Cr$_3^+$, Nd$_3^+$ multisites, pairs and energy transfer processes in laser crystal YAlO$_3$

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Abstract

Detailed spectroscopic studies of YAlO\(_3\):Nd, YAlO\(_3\):Cr and YAlO\(_3\):Nd,Cr have shown that these crystals contain up to eight Nd\(^{3+}\) multisites and three Cr\(^{3+}\) ones. Cr\(^{3+}\) \(\rightarrow\) Nd\(^{3+}\) energy transfer is observed between various multisites and is starting from \(^{3}E\) Cr\(^{3+}\) energy level. Cr\(^{3+}\) donor decay can be adequately fit with the standard Inokuti-Hirayama theory but an assumption of a spatial correlation between Cr\(^{3+}\) donors and Nd\(^{3+}\) acceptors does a much better fit of Nd\(^{3+}\) fluorescence decay.

1. Introduction

Neodymium doped yttrium aluminium perovskite YAlO\(_3\) (YAP) is one of the most important solid state laser crystals [1]. Cr\(^{3+}\) and Ce\(^{3+}\) codoping ions are added to Nd\(^{3+}\) lasing ions in YAlO\(_3\) crystal for an improvement of the pumping efficiency (due to Cr\(^{3+}\) \(\rightarrow\) Nd\(^{3+}\) or Ce\(^{3+}\) \(\rightarrow\) Nd\(^{3+}\) energy transfers). Cr\(^{3+}\), Nd\(^{3+}\) multisites, ionic pairs and energy transfer processes in YAlO\(_3\):Nd, YAlO\(_3\):Cr and YAlO\(_3\):Nd,Cr were investigated; the distribution of Nd\(^{3+}\), Cr\(^{3+}\) ions in the crystals is discussed based on the analysis of fluorescence decays according to models of standard (Inokuti-Hirayama) and non-uniform correlated distribution of ions in crystals [2].

To understand the energy transfer processes that occur between codopants (donors) and the dopants (acceptors) or between some of their multisites, one must consider non-uniform distribution of donors and acceptors [2–6]. This is not because overall the donors and acceptors are non-uniformly distributed; rather each multisite, with its unique crystal site, may have unique absorption and emission lines (see [7] for an extensive analysis of such multisites in chromium–thulium–holmium YAG). Such sites effectively see different distribution than the ordinary sites and act accordingly.

With the new experimental data, we are able to understand the optical and energy transfer processes in Nd\(^{3+}\) doped and Cr\(^{3+}\) codoped YAlO\(_3\) crystals. We report here the spectroscopic properties and energy transfer processes obtained by high-resolution and time-resolved spectroscopies of YAlO\(_3\):Nd and YAlO\(_3\):Nd,Cr crystals together with the

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analysis of various Cr³⁺ and Nd³⁺ fluorescence decays of different multisites.

2. Results and discussion

The YAlO₃:Nd, YAlO₃:Cr and YAlO₃:Nd,Cr crystal samples were grown by Preciosa a.s., Division Monokryszty in Turnov, Czech Republic. Cr³⁺ and Nd³⁺ fluorescence spectra were excited by a Lumonics dye laser, the spectra and decays were stored with a Canberra multichannel analyzer.

Selectively excited Nd³⁺ and Cr³⁺ emission spectra and the excitation spectra for various emission lines have been studied in detail. Some of the spectra are given in Fig. 1. These studies have shown that in YAlO₃:Nd or YAlO₃:Cr crystals are up to eight Nd³⁺ nonequivalent centres (multisites) and three Cr³⁺ nonequivalent centres (multisites).

For the first times it was observed that Cr³⁺ → Nd³⁺ energy transfer is from ²E Cr³⁺ energy level and that this transfer is observed between almost all Cr³⁺ and Nd³⁺ multisites. Fluorescence decay studies have shown that there is also energy transfer between Cr³⁺ multisites. However, it appears likely that there are anomalous shortrange interactions that occurs in pairs (either in Cr³⁺ ones or in pair centres Cr³⁺ – Nd³⁺).

Now, we have first results from the treatments of Cr³⁺ and Nd³⁺ fluorescence decays. Firstly, we consider the decay resulting from YAlO₃:Cr,Nd crystals where the Cr³⁺ donor concentration is C [%] and Nd³⁺ ions are found only as traces in crystals. The measured Cr³⁺ fluorescence decay for \( \lambda_{ex} = 724.017 \) nm pumped at \( \lambda_{ex} = 721.46 \) nm is well matched by the standard model where the relevant parameters are \( R_n = 4.77 \) nm and \( \tau_0 = 53.2 \) ms.

However, when the standard model for donor–acceptor energy transfer is compared to the acceptor data for \( \lambda_{em} = 875.65 \) nm of Nd³⁺ ions a poor fit is obtained, see Fig. 2. Evidently, the Nd³⁺ emission at \( \lambda_{em} = 875.65 \) nm does not represent the overall Nd³⁺ acceptor response; the assumed decay time of the Nd³⁺ acceptor was \( \tau = 214.6 \) μs.

We observe that both the Cr³⁺ donor and Nd³⁺ acceptor excited concentrations show a sudden deactivation at very short times. This indicates that many Cr³⁺ and Nd³⁺ ions are paired together, in essentially enhanced correlated placement. The fit for this enhanced placement for \( R_n = 4.77 \) nm, \( a = 2.20 \times 10^9 \) and \( b = 3.24 \) (according to equation presented in [2]) has shown a much better fit. Essentially, we must assume that aside from the very fast initial decay, the Nd³⁺ decay being observed at I(λ) is representative of Nd³⁺ and Cr³⁺ ions correlated each other. We therefore have an overall enhanced model with many pairs transferring immediately and the remaining ions fitting an enhanced correlation model.

3. Conclusions

The conclusions we have reached are very similar to those which were arrived for Y₃Al₅O₁₂:Cr,Tm,Ho [7]:

1) The Cr³⁺ donor decay can be adequately fit with the standard Inokuti–Hirayama theory.
2) The specific acceptor (some Nd\textsuperscript{3+} sites) decays we studied do not fit the standard model. This is true despite changing all possible parameters in the model ($R_a$ and $Q_a$). Evidently, the Nd\textsuperscript{3+} acceptor does not receive its energy equally from all donors.

3) An assumption of a spatial correlation between the Cr\textsuperscript{3+} donors and the Nd\textsuperscript{3+} acceptor, does a much better job fitting for the acceptor.

References


Fig. 1 (a) Nd\textsuperscript{3+} excitation spectrum of YAlO\textsubscript{3}:Cr (Nd traces) crystal at $T = 10$ K for $\lambda_{em} = 875.947$ nm; (b) Cr\textsuperscript{3+} selectively excited emission spectrum (in the spectral range of $R_1$ line) of YAlO\textsubscript{3}:Cr (Nd traces) crystal at $T = 6$ K for $\lambda_{ex} = 721.68$ nm.
Fig. 2 Nd$^{3+}$ fluorescence decay curve (1), ..., are experimental points of YAlO$_3$:Cr (Nd traces) crystal at $T = 10$ K and $\lambda_{em} = 875.65$ nm and the calculated curves: (2) standard model, (3) correlated model.