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Spectroscopic and crystallographic studies of YAG:Pr^{4+} single crystals

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Abstract

$Y_3Al_5O_{12}$ single crystals doped with praseodymium and magnesium ions have been prepared. The reversible color change of these crystals are observed when annealing in oxidizing or reducing atmospheres. The change is ascribed to the formation of Pr^{4+} in the as-grown crystal, caused by the second dopant, Mg^{2+}. The absorption spectra of YAG:Pr,Mg in the range 200–1100 nm, as grown and annealed in air and H_2/N_2 atmosphere, are presented and discussed. Additional broad absorption bands are observed for the as-grown crystals and those annealed in oxidizing atmosphere. Crystallographic investigations of the original crystal and after annealing in a reducing atmosphere as described above, show no distinct structural differences. A redox mechanism is proposed to explain the color change during annealing. © 1998 Elsevier Science S.A.

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1. Introduction

Yttrium–aluminum garnet $Y_3Al_5O_{12}$ (YAG) doped with different active elements is the most widely used laser material for solid state lasers. The crystal structure of YAG has been solved and refined several times using neutron and X-ray diffraction measurements. Yttrium–aluminum garnet crystallizes in a cubic lattice within the Ia-3d space group. The oxygen ions form a three-dimensional structure in which three kinds of sites exist: dodecahedral (c), octahedral (a) and tetrahedral (d). Yttrium cations are located in dodecahedral sites, and aluminum cations are located in both octahedral and tetrahedral sites. Lanthanide dopants are usually located in dodecahedral sites and other smaller dopants in the octahedral and tetrahedral sites, depending on the ionic radius of the doped cation [1].

In YAG crystals doped with praseodymium, the latter exists in the 3+ oxidation state. Such crystals are already known, and different types of investigations have already been reported [2,3].

The last few years has seen a growing interest in Pr^{4+} as a dopant in the solid state [4–6]. There are a few articles on this subject, in which all the investigations were made on oxide compounds in polycrystalline form. The work of Gramsch and Morss [4] is related to Pr^{4+} as a dopant in a yttrium–gallium garnet lattice.

In this paper, we present the results of our investigations on praseodymium and magnesium doped yttrium–aluminum garnet single crystals with Pr^{4+}. The 4+ oxidation state of praseodymium was obtained by incorporating a second dopant into the YAG host, namely Mg^{2+}. This codopant causes a loss of charge balance in the crystal, which is restored by a change of the oxidation state of some praseodymium ions to the 4+ state. Doped with Pr^{3+}, YAG single crystals have a green color which is permanent, i.e. annealing at high temperature and in different atmospheres does not change it. When doped with Pr^{3+} and Mg^{2+}, the YAG single crystals have a brown coloration, which is sensitive to thermal treatment.

Spectroscopic and structural measurements on YAG:Pr,Mg crystals under thermal treatment are presented.

2. Experimental

2.1. Crystal growth

The crystals were grown by the Czochralski method using MSR-3 Malvern-type devices and a r.f. heated iridium crucible in a N_2 atmosphere with about 3% O_2.

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The crucible loading was prepared in stoichiometric composition using high purity (not less than 4.5 N) Y_2O_3, Al_2O_3, Pr_6O_{11} and MgO oxides, according to the formula

$$(Y_{1-x-y}Pr_xMg_y)_3Al_5O_{12}$$

where $x = 0.012$ and $y = 5\times10^{-6}$, which corresponds to concentrations, n, of Pr and Mg ions of: $n(\mathrm{Pr}) = 1.7\times10^{20}\ \mathrm{cm}^{-3}$ and $n(\mathrm{Mg}) = 10^{17}\ \mathrm{cm}^{-3}$.

The as-grown crystal had a brown coloration and high optical quality, checked by elastometric methods. The concentrations of praseodymium and magnesium ions were checked by the chemical ICP method. Note that the concentration given for magnesium ions may be affected by a significant error.

A YAG crystal doped only with praseodymium ions (with a similar concentration of Pr ions as for the crystal described above) was also studied. This crystal was grown under the same conditions as for the previous crystal. The YAG:Pr crystal has a green coloration due to Pr^{3+}.

2.2. Thermal treatment

The "as-grown" YAG:Pr,Mg crystals were annealed in oxidizing and reducing atmospheres. For hermetic reducing conditions, a hydrogen furnace with a molybdenum heater was used. The annealing was carried out in a 33.3% H_2/66.7% N_2 atmosphere at 1200°C. A kanthal furnace was used to obtain the oxidizing conditions. The latter annealing was performed in air at 1200°C.

2.3. Spectroscopic measurements

Optically homogenous parts of the brown, as-grown YAG:Pr,Mg crystal were cut to obtain samples for measurements. Similarly, an optically homogeneous part of the green, as-grown YAG:Pr crystal was cut to obtain a sample. Several annealing processes were carried out on the samples in air and H_2/N_2 atmospheres.

