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N. Viegas, B. Teisseire, G. Aka, A. Kahn-Haradi, D. Vivien. Optical properties of modified YAB single crystals: $\text{Y}_{1-x}\text{Ln}_x(\text{Al}_{1-y}\text{Ga}_y)_3(\text{BO}_3)_4$. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-357-C4-360. 10.1051/jp4:1994485 . jpa-00252748

HAL Id: jpa-00252748

<https://hal.science/jpa-00252748>

Submitted on 1 Jan 1994

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Optical properties of modified YAB single crystals: $Y_{1-x}Ln_x(Al_{1-y}Ga_y)_3(BO_3)_4$

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Abstract

One of the best self frequency-doubling materials is NYAB, $Y_{1-x}Nd_xAl_3(BO_3)_4$. Optical properties of isomorphous modified NYAB, obtained by gallium substitution to aluminum (NYAB-Ga) or Yb doping ion, are investigated.

Introduction

A way to develop solid state coherent sources in the visible range (blue-green) is the direct emission of visible light by internal second harmonic generation of the IR laser emission, thanks to the non linear optical properties of the matrix. One of the best self frequency-doubling materials is NYAB, $Y_{1-x}Nd_xAl_3(BO_3)_4$.^(1, 2)

Yet this material is still to be improved: NYAB crystals, prepared by flux methods, are not large ($5 \times 5 \times 10 \text{ mm}^3$). Moreover, this compound exhibits a Nd^{3+} absorption at 532 nm, reducing the yield of the expected visible emission.

Therefore, isomorphous compounds, obtained by gallium substitution to aluminum (NYAB-Ga) or Yb doping of YAB, are investigated in order to improve the crystal growth and try to minimize the re-absorption losses in the visible range.

I - Study of modified NYAB:

Gallium containing NYAB compounds, with $Y_{1-x}Nd_x(Al_{1-y}Ga_y)_3(BO_3)_4$ general formula are obtained by solid state reaction, for $0 < y < 0.9$ Ga and $0 < x < 0.25$ Nd. Crystals are grown by a flux method, using potassium trimolybdate $K_2Mo_3O_{10}$ as solvent. Fairly perfect pink crystals of $Y_{1-x}Nd_x(Al_{1-y}Ga_y)_3(BO_3)_4$ ($0 < x < 0.5$) are

obtained ($3 \times 3 \times 5 \text{ mm}^3$) with good optical quality. All crystals have hexagonal prismatic habits with rhombohedral structure (space group R32).

In NYAB lattice, the active neodymium ion is found on Y^{3+} sites, in D_3 site symmetry, Al^{3+} ions in site symmetry C_2 . Boron ions are arranged in sheets of connecting $[BO_3]$ triangles, perpendicular to $[111]$.

Refinements of the NYAB structure performed, on single crystals, point out the modifications introduced around Nd^{3+} by the presence of gallium :

- Ln-Ln distances increase with increasing values of y

- Ln-O bond lengths increase with the Ga content, this suggests a weaker crystal field around Ln^{3+} active ion. This should be favourable to avoid quenching by cross relaxation process.-

The B_1 boron atom has a more symmetrical site than B_2 , the environment of which undergoes more distortion when the Ga proportion increases.

Optical study of Nd^{3+} in NYAB-Ga

Experiments were conducted on NYAB-Ga crystals containing 30 % gallium, for two Nd^{3+} compositions: ($Y_{1-x}Nd_x(Al_{0.7}Ga_{0.3})_3(BO_3)_4$ with $x=0.05$ and 0.15). The optical behavior was compared to that of NYAB.

1 - Polarized absorption measurements

The σ ($E \perp c$) and π ($E // c$) polarized absorption spectra recorded for NYAB-Ga present the same particularities as NYAB (fig.1). The σ polarization spectrum is much more intense than for π polarization.

3 - Fluorescence lifetimes

Fluorescence decays of NYAB and NYAB-Ga are exponential for all studied samples. In NYAB -Ga, the ${}^4F_{3/2}$ state luminescence lifetimes τ_{lum} are short (48 μ s), which is close to the reported NYAB τ_{lum} values (50-60 μ s). Significant temperature dependence was not observed in the range 300-15 K. The total radiative transition rate and the branching ratio for electric-dipole transition from ${}^4F_{3/2}$ to 4I_j manifold were calculated. Branching ratios for NYAB-Ga are compared to those of NYAB in table III.

