Conference paper

OPTO-ELECTRONICS REVIEW 7(2), 149–152 (1999)

Growth and optical properties of Nd:YVO_4 laser crystals♣

S.M. KACZMAREK[1*], T. ŁUKASIEWICZ[2,3], W. GIERSZ[2], R. JABŁOŃSKI[2], J.K. JABCZYŃSKI[1], M. ŚWIRKOWICZ[2], Z. GAŁĄZKA[2], W. DROZDOWSKI[4] and M. KWAŚNY[1]

[1]Institute of Optoelectronics, MUT, 2 Kaliskiego Str., 00-908 Warsaw, Poland
[2]Institute of Electronic Materials Technology, 133 Wólczyńska Str., 01-919 Warsaw, Poland
[3]Institute of Applied Physics, MUT, 2 Kaliskiego Str., 00-908 Warsaw, Poland
[4]Institute of Physics CU, 5 Grudziądzka Str., 87-100 Toruń, Poland

Growth conditions for Nd:YVO_4 crystals and some optical properties are presented. The obtained Nd: YVO4 crystal shows lower content of point defects and consequently, lower susceptibility to ionising radiation. ESR measurements show the presence of V ions in interstitial sites with another than 5t valency. Obtained by Czochralski method crystals reveal very good optical properties, some of which are better than for Nd:YAG.

Keywords: crystal growth, absorption, electron spin resonance, gamma and electron irradiations

1. Introduction

Yttrium ortovanadate single crystals YVO_4 doped with rare earth elements are very attractive laser material currently used for micro and diode laser pumped solid-state laser. Physical properties make them superior to Nd: YAG [1]. In comparison with Nd: YAG for diode laser pumping Nd:YVO_4 lasers reveal the advantages of lower dependence of pump wavelength on temperature, high slope efficiency, lower lasing threshold, linearly polarised emission and tend to the single-mode output. The peak pump wavelength for these two crystals is 808 nm, the standard wavelength of currently manufactured high power diodes for laser pumping. For the applications in which compact design and the single longitudinal-mode output is needed Nd:YVO_4 shows its particular advantages over other laser crystals used at present.

The material shows high absorption coefficient, high optical transparency in the 400–5000 nm range, large stimulated emission cross section at lasing wavelength (25×10^{-19} cm^2), strong birefringence (n_o = 1.958, n_e = 2.168 at 1064 nm), good optical, physical, and mechanical properties (crystal structure – tetragonal: a = b = 7.12 Å; c = 6.29 Å. Density: 4.22 g/cm^3. Mohs hardness ~5. Thermal expansion coefficient: $\alpha_a = 4.43 \times 10^{-6}$/K. Thermal conductivity coefficient: $\|c\ \lambda = 0.0523$ Wcm/K, $\perp c\ \lambda = 0.0510$ Wcm/K).

However, for the above mentioned applications, scattering free Nd:YVO_4 single crystals of high quality are required. Since scattering is related to the defect structure of the crystal, special attention must be paid to the growth conditions [2]. The best quality and largest single crystals have been obtained by means of Czochralski method [3]. Growth conditions for Nd:YVO_4 single crystals and investigation of some optical properties are presented.

2. Growth conditions

Growth of yttrium ortovanadate crystals is connected with some difficulties that seriously complicate growth process. It is caused by vaporisation behaviour and the non-stoichiometry of vanadium pentoxide and the YVO_4 compound. The congruent composition in the case of YVO_4 is slightly off stoichiometric composition. It is mainly created by in-

* e-mail: skaczmar@wat.waw.pl

♣ The paper presented there appears in SPIE Proceedings Vol. 3724, pp. 324–328.

correct valency states of vanadium ions. Vanadium can exist in yttrium ortovanadate in different state of valency and all of the V_2O_5 starting materials can have a limited concentration of non-pentavalent vanadium ions. Concentration of the non-pentavalent ions can be changed because of the high vapour and oxygen partial pressures. Schematic phase diagram published by Erdei et al. [3] shows that congruently melting composition is shifted toward the yttrium excess and contains 50.7 ±0.2 mol.% of Y_2O_3 and 49.3 ±0.2 mol.% V_2O_5. During the growth process, composition of the melt continually changes. Oxygen-deficient can create a complex solid solution with oxygen--deficiency-free yttrium or vanadium excess solid solution and presence of $YVO_4 \rightarrow YVO_3$ solid solution is possible. Thus, the growth of oxygen-deficiency-free YVO_4 from melt with different vanadium oxides is rather difficult. YVO_4 and Nd:YVO_4 crystals were grown by Czochralski method with inductive heating from stoichiomteric mixture of Y_2O_3 and V_2O_5 oxides. As container iridium crucible with afterheater was used. Crucible was located on the balance, recording its loss in weight during the growth, as equivalent weight gain of growing crystal. Parameters of the growth process were controlled by computer. As usually in the Czochralski method we have three parameters for the process controll; power supply influencing melt temperature, the rate of pulling, and rate of seed rotation. For Nd:YVO_4 growth we have found: pulling rate 1–1.2 mm/h and rotation rate 5 rot/min.

