Special Anniversary Issue: Professor Jan Czochralski Year 2013 — Invited Paper

Growth and Characterization of Vanadate Laser Crystals

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Based on the invention and widely application of the Czochralski pulling method, vanadate crystals have been grown and commercialized in recent decades. In this paper, the growth and characterization of a series of neodymium doped vanadate crystals have been reviewed, including Nd:YVO_4, Nd:$GdVO_4$, and Nd:$LuVO_4$. The excellent thermal-mechanical and laser property make them to be used in many respects.

DOI: 10.12693/APhysPolA.124.301

PACS: 81.10.Fq, 42.55.Px

1. Introduction

Since the invention of the Czochralski (Cz) pulling method in 1916 [1], this technology has been well developed and applied as an important tool for exploration and investigation of many new and novel crystals. With the development of lasers, investigation on the growth of laser crystals, especially for those which can be grown with the Cz method, has attracted wide attention. Neodymium (Nd) doped garnet and vanadate crystals are the best examples for the application of Cz method. Owing to the development of laser-diode lasers, the neodymium vanadate crystals have become an important series gain materials in the low and even moderate power lasers.

Nd:YVO_4 is the most famous one. Nowadays, its quality has been highly improved and its growth cycle has been reduced using the well known Cz method. This crystal has been commercial and widely adopted in laser processing, generation of visible lasers, etc. Replacing Y ions by Gd or Lu ions, another vanadate crystal Nd:$GdVO_4$ or Nd:$LuVO_4$ would be grown. Compared with Nd:YVO_4, Nd:$GdVO_4$ has the highest thermal conductivity and Nd:$LuVO_4$ possesses the largest emission cross-section among them. In this paper, we review the growth and characterization of a series of vanadate crystals including Nd:YVO_4, Nd:$GdVO_4$ and Nd:$LuVO_4$.

2. The growth and property of vanadate crystals

2.1. *Nd:YVO_4 crystals*

The compound of YVO_4 material is not chemically existing in nature. In 1928, Goldschmidt and Haralden synthesized this compound firstly [2]. From 1960s, this crystal has been heavily investigated and grown by various flux, zone melting, hydrothermal methods, etc. But the size and quality of the crystal could not meet the need of laser applications. Until 1966, Rubin and Van Uitert have grown high-quality YVO_4 crystal with the Czochralski method [3], which opened the door to commercialization of this crystal. In 1987, Fields et al. first reported the laser-diode pump [4] Nd:YVO_4 laser performance, then this crystal has attracted increasing attention as a gain material for all solid-state lasers.

Fig. 1. Photo of as-grown Nd:YVO_4 crystal with doping concentration of 1 at.%.

Fig. 2. Photos of Nd:Cr:YVO_4 crystals with the doping concentration of 0.79 at.% Nd and 1.40 at.% Cr.

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A Nd:YVO_4 crystal grown by the Czochralski method is shown in Fig. 1. Compared with the early grown vanadate crystal, the Nd:YVO_4 crystal of Fig. 1 has an excellent quality (no scatter pellets can be observed under 5 mW He–Ne laser). This crystal is tetragonal with space phase of D_{4h}^{19}-$I4_1amd$. Their properties are shown in Table [5]. It can be found that the thermal conductivity of Nd:YVO_4 are much small compared with the Nd:YAG crystal. However, its large absorption and emission cross-section and wide spectra determine its important applications in low and even moderate lasers. Due to the high melting points, Nd:YVO_4 crystal should be grown in oxygen free atmosphere. There were four kinds of defects which would appear in the vanadate crystal: color centers, inclusions, substructure, and uneven distribution of Nd^{3+} concentration [6]. Therefore, the annealing and suitable controlled growing technology are necessary. The doping maximum concentration of 3.2 at.% has been reported, however, the concentration quenching became evident when the Nd^{3+} doping concentration is larger than 2 at.% [7]. The effective segregation coefficient of Nd^{3+} ions was measured to be 0.63 [8]. Generally, the concentrations of the Nd^{3+} ions in the shoulder or diameter part are higher than the tail part. Up to now, the maximum of over than 110 W continuous-wave and mode-locked Nd:YVO_4 laser has been achieved [9, 10]. Besides the laser performance, Nd:YVO_4 is also a self-Raman laser crystal and the output power of 7.9 W yellow laser has been achieved with the slope efficiency of 43% [11].

