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Spectroscopy and lasing of new mixed Nd-doped (Sc,Y)VO_4 crystals

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Abstract We report the first successful growth of Nd-doped $Sc_xY_{1-x}VO_4$ crystals ($0 < x \leq 1$) by the Czochralski technique. For a successful synthesis, the upper limit of the Sc concentration in the YVO_4 melt was found to be below 10 at%. The spectroscopic characterization of an Nd-doped laser crystal, i.e., Nd:$Sc_{0.011}Y_{1.003}V_{0.986}O_{3.986}$, is discussed. Diode pumping of a *c*-cut crystal yielded an output power of 1.1 W at a wavelength of 1.06 μm with a slope efficiency of 43%: The slope efficiency of an *a*-cut crystal was 37%.

1 Introduction

Highly efficient ultrashort-pulse lasers are beneficial for a variety of applications, such as micro-machining of hard materials (sapphire, diamond), metals, or dielectrics in the semiconductor industry. The duration of a laser pulse is inversely proportional to the gain bandwidth of the amplifying medium. That is, to achieve short pulses, active media with broad luminescence bands are required. For good efficiency, it is mandatory that the active medium can be diode pumped and has good optical, thermal, and mechanical properties. Promising candidates are Nd-doped mixed vanadates which have a distorted crystal structure and exhibit an inhomogeneously broadened luminescence spectrum. The first mixed vanadate crystal (Nd:$Gd_{0.5}La_{0.5}VO_4$) was grown and investigated in 1996 [1]. Afterwards, several other mixed vanadate crystals, such as Nd:$Gd_{0.8}La_{0.2}VO_4$ [2, 3], $Y_{1-x}La_xVO_4$ [4], Nd:$Gd_xY_{1-x}VO_4$ [5, 6], or Nd:$Lu_xGd_{1-x}VO_4$ [7], were studied. For all crystals, the luminescence bands were found to be broader than those of Nd:YVO_4 or Nd:$GdVO_4$ [8].

Based on the achievements in crystal growth and the excellent optical, thermal, and mechanical properties, diode-laser pumping of Nd:YVO_4, Nd:$GdVO_4$, or mixed Nd:$Gd_xY_{1-x}VO_4$ laser materials has seen a rapid and successful development. Vanadate crystals excel Nd:YAG both in laser characteristics and thermal properties. For example, an Nd:$GdVO_4$ crystal has a seven times larger absorption cross-section for π-polarization (5.2×10^{-19} cm^2) and a three times larger emission cross-section (7.6×10^{-19} cm^2) than Nd:YAG [9]. The thermal conductivity of 14.5 W m^{-1} K^{-1} along the crystallographic *c*-axis of an Nd:YVO_4 crystal considerably exceeds the 11.1 W m^{-1} K^{-1} of a 0.9 at% Nd:YAG crystal [10].

In order to further increase the width of the Neodymium luminescence spectrum, it was proposed to replace the Y^{3+} ions in YVO_4, by the smaller Sc^{3+} ions. This should decrease the dodecahedral lattice sites and should result, first, in a decreasing segregation coefficient for the Nd^{3+} ions and, second, in a broadening of the Nd^{3+} luminescence spectrum. The Sc^{3+} ions occupy the same lattice sites within the crystal as the Gd^{3+} and the Y^{3+} ions in the other orthovanadates $GdVO_4$ and YVO_4, and have the site symmetry D_{2d}. The first polycrystalline samples of Nd-doped $ScVO_4$ were prepared by sintering (two-stage solid-state re-

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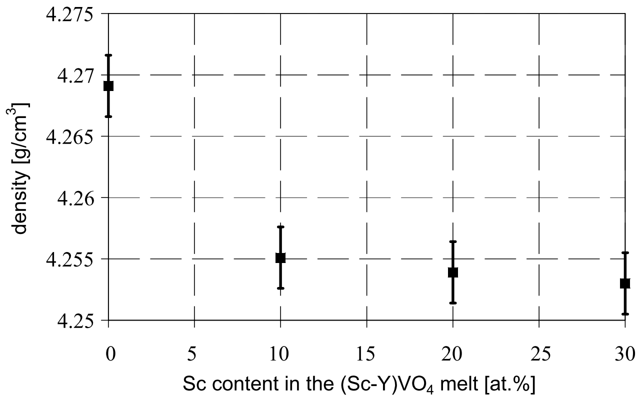