3. Experimental setup for optical investigations

The as grown crystals were cut and polished into the samples with approximate dimensions; 10 mm length and 1 mm thick. After measurement of the transmission, the absorption (K) and then, after a treatment, the additional absorption value, ΔK, were calculated according to the formula

$$\Delta K(\lambda) = 1/d \ln(T_1(\lambda)/T_2(\lambda)) \quad (1)$$

where λ is the wavelength, d is the sample thickness, T_1 and T_2 are the transmissions of the sample before and after an appropriate treatment procedure, respectively.

Absorption spectra were taken at a temperature of 300 K in the spectral range 190–7000 nm using the Perkin-Elmer spectrophotometer (190–1100 nm) and a FTIR spectrometer (1400–25000 nm) before and after gamma irradiation. The samples were irradiated by gamma photons, immediately after the crystal growth process. The gamma source of ^{60}Co with strength of 1.5 Gy/s was used. The gamma doses applied were up to 10^6 Gy. Radioluminescence spectra were measured in the range 200–850 nm using excitation with X-rays (DRON, 35 kV/25 mA) and Spectrograph ARC SpectraPro-500i (Hol-UV 1200 gr/mm grating, 0.5 mm slits), PMT Hamamatsu R928 (1000 V).

The dimensions of samples for ESR investigation were the following 3.5 × 3.5 × 2 mm. They were investigated in the Bruker ESP300 ESR spectrometer (X-band). The spectrometer was equipped with helium flow cryostat type ESR900 Oxford Instruments. The ESR investigations were performed in the temperature range from 4 to 35 K and microwave power from 0.002 to 200 mW.

For rods with a length of 5–10 mm transmission measurements were performed with application of Nd: YAG (1.06 μm) beam of 200 mW power.

4. Results and discussion

4.1. Absorption measurements

Figures 1 and 2 present absorption of a pure and Nd doped YVO_4 single crystal compare to YAG's. As it is seen, fundamental absorption edge (FAE) is shifted about 50 nm towards longer wavelengths, while lattice absorption starts about 500 nm earlier for YVO_4 crystals compare to YAG's.

Absorption of Nd doped YVO_4 crystal is higher than YAG crystal for the same level of doping (1at.%). It is clearly seen in Fig. 3 where absorption of these crystals in the range 750–850 nm, characteristic for laser diode pumping, is presented. Ratio of

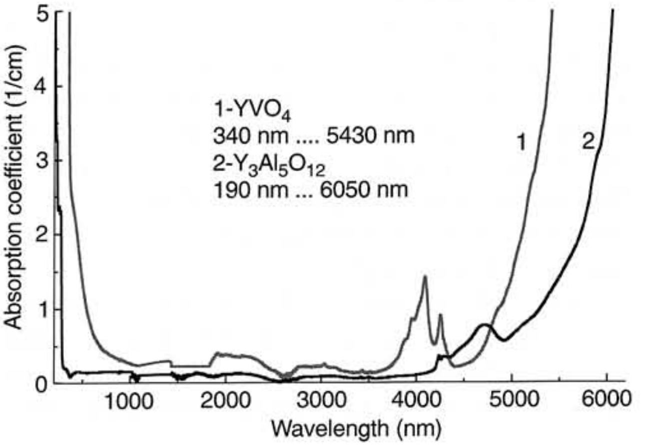

Fig. 1. Absorption of pure YVO_4 single crystal in comparison with YAG one.

the absorptions for $\lambda = 808$ nm is as high as 4 (YVO_4 with respect to YAG).

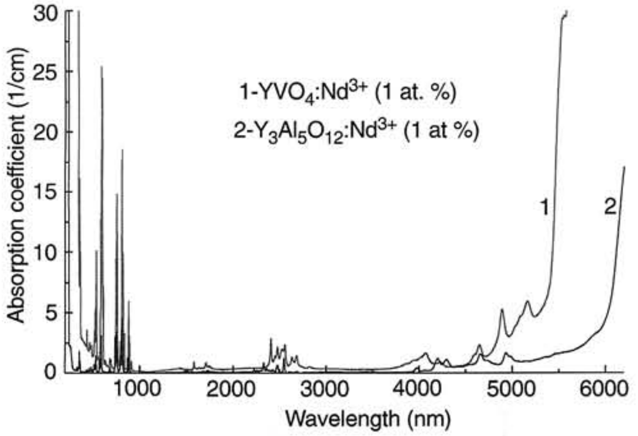

Fig. 2. Absorption of Nd doped YVO_4 single crystal in comparison with YAG one.

