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Cr³⁺, Nd³⁺ multisites, pairs and energy transfer processes in laser crystal YAlO₃

J.A. MARES, G. BOULON*, A. BRENIER*, L. LOU^{*,(1)}, S.R. ROTMAN** and H. LURIA**

Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 162 00 Praha 6, Czech Republic

** LPCML, URA 442 du CNRS, Université Lyon I, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex, France*

*** Ben Gurion University of the Negev, Department of Electrical and Computer Engineering, 84105 Beer-Sheva, Israel*

Abstract

Detailed spectroscopic studies of YAlO₃:Nd, YAlO₃:Cr and YAlO₃:Nd,Cr have shown that these crystals contain up to eight Nd³⁺ multisites and three Cr³⁺ ones. Cr³⁺ → Nd³⁺ energy transfer is observed between various multisites and is starting from ²E Cr³⁺ energy level. Cr³⁺ donor decay can be adequately fit with the standard Inokuti–Hirayama theory but an assumption of a spatial correlation between Cr³⁺ donors and Nd³⁺ acceptors does a much better fit of Nd³⁺ fluorescence decay.

1. Introduction

Neodymium doped yttrium aluminium perovskite YAlO₃ (YAP) is one of the most important solid state laser crystals [1]. Cr³⁺ and Ce³⁺ codoping ions are added to Nd³⁺ lasing ions in YAlO₃ crystal for an improvement of the pumping efficiency (due to Cr³⁺ → Nd³⁺ or Ce³⁺ → Nd³⁺ energy transfers). Cr³⁺, Nd³⁺ multisites, ionic pairs and energy transfer processes in YAlO₃:Nd, YAlO₃:Cr and YAlO₃:Nd,Cr were investigated; the distribution of Nd³⁺, Cr³⁺ 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 Nd³⁺ doped and Cr³⁺ codoped YAlO₃ crystals. We report here the spectroscopic properties and energy transfer processes obtained by high-resolution and time-resolved spectroscopies of YAlO₃:Nd and YAlO₃:Nd,Cr crystals together with the

⁽¹⁾ L. Lou is leaving from the University of Science and Technology of China, 230026 Hefei, Anhui, The People's Republic of China

analysis of various Cr^{3+} and Nd^{3+} fluorescence decays of different multisites.

2. Results and discussion

The $\text{YAlO}_3\text{:Nd}$, $\text{YAlO}_3\text{:Cr}$ and $\text{YAlO}_3\text{:Nd,Cr}$ crystal samples were grown by Preciosa a.s., Division Monokrystaly in Turnov, Czech Republic. Cr^{3+} and Nd^{3+} fluorescence spectra were excited by a Lumonics dye laser, the spectra and decays were stored with a Canberra multichannel analyzer.

Selectively excited Nd^{3+} and Cr^{3+} 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 $\text{YAlO}_3\text{:Nd}$ or $\text{YAlO}_3\text{:Cr}$ crystals are up to eight Nd^{3+} nonequivalent centres (multisites) and three Cr^{3+} nonequivalent centres (multisites).

For the first times it was observed that $\text{Cr}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer is from ${}^2\text{E}$ Cr^{3+} energy level and that this transfer is observed between almost all Cr^{3+} and Nd^{3+} multisites. Fluorescence decay studies have shown that there is also energy transfer between Cr^{3+} multisites. However, it appears likely that there are anomalous shortrange interactions that occurs in pairs (either in Cr^{3+} ones or in pair centres $\text{Cr}^{3+} - \text{Nd}^{3+}$).

Now, we have first results from the treatments of Cr^{3+} and Nd^{3+} fluorescence decays. Firstly, we consider the decay resulting from $\text{YAlO}_3\text{:Cr,Nd}$ crystals where the Cr^{3+} donor concentration is C [%] and Nd^{3+} ions are found only as traces in crystals. The measured Cr^{3+} fluorescence decay for $\lambda_{\text{em}} = 724.017$ nm pumped at $\lambda_{\text{ex}} = 721.46$ nm is well matched by the standard model where the relevant parameters are $R_0 = 4.77$ nm and $\tau_p = 53.2$ ms.

However, when the standard model for donor-acceptor energy transfer is compared to the acceptor data for $\lambda_{\text{em}} = 875.65$ nm of Nd^{3+} ions a poor fit is obtained, see Fig. 2. Evidently, the Nd^{3+} emission at $\lambda_{\text{em}} = 875.65$ nm does not represent the overall Nd^{3+} acceptor response; the assumed decay time of the Nd^{3+} acceptor was $\tau = 214.6$ μs .

We observe that both the Cr^{3+} donor and Nd^{3+} acceptor excited concentrations show a sudden deactivation at very short times. This indicates that many Cr^{3+} and Nd^{3+} ions are paired together, in essentially enhanced correlated placement. The fit for this enhanced placement for $R_0 = 4.77$ 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 Nd^{3+} decay being observed at $I(\lambda)$ is representative of Nd^{3+} and Cr^{3+} 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 $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Cr,Tm,Ho}$ [7]:

- 1) The Cr^{3+} donor decay can be adequately fit with the standard Inokuti-Hirayama theory.

- 2) The specific acceptor (some Nd^{3+} sites) decays we studied do not fit the standard model. This is true despite changing all possible parameters in the model (τ_0^A and R_0). Evidently, the Nd^{3+} acceptor does not receive its energy equally from all donors.
- 3) An assumption of a spatial correlation between the Cr^{3+} donors and the Nd^{3+} acceptor, does a much better job fitting for the acceptor.

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Fig. 1 (a) Nd^{3+} excitation spectrum of $\text{YAlO}_3:\text{Cr}$ (Nd traces) crystal at $T = 10$ K for $\lambda_{\text{em}} = 875.947$ nm; (b) Cr^{3+} selectively excited emission spectrum (in the spectral range of R_1 line) of $\text{YAlO}_3:\text{Cr}$ (Nd traces) crystal at $T = 6$ K for $\lambda_{\text{ex}} = 721.68$ nm.

Fig. 2 Nd^{3+} fluorescence decay curve (1), $\dots$ are experimental points of $\text{YAlO}_3\text{:Cr}$ (Nd traces) crystal at $T = 10\text{ K}$ and $\lambda_{\text{em}} = 875.65\text{ nm}$ and the calculated curves: (2) standard model, (3) correlated model.