Fig. 1 The dependence of density of the $Sc_xY_{1-x}VO_4$ crystals on Sc contents in the melts

action) of scandium oxide and vanadium pentoxide in 1973 by Ageeva et al. [11]. A comparison of the Nd excitation spectra in different orthovanadates showed that the broadest and most intense bands are found in $ScVO_4$ [11], making it the most promising host matrix for the Nd^{3+} ions. However, up to now all efforts to grow single crystals have failed.

This paper reports on the first successful growth of Nd-doped (Sc,Y)VO_4 mixed crystals from a 1.1 at.% Nd:$Sc_xY_{1-x}VO_4$ melt, with x ranging from 0 to 1, and their spectroscopic properties and laser performance.

2 Crystal growth

The orthovanadates $ScVO_4$, $GdVO_4$, and YVO_4 possess the same $ZrSiO_4$ structure and belong to the tetragonal symmetry space group $I4_{1/amd}$. Therefore, it is expected that the $ScVO_4/YVO_4$ mixed crystals may be grown as solid solution single crystals. However, the growth of laser-quality scandium containing vanadate crystals by the Czochralski method leads to technical difficulties, which are due to the small ion radius of Sc^{3+} in the dodecahedral sites of the orthovanadate lattice. Consequently, several attempts to grow $ScVO_4$ single crystals by the Czochralski technique have failed, and typically only black polycrystalline samples were obtained.

Mixed Sc–Y vanadate single crystals of good optical quality were grown from a melt of 10 at% $ScVO_4$/90 at% YVO_4 and a melt of 20 at% $ScVO_4$/80 at% YVO_4. The growth of a single crystal from a melt of 30 at% $ScVO_4$/70 at% YVO_4 failed. The density of the mixed (Sc,Y)VO_4 crystals was measured by the hydrostatic weighing method. A 0.7 at% Nd:$Y_{1.014}V_{0.986}O_{3.986}$ crystal containing no scandium had the highest density, and the densities of the crystals grown from the Y–Sc melts were significantly lower as shown in Fig. 1.

Within the error bars, the measured densities of the crystals with 10 at%, 20 at%, and 30 at% of scandium were about the same, although a slight decline of the density with increasing Sc content may be inferred. We suspect that this decline may be related to defects in the crystal which become more likely with an increasing compositional shift of the melt. An X-ray microprobe analysis of the crystal grown from the 1.1 at% Nd^{3+}:$Sc_{0.304}Y_{0.694}V_{0.986}O_{3.986}$ composition of the melt revealed a composition of $Nd_{0.008}Sc_{0.011}Y_{0.995}V_{0.986}O_{3.986}$. That is, instead of about 30 at% Sc only about 1 at% Sc is incorporated in the crystal. Consequently, the crystals grown from the melts with 10 at%, 20 at%, and 30 at% Sc have nearly the same composition and, thus, similar densities. Excess Sc results in a seriously defective crystalline structure which lowers the density slightly.

3 Spectroscopy and laser experiments

Laser crystals of 0.6 at% Nd:$Sc_{0.011}Y_{1.003}V_{0.986}O_{3.986}$ were studied spectroscopically in different crystallographic orientations. Polarization-dependent absorption spectra are recorded with a commercial spectrophotometer (*Shimadzu* UV-3101PC). For luminescence excitation, we used a 12-W cw laser diode operated at a wavelength of 808 nm with the polarization either parallel or perpendicular to the c-axis of the crystal. To minimize reabsorption, the sample thickness was 270 µm. The polarization-dependent luminescence was measured at room temperature with a spectrometer based on an autocollimation tube (UV-90) and a detector (*Toshiba* TSD1304JK) with a resolution of 0.1 nm/mm.

