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Optical spectroscopy of Nd^{3+} ions in $Gd_XY_{1-X}Al_3(BO_3)_4$

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Abstract

In this work, the optical spectroscopy (absorption and luminescence) of a new Nd^{3+} activated non-linear crystal, $Gd_XY_{1-X}Al_3(BO_3)_4$, with $x=0.25$, has been investigated. The crystal structure of this system is quite similar to that of one of the best self frequency doubling crystals, $YAl_3(BO_3)_4$ (YAB). Results show absorption bands very similar, but broader than those observed in Nd:YAB. This suggests the possibility of two non-equivalent environments for the Nd^{3+} ions, corresponding to the replacement of Y^{3+} and Gd^{3+} lattice sites.

Keywords: Solid state lasers; Crystal structure; Optical spectroscopy

1. Introduction

Aluminum borate crystals of the general composition $RAl_3(BO_3)_4$ are widely known non-linear materials. In particular, the $YAl_3(BO_3)_4$ (YAB) crystal has been proved to be an excellent frequency doubling material. In fact, doping with Nd^{3+} ions it has been used to make an excellent Self-Frequency Doubling (SFD) laser [1]. In addition, Red, Green and Blue (RGB) laser light has been obtained from a single Nd:YAB crystal [2]. Tunable UV laser light has been also demonstrated [3].

The present work concerns the spectroscopic characterization of Nd^{3+} ions in a new non-linear optical material, the $Gd_XY_{1-X}Al_3(BO_3)_4$, with $x=0.25$ (GYAB). This host is isostructural to that of YAB, although a percentage of the Y^{3+} ions has been replaced by Gd^{3+} ions [4]. The problem of concentration quenching in Nd:YAB (the concentration in laser crystals has been limited to a 5 at.%) could be slightly improved according to the better match of the Nd^{3+} ionic radius with Gd^{3+} in comparison with Y^{3+}. This should improve the visible laser characteristics in spite of the slight decrease in the nonlinear coefficient of GYAB [5].

2. Experimental results

A crystal of $Gd_XY_{1-X}Al_3(BO_3)_4$, with $x=0.25$ and doped with 5% of Nd^{3+} in the melt, has been grown by the flux method in the Fujian Institute of Research on the Structure of Matter, China [4]. A sample of 1.6 mm thickness was cut and oriented for frequency doubling the Nd:YAG infrared laser light and then carefully polished up to laser quality.

Absorption spectra were taken in a 0.1 nm resolution two beam Spectrophotometer (Hitachi model U-401). In the fluorescence spectra a CW Ar^{+} pumped Ti:sapphire laser was used as pump source, whereas the emitted light was detected with a 0.5 M Spex monochromator (0.01 nm resolution) and a Hamamatsu R636 photomultiplier. A 10 K absorption measurement was performed with a Leybold close cycle Helium cryostat. Luminescence measurements were carried out with a Liquid Nitrogen (LN) cryostat.

The 10 K absorption spectrum of Nd^{3+} in GYAB consists of several groups of lines corresponding to transitions among the Stark sublevels of $^{2S+1}L_J$ states within the $4f^3$ electronic configuration of the Nd^{3+} ion. All these absorption bands are similar but broader than those observed in Nd:YAB. This fact can be clearly visualised in Fig. 1, where the 10 K absorption spectra corresponding to the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition for both Nd:YAB [6] and Nd:GYAB are shown. The broadening of the absorption bands in Nd:GYAB suggests the presence of two non-equivalent Nd^{3+} centers associated with the possibility of two non-equivalent environments for the Nd^{3+} ions, corresponding to the replacement of Y^{3+} and Gd^{3+} lattice

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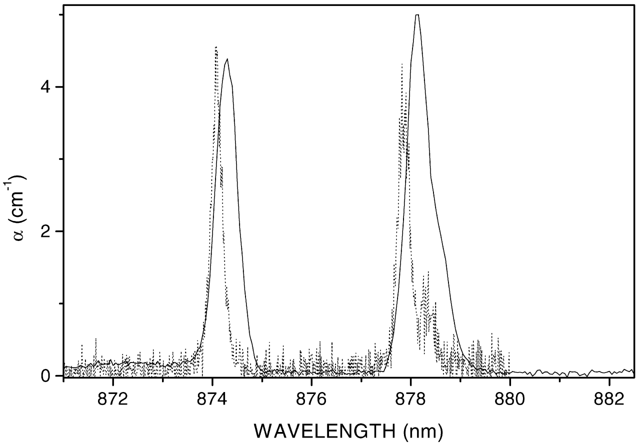

Fig. 1. 10 K absorption spectra of Nd:GYAB (continuous line) and Nd:YAB (dotted line) in the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ region.