The transmission spectra of the samples were recorded with spectrophotometers (Perkin-Elmer LAMBDA-2 within the 200–1100 nm range; Beckmann ACTA MVII within 1.1–1.4 μm and Perkin-Elmer FTIR 1725 within 1.4–2.5 μm; and Hitachi-Perkin Elmer model 340 within the range 200–1100 nm). The measured transmission values were used to compute the absorption spectra.

3. Results and discussion

The brown as-grown YAG:Pr,Mg monocrystals were annealed in air (1200°C). This intensifies the brown coloration of the sample. The same monocrystals annealed in a H_2/N_2 atmosphere (1200°C) changed color to green. The conversion is reversible, when repeating the thermal treatment in reducing or oxidizing atmospheres. The green as-grown YAG:Pr monocrystal treated in the same way does not show any color changes, i.e. its color is permanent. This behavior of YAG:Pr,Mg monocrystals suggests that the color changing process in red/ox conditions is associated with a red/ox process of the praseodymium ion changing its oxidation state. The oxidizing process is a long-term process, which is associated with the diffusion of the oxidizing agent. The reduction process, as we can see from our experiments, is very fast. Even annealing for 15 min in a H_2/N_2 atmosphere changes the color to green.

The absorption spectra of YAG:Pr,Mg single crystalline samples are presented in Fig. 1 for the range 300–1100 nm. The spectra of both samples exhibit the characteristic absorption lines for Pr^{3+} (in the regions 430–500, 570–620 and 960–1040 nm). The spectrum of the crystal annealed in a H_2/N_2 atmosphere (spectrum 2), having a green coloration, contains only absorption lines of Pr^{3+}. The absorption coefficient is identical to praseodymium only doped YAG crystals. The spectrum of the as-grown brown crystal (spectrum 1) contains additional broad features in the range 300–570 nm.

The differential absorption coefficient spectra of the examined crystals are presented in Fig. 2. They mainly exhibit the wide absorption bands characteristic for brown crystals. The absorption maxima of these bands occur at around 330 and 395 nm. Additionally, a very broad region of the differential absorption extends up to about 550–570 nm. These bands overlap one another. The short-wavelength part of these bands is located on the shoulder of much stronger bands with maxima between 200 and 300 nm.

The absorption of thin (about 100 μm) brown (as grown) and green (annealed in H_2/N_2) samples in the region 200–320 nm is presented in Fig. 3. Two very strong absorption bands are visible in the spectra of both samples, with maxima at 239 and 290 nm. The absorption coefficient of the brown (as-grown) sample is about 15% larger than that of the green (annealed in H_2/N_2) sample. The

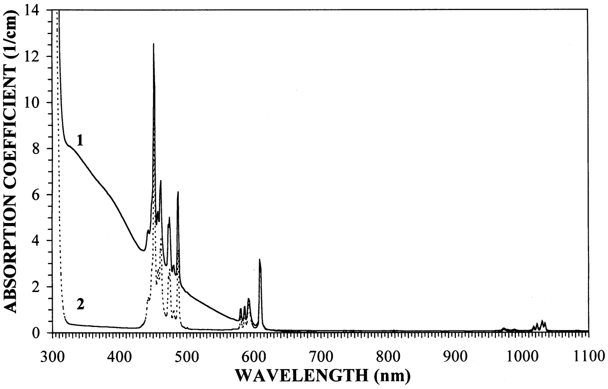

Fig. 1. Changes in the absorption spectrum of YAG:Pr,Mg crystals under thermal treatment: (1) brown crystal "as grown"; (2) green crystal after annealing in a H_2/N_2 reducing atmosphere, 8 h, 1200°C.

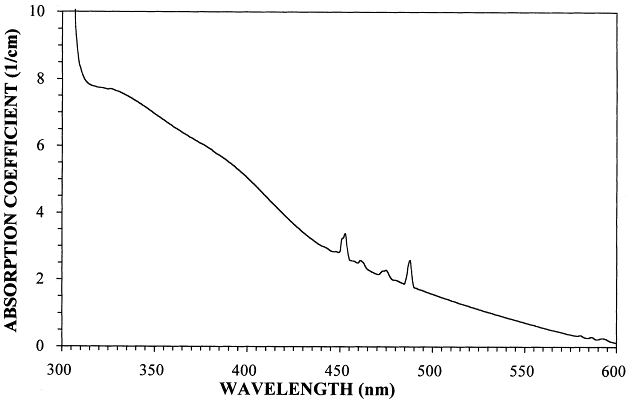

Fig. 2. Difference between absorption of the “as-grown” YAG:Pr,Mg crystal and the crystal annealed in a H_2/N_2 reducing atmosphere. The lines between 450 and 500 nm are the residuals of the Pr^{3+} spectrum.

same absorption bands are also present for the YAG:Pr^{3+} sample not codoped with Mg^{2+} ions.

Pr^{4+} is isoelectronic with Ce^{3+}. The Ce^{3+} dopant in YAG and in the other oxide hosts has been the subject of extensive studies in the past due to the possible application as scintillators. It has been established that the absorption spectrum of YAG:Ce^{3+} is associated with 4f→5d transitions [7–9]. The spectrum consists of five 4f→5d transitions in the region 460–200 nm. Similar results can be expected in the case of Pr^{4+}.