From the isomorphous replacement of the Y^{3+} ions in YVO_4 by the Sc^{3+} ions we expected a broadening of the absorption spectra of the mixed Nd:(Sc,Y)VO_4 crystals. Yet, the observed absorption band between 740 nm and 840 nm was only slightly broader than the one of Nd:YVO_4 and also not shifted in position. Its maximum is found at 808.8 nm for both polarizations. The absorption coefficient for the π-polarization (electric field vector parallel to the c-axis of the crystal) was measured to be 65.82 cm^{-1}, resulting in an absorption cross section of 8.6×10^{-19} cm^2. The full width at half maximum (FWHM) was 1.6 nm. For σ-polarized excitation light, the absorption coefficient was 16.04 cm^{-1}, and the absorption cross section was calculated to 2.1×10^{-19} cm^2. The FWHM was 2.2 nm.

The room temperature luminescence spectra in the wavelength range between 1055 nm and 1087 nm, i.e., the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, are presented in Fig. 2. The luminescence spectrum of a c-cut Nd:(Sc,Y)VO_4 crystal (irrespective of the polarization of the pump light) consists of three transitions with the strongest line centered at 1064.6 nm and two somewhat weaker lines at 1062.7 nm and 1066.4 nm, respectively. With 5.484 nm, the FWHM of the luminescence spectrum is slightly broader than that

Table 1 Comparison of the full widths at half maximum (FWHM) of the Nd-doped Y, Gd, La, and Sc mixed vanadates at 1.06 μm measured at 300 K

	C-cut sample		A-cut sample			Ref.
	λ_{max}, nm	FWHM	λ_{max}, nm	FWHM		
				$E \perp c$	$E \parallel c$	
$GdVO_4$	1065.5	4.5	1063.17	3.7	1.4	Present work
YVO_4	1066.1	5.151	1064.1	4.4	1.0	Present work
$Y_{0.3}Gd_{0.7}VO_4$	1065.4	5.1	1063.3	–	1.7	[8]
$Y_{0.36}Gd_{0.64}VO_4$	–	–	~1063	–	3.5	[12]
$Y_{0.5}Gd_{0.5}VO_4$	–	–	1065.15	–	~10	[5]
$La_{0.2}Gd_{0.8}VO_4$	–	–	~1064	~4	~2.8	[2]
$La_{0.5}Gd_{0.5}VO_4$	–	–	~ 1064	5.3	4.8	[1]
$Sc_{0.011}Y_{1.003}VO_4$	1064.6	5.484	1064.4	4.51	1.43	Present work

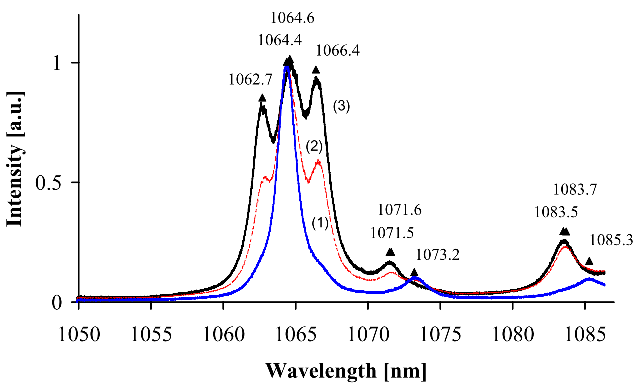

Fig. 2 Normalized luminescence spectra of the Nd:(Sc,Y)VO_4 crystal pumped along the *a*-axis: (1) π-polarization (*blue line*), (2) σ-polarization (*dotted red line*), and (3) a crystal pumped along the *c*-axis (*black line*) at 300 K