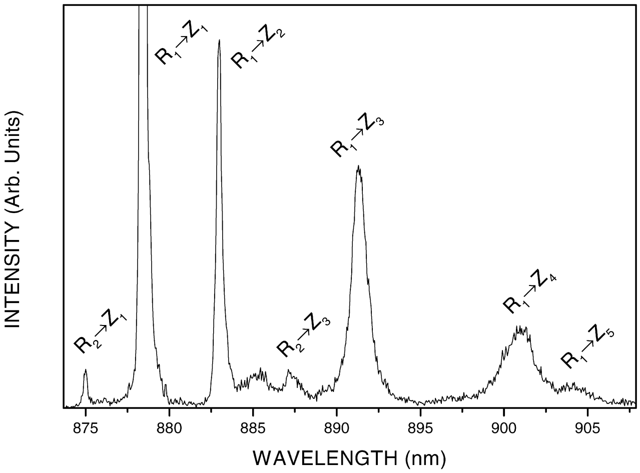

Fig. 3. LN emission spectrum of Nd:GYAB exciting at 879 nm.

sites. In fact, Fig. 2 shows how two gaussian bands at 878.1 and 878.6 nm (associated with the two expected centers) can be used to fit the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ (R_1) absorption band. Considering the great similitude between the absorption bands of Nd^{3+} ions in GYAB and YAB, and the fact that, in principle, our crystal contains three times more Y^{3+} than Gd^{3+} available sites, it is reasonable to think that Nd^{3+} ions might be occupying predominantly Y^{3+} lattice sites in the same proportion (3:1). Moreover, it is not expected a preference of one of these two Y^{3+} or Gd^{3+} lattice sites for the Nd^{3+} ions in view of the similar ionic radii; Y^{3+} (1.05 Å) and Gd^{3+} (1.06 Å). Thus, the highest gaussian component (peaking at 878.1 nm) in the spectrum of Fig. 2 could be attributed to Nd^{3+} ions replacing Y^{3+} lattice cations, while the other component (peaking at 878.6 nm) would be related to Nd^{3+} ions replacing Gd^{3+} sites. In fact, the intensity proportion of these two components fit is near 3:1, according to the expected available ratio.

As for Nd:YAB, the two Stark components R_1 and R_2 of the $^4F_{3/2}$ excited state are separated only ~53 cm^{-1}, and hence, thermalisation effects are minimised at temperature lower than 20 K. At higher temperatures (>20 K), it can be observed the appearance of thermal transitions. Fig. 3 shows, as an example, the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission spectrum, at LN temperature, recorded under excitation within the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ (R_1) absorption band at 878 nm. Seven peaks are clearly observed (included the pump peak), instead of the five peaks expected from $^4I_{9/2}$ ground state degeneracy. This is due to a thermal population of the R_2 sublevel from the R_1 one of the $^4F_{3/2}$ state. As consequence an anti-Stoke emission, corresponding to the $^4F_{3/2}(R_2) \rightarrow {}^4I_{9/2}$ (Z_1) transition, can also be observed. Such emission spectrum is very similar to that of Nd:YAB, taken under the same conditions. Thus, the major fraction of Nd^{3+} ions incorporated in the host is expected to retain the environment to the Y^{3+} lattice site, which is trigonal D_3 symmetry. Within such local symmetry all $^{2S+1}L_J$ states appear split by the crystalline field into the maximum number of Kramers levels (2J+1)/2. At the present, we are performing polarised and site selective laser spectroscopy at 10 K with other crystal compositions in order to confirm the presence of the two non-equivalent Nd^{3+} centers, which could be associated with Nd^{3+} ions replacing Y^{3+} and Gd^{3+} lattice sites, as well to determine their spectral characteristics.

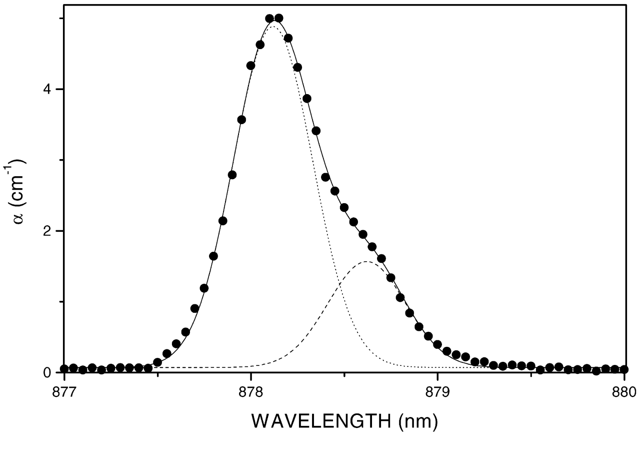

Fig. 2. 10 K absorption spectrum corresponding to the $^4I_{9/2} \rightarrow {}^4F_{3/2}(R_1)$ transition.

3. Conclusions

From a first analysis of the absorption and luminescence properties of Nd:GYAB in the near infrared region the presence of two non-equivalent Nd^{3+} centers, associated with the possibility of Nd^{3+} ions replacing Y^{3+} and Gd^{3+} lattice cations, has been suggested. The dispersion of Nd^{3+} ions among these two lattice sites seems to be strongly related to the available Y^{3+} and Gd^{3+} cation proportion for a particular crystal composition.

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