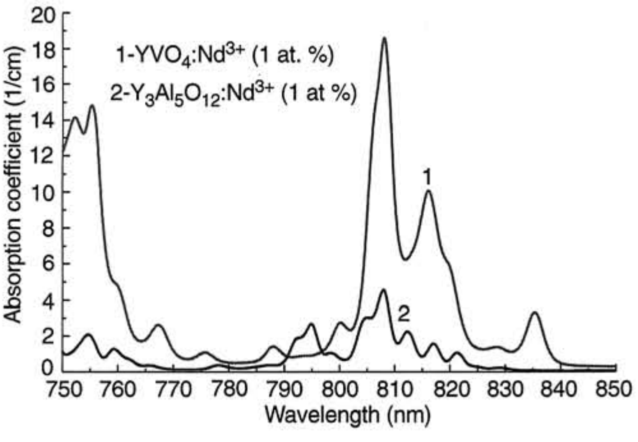

Fig. 3. Absorption in the laser diode pumping range for Nd doped YVO_4 and YAG single crystals.

4.2. Additional absorption after gamma irradiation

Figure 4 shows additional absorption after gamma irradiation with a dose of 10^5 Gy in YVO_4 and Nd:YVO_4 single crystals compared to YAG' s. As it can be seen, YVO_4 single crystal is less susceptible to gamma irradiation than YAG (maximum of additional absorption for YVO_4 crystal has a value of about 0.25 cm^{-1} while for YAG crystal this value is equal to about 1 cm^{-1}). Moreover, in the additional absorption spectrum there is not seen the presence of Fe ions absorption (256 and 310 nm for YAG and Nd: YAG crystals) and F-center absorption (400–450 nm for YAG and Nd: YAG crystals). So, we can conclude that in YVO_4 crystal lower amount of growth defects arises than in YAG one and that YVO_4 crystal shows absence of non-controlled impurity (optically active) absorption. Irradiations with gamma quanta performed for greater doses (10^6 Gy) show that further increase in additional absorption value is not observed. So, saturation phenomenon is stated for the doses as high as 10^5 Gy (all the point defects undergo a recharging process).

4.3. Radioluminescence measurements

More accurate analysis of the photoluminescence features one can obtain using radioluminescence method. Fig. 5 shows radioluminescence measurements of pure (a) and Nd doped (b) YVO_4 single crystals. As it can be seen FAE is described as previously for absorption measurements (340 nm) and some non-controlled impurities can be seen at 485 and 575 nm for pure YVO_4 crystal, while for Nd:YVO_4 crystals all the emissions are damped by Nd ions, which do not give any self-emission. Both characteristics were obtained for current input range equal to 10^{-8} A.

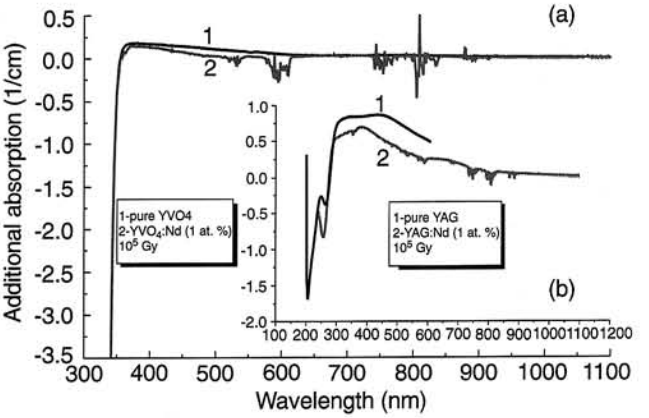

Fig. 4. Additional absorption after gamma irradiation with a dose of 10^5 Gy in YVO_4 and Nd:YVO_4 single crystals in comparison with YAG one.

