570 nm, and T = 6 K.

Figure 1 shows normalized low-temperature emission spectra from two samples of Nd, Cr: YAP which are similar except that one has been intentionally doped with 1.4 at% Nd, while the other contains only unavoidable traces. The Cr concentrations in the two samples are both about 0.15 at%. The excitation wavelength for both spectra is approximately 570 nm, which is near the center of the T₁ band for Cr³⁺ ions, and at the high-energy limit of the Gₛ² and Gₐ₂ Nd³⁺ levels. The most significant difference between these two spectra is the relative intensity of the chromium pair lines near 731 nm in comparison to that from the R₁ line near 740 nm.

There are three possible explanations for this observation. (1) Cr³⁺-Cr³⁺ pairs transfer energy efficiently to Nd³⁺ ions. (2) Substitution of Nd for Y inhibits the formation of chromium pairs without changing the uniform distribution of dopant ions. (3) As the concentration of Nd³⁺ ions is increased, Cr³⁺ ions pair with them, rather than with other Cr³⁺ ions, so that the dopant distribution is nonuniform.

Figures 2 and 3 compare the low-temperature excitation spectra of Nd³⁺ ⁴F₅/₂ emission in the two samples. The samples were excited by an excimer-pumped dye laser, and the emission detected with a photomultiplier and photon counter. The line at 876 nm, which was monitored in both samples, is due to a transition between the lowest energy states of ⁴F₅/₂ and ⁴I₉/₂. The lines at 885 and 892 nm correspond to transitions from the same upper state to the first two excited states of the ⁴F₉/₂ multiplet. These emissions were too weak in the lightly-doped crystal to obtain useful excitation spectra.

The Cr³⁺ R lines are present in the excitation spectrum of the lightly-doped sample (fig. 2), indicating that in this sample isolated chromium ions contribute energy to the Nd³⁺ emission. However, the R lines do not appear in the excitation spectra from the Nd-doped sample (fig. 3), showing that individual Cr³⁺ ions are not significant energy donors for Nd³⁺ emission in YAP laser crystals.
No Cr\textsuperscript{3+}-Cr\textsuperscript{3+} pair lines appear in either figure 2 or figure 3. Thus, chromium pairs are also not important in the fluorescence dynamics. This means that most of the energy transfer between Cr\textsuperscript{3+} and Nd\textsuperscript{3+} in YAP probably involves Cr\textsuperscript{3+}-Nd\textsuperscript{3+} pairs (i.e., a nonuniform distribution of Cr\textsuperscript{3+} ions with respect to Nd\textsuperscript{3+} ions).

The four intense lines in each of the excitation spectra are in the energy range of the Nd\textsuperscript{3+} \textsuperscript{2}F\textsubscript{7/2} and \textsuperscript{4}S\textsubscript{3/2} levels.\textsuperscript{18} At 5K, the dominant fluorescence decay time of the Nd\textsuperscript{3+} \textsuperscript{2}F\textsubscript{7/2} emission is approximately 370 \mu s in the Nd-doped sample for excitation in each of these excitation lines, which indicates that these are indeed Nd\textsuperscript{3+} transitions. In the sample containing only traces of Nd, the lifetime of the 876 nm Nd emission is approximately 430 \mu s for the same excitations, showing that the Nd concentration in the intentionally-doped crystal is large enough to cause a small amount of concentration quenching through Nd\textsuperscript{3+}-Nd\textsuperscript{3+} interactions.

![Excitation spectrum of the 876 nm emission in a Nd,Cr:YAP crystal containing only traces of Nd. T = 5 K.](image)

The lifetime of Cr\textsuperscript{3+}-Cr\textsuperscript{3+} pairs is much shorter than that of the R lines (1 ms for pairs vs. 50 ms for the R lines at low temperature),\textsuperscript{19,20} but is comparable to that for Nd\textsuperscript{3+} transitions. There are indications of complex initial transients for some of our decay curves, although these features are not well-resolved. None of our experimental decay curves shows a significant residual slow decay, which supports the conclusion that individual Cr\textsuperscript{3+} ions are not an important energy donor. (These decay curves alone would not entirely rule out some energy transfer from chromium pairs, as the difference in decay time between Nd\textsuperscript{3+} alone and that of chromium pairs is not very large.) The existence of processes with a shorter time scale than the Nd\textsuperscript{3+} decay time suggests the involvement of Nd\textsuperscript{3+}-Cr\textsuperscript{3+} pairs. Further study of these decays will be presented in a future communication.

The relative intensities of the strong Nd\textsuperscript{3+} lines in the three excitation spectra of the Nd-doped sample shown in figure 3 also suggest that the fluorescence dynamics may be quite complex. The intensities of the excitation lines at 734.7 and 735.7 nm change with respect to those of the excitation lines at 732.2 and 737.0 nm, depending on the terminal Nd\textsuperscript{3+} \textsuperscript{4}I\textsubscript{15/2} state which is monitored. Since all the emission lines studied have the same upper level, this result indicates that the fluorescence cannot be explained by a simple branching ratio model.
In summary, the emission and excitation spectra and fluorescence decay curves of Nd,Cr:YAP for excitations between 720 and 740 nm indicate that neither individual Cr$^{3+}$ ions nor Cr$^{3+}$-Cr$^{3+}$ pairs are important energy donors for the Nd$^{3+}$ $^4F_{3/2}$ upper laser level in laser crystals. Our results are consistent with the hypothesis that Cr$^{3+}$ ions have a nonuniform distribution with respect to Nd$^{3+}$ ions.

References