Table III- Branching ratios for ${}^4F_{3/2} \rightarrow {}^4I_j$ transitions in NYAB-Ga and NYAB

Transition	NYAB - Ga		NYAB		
	$\lambda(\text{nm})$	β_{π}	β_{σ}	β_{π}	β_{σ}
${}^4F_{3/2} \rightarrow {}^4I_{9/2}$	867	0.329	0.368	0.27	0.37
${}^4F_{3/2} \rightarrow {}^4I_{11/2}$	1063	0.522	0.500	0.56	0.50
${}^4F_{3/2} \rightarrow {}^4I_{13/2}$	1350	0.146	0.129	0.17	0.13
${}^4F_{3/2} \rightarrow {}^4I_{15/2}$	1880	0.003	0.003	0.004	0.003

The calculated radiative lifetime was found to be $\tau_{rad} = 174 \mu$ s, whereas the radiative lifetime in NYAB is $\tau_{rad} = 267 \mu$ s. Hence, the quantum efficiency of ${}^4F_{3/2}$ emission state in Nd^{3+} is about 27.4% in NYAB-Ga. The origin of this low quantum efficiency could be cross relaxation and/or non radiative transition.

- In the structure of NYAB-Ga, Nd^{3+} ions are shielded by the B-O-Al triangular prisms, and the Nd-Nd distance is relatively large (5.908 Å). Therefore Nd-Nd interaction should be weak (no cross relaxation).
- From 5 to 15% Nd^{3+} content, no appreciable variations of the luminescence lifetime were detected (no concentration quenching).

The low quantum efficiency in these materials could then results from a multiphonon non-radiative process.

Absorption spectra show that partial replacement of Al^{3+} by Ga^{3+} ions in NYAB

does not change the high energy phonons which are related to $(BO_3)^{3-}$ anions.

The largest observed phonon energy is about 1347 cm^{-1} and the energy gap ΔE between ${}^4F_{3/2}$ and ${}^4I_{15/2}$ states is about 5400 cm^{-1} . Therefore, the emission of only a few phonons with such energy is required to fill this energy gap.

A theoretical value of the ${}^4F_{3/2}$ luminescence lifetime was computed and the non-radiative emission rate evaluated, using the Reisberg and Moos theoretical approach⁽⁴⁾ of multiphonon relaxation process. The resulting computed theoretical luminescence lifetime is $\tau_{lum} = 49.9 \mu$ s (at 300K), which is very close to the experimental values ($\tau_{lum} = 47.8 \mu$ s).

This theoretical approach looks consistent with the non significant temperature dependence of the Nd^{3+} fluorescence lifetime. Therefore the low quantum efficiency in these materials probably arises from the non-radiative ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition, which has a high probability, by emitting four 1344 cm^{-1} phonons.

Discussion

A partial substitution of Ga^{3+} to Al^{3+} ions in NYAB structure seems to induce positive effects, as listed in the following :

- 1 - Second harmonic generation from a pulsed Nd^{3+} : YAG laser has been demonstrated, using a NYAB-Ga crystal grown by flux methods.
- 2 - Oscillator strengths are higher in NYAB-Ga than in NYAB. However, the ${}^4F_{3/2}$ excited state lifetime is as short as the NYAB one.
- 3 - Ga substitution to Al induces a weaker crystal field around the active ion. Nd^{3+} fluorescence bands become broader when the gallium content increases in the host lattice. This corresponds to a structural disorder of Nd^{3+} environment and a lower Nd site symmetry, probably responsible for

Fig 1 - Polarized absorption spectra of NYAB-Ga. Nevertheless, the band peaking at 805 nm seems less sensitive to the direction of polarization.

The Judd-Ofelt intensity parameters are obtained by a linear least squares fit of the absorption line strengths using calculated reduced matrix elements between the states involved⁽³⁾. Table I lists polarized intensity parameters as well as the Ω^{eff} .