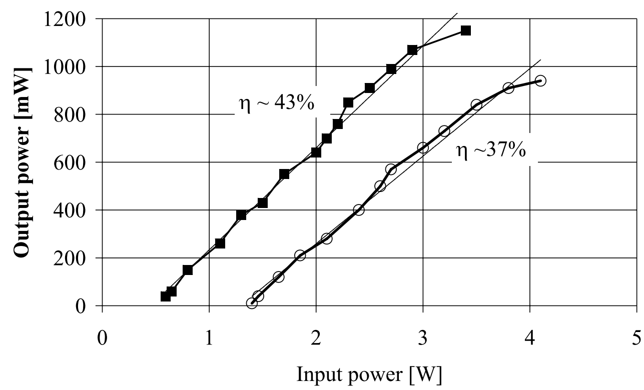

Fig. 3 Laser output power versus absorbed pump power for a 0.6 at% Nd:$Sc_{0.011}Y_{1.003}V_{0.986}O_{3.986}$ crystal. *Circles*: pump polarization along the *a*-axis; *squares*: pump polarization along the *c*-axis

of Nd:YVO_4 crystals with 5.151 nm. For an *a*-cut crystal, the π- and σ-polarized spectra differ substantially. For σ-polarized excitation light, the luminescence spectrum resembles that of a *c*-cut crystal only with a somewhat reduced intensity of the two side peaks. Conversely, for π-polarized excitation light, the two side peaks have almost disappeared, and the FWHM is reduced to 1.43 nm. Sc–Y disorder in the ScYVO_4 crystals makes the luminescence peaks slightly broader than in $GdVO_4$ and YVO_4, but an FWHM is less than in the other known mixed vanadate crystals. However, taking into account a quantity of Sc entered into the YVO_4 crystal structure (1.1 at% of the Sc ions only replaced Y in mixed Sc–Y vanadate), we reach to the conclusion that a disorder in mixed Sc–Y vanadate is much stronger than in the other mixed vanadates; the FWHM of YVO_4, $GdVO_4$, and Y–Gd, La–Gd mixed vanadates are summarized in Table 1.

Laser experiments at 1064 nm were performed with a 4-mm wide and 4-mm long 0.6 at% Nd:$Sc_{0.011}Y_{1.003}V_{0.986}O_{3.986}$ crystal mounted on a copper heat sink. The side faces where plane parallel and had no antireflection coating. The resonator was 20-mm long and consisted of a plane HR mirror and a plane output coupler with a transmission of 8%. The crystal was pumped by a laser diode operated at 808 nm and a maximum output power of 4 W. The pump light was focused to a spot size of 200 μm, and the crystal was long enough to absorb the entire pump light. The input–output curves are shown in Fig. 3. When the pump light is polarized along the *c*-axis, we measure a laser threshold of about 1.4 W and a slope efficiency of 37%. The maximum output power is approximately 0.95 W at a pump power of 4.2 W. For a polarization parallel to the *a*-axis, the laser threshold reduces to approximately 0.6 W, and the slope efficiency increases to 43%. The highest output power of 1.15 W is found for a pump power of about 3.4 W. We believe that in both cases the slope efficiency was partially limited by the optical quality of the laser crystal which was grown from the 10% Sc/90% Y vanadate melt. Higher output powers for the pump light parallel to the *a*-axis can be expected for crystals with an optimal length and with an AR coating.

4 Conclusion

A series of the mixed Nd-doped $Sc_xY_{1-x}VO_4$ ($0 < x < 1$) crystals has been successfully grown, to our knowledge for the first time, by Czochralski technique. The attempts to grow an Nd:$ScVO_4$ single crystal, i.e., $x = 1$, by the directional crystallization method failed (the Czochralski technique is a special case of the directional crystallization). The crystals grown from the YVO_4 melts containing the 10%, 20%, and 30% of $ScVO_4$ had approximately the same $Nd_{0.008}Sc_{0.011}Y_{0.995}V_{0.986}O_{3.986}$ composition.

The luminescence spectra of the 0.6 at% Nd:$Sc_{0.011}Y_{1.003}V_{0.986}O_{3.986}$ laser crystal revealed that the FWHM of 5.484 nm of Sc–Y vanadate is slightly larger than the FWHM of an Nd:YVO_4 crystal (5.151 nm). The additional broadening is caused mainly by the distorted crystal structure of the lattice. A slope efficiency of 37% with respect to the absorbed pump power was achieved when the laser sample was oriented with the c-axis parallel to the polarization of the diode laser, and a slope efficiency of 43% occurred with the a-axis parallel to the polarization of a diode-laser.

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