Therefore, we associate the bands in the region 300–570 nm with the 4f→5d transitions of Pr^{4+} [10]. The intensity of this band increases if green crystals (previously annealed in H_2/N_2) are annealed in air and reaches saturation after about 10 h of annealing. This indicates that the quantities of Pr^{4+} and Mg^{2+} in the crystal have equalized.

The strong bands observed in the region 200–300 nm are also sensitive to thermal treatment, although they do not disappear completely after annealing in a reducing atmosphere. There is a chance of accidental overlap of the higher energy bands associated with the Pr^{4+} f–d transitions with absorption bands associated with the other charge-transfer states. These charge-transfer bands could be associated with an unidentified dopant, sensitive to thermal treatment. Additional studies are necessary to explain the origin of the bands observed in this spectral region.

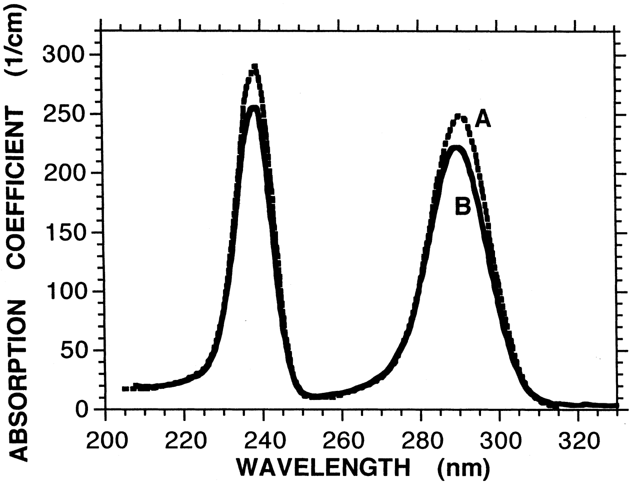

Fig. 3. Absorption coefficient of the “as-grown” sample (A), and the sample annealed in a H_2/N_2 reducing atmosphere (B) in the region 200–320 nm.

An attempt was made to detect luminescence from Pr^{4+}. Unfortunately, such luminescence was not observed. Emission from Pr^{3+} only was detected. The energy transfer from Pr^{4+} to Pr^{3+} can explain the lack of Pr^{4+} luminescence.

The composition of our crystals is given by the formula

$$Y^{3+}_{3-x-y}Pr^{3+}_{x-z}Mg^{2+}_{y}Pr^{4+}_{z}Al_5O_{12}$$

where $0 \leq z \leq x$. During crystallization from the melt, a relatively small amount of Pr atoms is incorporated into the crystal as Pr^{4+}, and the remaining atoms as Pr^{3+}. Further, Pr^{3+} to Pr^{4+} oxidation (up to $z=x$) must be performed in the solid phase by heating the crystal in an oxidizing atmosphere.

The stoichiometric state of the YAG:Pr,Mg crystal is when $z=x$. It is the state of saturation, when the change of each Mg^{2+} is compensated by a Pr^{4+} ion. During annealing of the stoichiometric crystal in a hydrogen atmosphere, non-stoichiometric conditions are generated, causing defects to arise in the oxygen sublattice. This is in spite the fact that vacancy formation in garnet structures is usually quite difficult [11]. The loss of oxygen compensates the total charge balance. The process of thermal annealing in a reducing atmosphere proceeds according to the following expression:

$$\begin{gathered} Y^{3+}_{3-x-y}Pr^{3+}_{x-y}Mg^{2+}_{y}Pr^{4+}_{y}Al_5O_{12} \\ H_2\downarrow - O_2 \\ Y^{3+}_{3-x-y}Pr^{3+}_{x}Mg^{2+}_{y}Al_5O_{12-y/2} \end{gathered}$$

Unfortunately, the oxygen stoichiometry in this crystal cannot be measured accurately because the mass loss is too small. In the YAG crystal doped only with praseodymium ions, the stoichiometric state appears as

$$Y^{3+}_{3-x}Pr^{3+}_{x}Al_5O_{12}$$

and there is no possibility for any reversible change in reducing and oxidizing atmospheres.

Our X-ray study demonstrates that the structure of our crystal is in good agreement with literature data. Our data are very similar to those obtained for YAG:Nd ($x=0.042$) structures [12]. The measured lattice constants of the brown and green crystals differ significantly. The brown YAG:Pr,Mg crystal lattice parameter 12.0075(8) Å is smaller than that of the green YAG:Pr,Mg crystal, 12.0119(9) Å. This is in agreement with our hypothesis, since Pr^{4+} has a much smaller ionic radius ($VIII_{coord.}$ = 1.10 $Å_{(cr)}$, 0.96 $Å_{(ir)}$; $VI_{coord.}$ = 0.99 $Å_{(cr)}$, 0.85 $Å_{(ir)}$) than Pr^{3+} ($VIII_{coord.}$ = 1.266 $Å_{(cr)}$, 1.126 $Å_{(ir)}$), according to Shannon [13] (where cr is the crystal radius and ir is the effective ionic radius) (1.332 Å), and Espinosa [14].

Acknowledgements

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