Table I - Judd-Ofelt parameters of Nd³⁺ in various host lattices at 300K (units 10⁻²⁰cm²)

Ω parameters	NYAB-Ga/NYAB			Ca ₂ Al ₂ SiO ₇ (6)	Ca ₂ Ga ₂ SiO ₇ (7)
	π	σ	effective		
Ω_2	1.70/ 1.13	6.51/ 5.18	4.91/ 3.83	0.90	0.82
Ω_4	2.16/ 0.89	4.66/ 3.52	3.89/ 2.58	3.40	2.41
Ω_6	6.37/ 4.39	9.22/ 6.81	8.27/ 6.00	4.90	6.44
RMS	5.21 10 ⁻⁶ / 5.04 10 ⁻⁷	6.28 10 ⁻⁷ / 7.12 10 ⁻⁷			

This suggests that a laser diode could be used to pump NYAB-Ga crystals. In addition, to minimize re-absorption losses an efficient end pumping scheme of NYAB-Ga at 806 nm should be done with π polarization.

2 - Fluorescence measurements

Polarized fluorescence measurements and lifetime measurements look very similar for NYAB and NYAB-Ga (fig. 2).

The main fluorescence peak is centered at 1.063 μ m for σ and π polarizations and, in both compounds, the σ emission is more intense than the π one. Nevertheless, the NYAB-Ga emission is less sensitive to

polarization than the NYAB one, for which the intensity decreases dramatically with π polarization. Moreover, the spectral widths are slightly broader in NYAB-Ga. The emission cross section is of the same order of magnitude in NYAB-Ga and in NYAB, as shown in table II.

fig.2 - Polarized fluorescence spectra of NYAB-Ga and NYAB at 100 K, for the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition

This confirms that a partial substitution of Ga³⁺ to Al³⁺ ions induces positive effects on the material optical behavior.

Table II - Optical parameters for NYAB-Ga, compared to NYAB

Parameters	NYAB-Ga	NYAB
$\sigma_e(\text{cm}^2)$ π	$1.28 \cdot 10^{-19}$	$1.25 \cdot 10^{-19}$
σ	$2.47 \cdot 10^{-19}$	$2.60 \cdot 10^{-19}$
Nd concentr.	$8.16 \cdot 10^{20}$	$8.40 \cdot 10^{20}$
τ rad ($^4F_{3/2}$)	174 μ s	267 μ s
$^4F_{3/2}$ quantum efficiency	27.4 %	17.3 %

fig.3 -absorption(a), fluorescence (b) and energy-levels diagram(c) of Yb^{3+} -doped YAB crystals

the admixture of odd-parity transitions into the $4f^3$ configuration of Nd^{3+} .

All these results suggest that Ga^{3+} ions do not alter the optical properties of NYAB-like crystals. NYAB-Ga crystals could be pumped efficiently with a laser diode. In addition, to minimize re-absorption losses at 532 nm, during a self frequency doubling laser test, the most efficient end pumping scheme of NYAB-Ga should be done with π polarization.

II - Optical study of Yb^{3+} -doped YAB

$\text{Yb}^{3+}:\text{YAl}_3(\text{BO}_3)_4$ is studied to evaluate its emission and absorption properties in order to assess the potential self frequency doubling performance of this material. Indeed, Yb^{3+} is ideally suited for diode pumping, since it has quite a simple energy-level diagram to be used in a laser system.

Large size crystals ($7 \times 7 \times 5 \text{ mm}^3$) of Yb^{3+} -doped YAB, of good optical quality, have been grown by a flux method ($\text{Y}_{1-x}\text{Yb}_x\text{Al}_3(\text{BO}_3)_4$, with $x = 0.05, 0.02, 0.15$).

The absorption band around 480 nm (fig 3a) is quite broad (FWMH = 19 nm). It means that thermal requirements on the pumping laser diode would be less drastic than in Nd:

YAG for example. The computed value of oscillator-strength at 974 nm is 3.29×10^{-6} .

Fluorescence spectra are given in fig.3b from 300 to 20K, with a good resolution of the $2F_{5/2} \rightarrow 2F_{7/2}$ transition at 20 K. The main peaks are around 1000 and 1035nm. Yb^{3+} -energy level diagram in YAB is given in fig. 3 c and $\text{Yb}^{3+}:\text{YAB}$ is a quasi four-level system. Compared to other Yb doped matrices, this one shows a very narrow overlapping between absorption and emission wavelength ranges. The main emission line at 1035nm would result in a visible emission at 517nm by self doubling frequency, where no re-absorption occurs.

Therefore $\text{Yb}^{3+}:\text{YAB}$ non linear matrix could offer a number of advantages in a self frequency doubling operating laser.

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