4.4. ESR measurements

Nd^{3+} ion substitutes Y^{3+} in YVO_4 single crystal. The nearest neighbours of the Nd^{3+} are four O^{2-} ions that form a tetragonally distorted tetrahedron [4]. For Nd:YVO_4 single crystal and magnetic field parallel to (001) plane, an isotropic spectrum with two groups of eight hyperfine lines (hfs) and one single strong line with I = 0 were observed. The spectrum is described by following spin-Hamiltonian:

$$H = g_{\parallel}\beta H_x S_x + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}(I_x S_x + I_y S_y) \quad (2)$$

where H_x, H_y are the components of magnetic field, $S = 1/2$ is the electron spin, $I = 0$ for even-mass isotopes and I = 7/2 for ^{143}Nd and ^{145}Nd nucleus spin. $A_{\|}$ and $A_{\perp}$ are the hfs constants, g is the Lande factor and β is the Bohr magnethon. We obtained $g_{\|}$ = 0.9132, $g_{\perp}$ = 2.350(1), $^{143}A_{\perp}$ = 216×10^{-4} cm^{-1}, and $^{145}A_{\perp}$ = 138×10^{-4} cm^{-1}. $A_{\|}$ was not measured because for this direction the linewidth of each hfs was very wide.

It results from ESR investigations that these non-controlled impurities observed in radioluminescence spectrum, may be also the V ions with different then 5 valency, lying in interstitial sites. They are seen in ESR spectrum for "as grown" crystals and after gamma or electron irradiations the amount of ions in such a way defected increases. The only differences between electron and gamma irradiations are additional ESR lines for electrons, which can be connected with Frenkel defects. Similar phenomenon, but for vanadium doped YAG single crystals, was observed in Ref. 5.

4.5. Transmission measurements

Power measurement of laser beam passing through the rod was done with use of LabMaster gauge with a thermopile searcher. Measurement error was about 1%. We obtained transmission between 75–77.5%. The transmission of ideal Nd:YVO$_4$ crystal after Fresnel losses dimnish is equal to about 77.4%. It indicates that absorption and volume scattering losses are not greater then 1%.

5. Conclusions

The obtained by us YVO$_4$ and Nd doped YVO$_4$ single crystals have good optical quality, and great absorption coefficient in the range of diode laser pumping (about 19 cm^{-1} in the range 750–850 nm). They have got also small amount of non-controlled impurities without the presence of Fe ions (as compared to YAG crystals) and small amount of growth defects, such as oxygen vacancies.

Our crystals showed lower susceptibility to gamma irradiation in comparison with YAG's. It results ESR investigations result that these non-controlled impurities, observed in radioluminescence spectrum, may be also the V ions with different then 5 valency, lying in interstitial sites. Absorption and volume scattering losses, measured with the use of Nd: YAG laser are not greater then 1%.

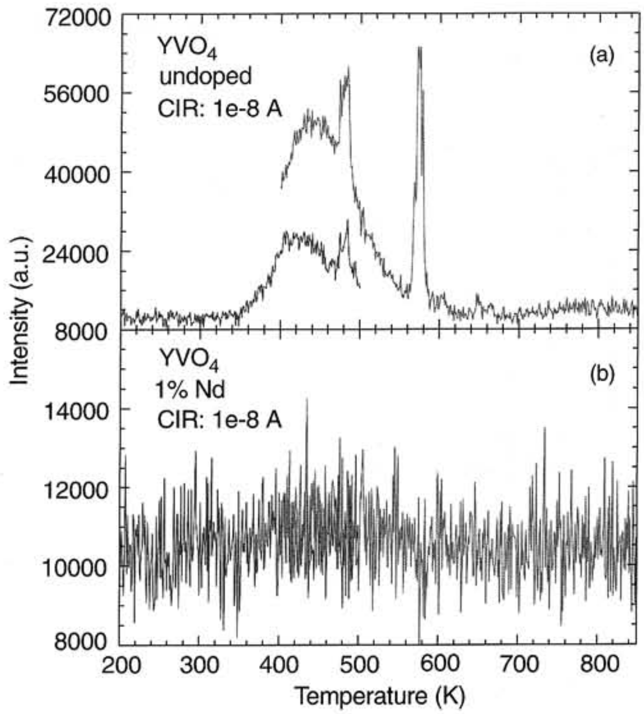

Fig. 5. Radioluminescence of YVO$_4$ and Nd: YVO$_4$ (1at.%) single crystals.

Acknowledgments

This work was sponsored by the Polish Committee for Scientific Research (project no 7T08A01510).

References

1. S. Erdei et al., *Journal of Crystal Growth* **172**, 466–472 (1997).
2. K. Chow and H.G. Knight, *Mat. Res. Bull.* **8**, 1343–1350 (1973).
3. S. Erdei et al., *Cryst., Res. Technol.* **29**, 815–828 (1994).
4. F.G. Anderson, P.L. Summers, H. Weidner, P. Hong, and R.E. Peale, "Interpretative crystal-field parameters: Application to Nd^{3+} in GdVO$_4$ and YVO$_4$", *Phys. Rev.* **B50**, 14802–14808 (1994).
5. R. Jabłoński, S.M. Kaczmarek, "Electron spin resonance and optical measurements in YAG:V^{3+} crystals", to be publish.