TABLE

Characterization of the neodymium doped vanadate crystals.

	Nd:YVO_4	Nd:$GdVO_4$	Nd:$LuVO_4$
cell parameters	$a = b = 0.7118$ nm, $c = 0.6293$ nm	$a = b = 0.7211$ nm, $c = 0.6350$ nm	$a = b = 0.70243$ nm, $c = 0.62316$ nm
melting point	1810 °C	1800 °C	1800 °C
Moh's hardness	4.6–5		
density	4.22 g/cm^3	5.48 g/cm^3	6.233 g/cm^3
thermal-optical coefficient dn_o/dT dn_e/dT	$8.5 \times 10^{-6}/°C$ $3.0 \times 10^{-6}/°C$	$4.7 \times 10^{-6}/°C$	
thermal conductivity a-axis c-axis	5.1 W/mK 5.23 W/mK	10.1 W/mK 11.4 W/mK	7.96 W/mK 9.77 W/mK
absorption peak	808.6 nm	808.4 nm	807 nm
width of absorption peak (full width at half maximum) at 808 nm	2 nm (1.0 at.% Nd)	1.6 nm (1.2 at.% Nd)	1.5 nm (0.36 at.% Nd)
absorption cross-section	5.7×10^{-19} cm^2	5.2×10^{-19} cm^2	6.9×10^{-19} cm^2
emission peak	1064 nm	1063 nm	1066 nm
width of emission peak (full width at half maximum) at 1064 nm	1.5 nm (≈ 1% Nd concentration)	1.2 nm (1.2 at.% Nd)	2.1 nm (1 at.% Nd)
emission cross-section	12×10^{-19} cm^2	7.6×10^{-19} cm^2	14.6×10^{-19} cm^2
fluorescence lifetime	76 μs	90 μs	82 μs
Sellmeier equation	$n_o^2 = 3.77834 + 0.069736/(\lambda^2 - 0.04724) - 0.01081133\lambda^2$ $n_e^2 = 4.59905 + 0.110534/(\lambda^2 - 0.04813) - 0.0122676\lambda^2$	$n_o^2 = 3.8714 + 0.0604/(\lambda^2 - 0.06119) - 0.03961\lambda^2$ $n_e^2 = 4.7331 + 0.1054/(\lambda^2 - 0.06112) - 0.02409\lambda^2$	

Nowadays, we have developed the self-Q-switched Nd:Cr:YVO_4 laser crystals as shown in Fig. 2 based on our previous investigation of Nd:YVO_4 [12, 13] with the size of $\oslash 32 \times 20$ mm^2. In this crystal, the V^{5+} ions are partly substituted by Cr^{5+} which has saturable absorbing property when they are localized in the tetragonal coordination. Based on the emission property of Nd ions and saturable absorbing property of Cr ions, this crystal can be used as a self-modulated pulsed laser gain material.

2.2. Nd:$GdVO_4$ crystals

From 1990s, the Nd:$GdVO_4$ crystal with small size has been investigated. Until 1992, the large size Nd:$GdVO_4$ crystal was firstly grown with the Czochralski method by

Zagumennyi et al. [14] and used as a gain material for the generation of lasers. In 1994, Jensen et al. investigated the spectral and laser properties of this crystal systematically [15]. In 1995, Studenikin et al. reported its thermal properties and refractive index [16]. From 1996, we started the investigation of growth and properties of this crystal. In 2002, we reviewed the laser properties of this crystal including its fundamental laser performance and applications in second harmonic generation [8]. Since then, this crystal has been widely studied and used in moderate and even high power lasers. Up to now, over 100 W $Nd:GdVO_4$ lasers have been achieved with the efficiency of 40% [17]. The shortest $Nd:GdVO_4$ laser pulse is 2.8 ps [18]. In the application of self-Raman lasers, the continuous-wave yellow laser of 5.3 W was achieved with $Nd:GdVO_4$ as the gain and Raman material [19] where the optical efficiency is 21%.

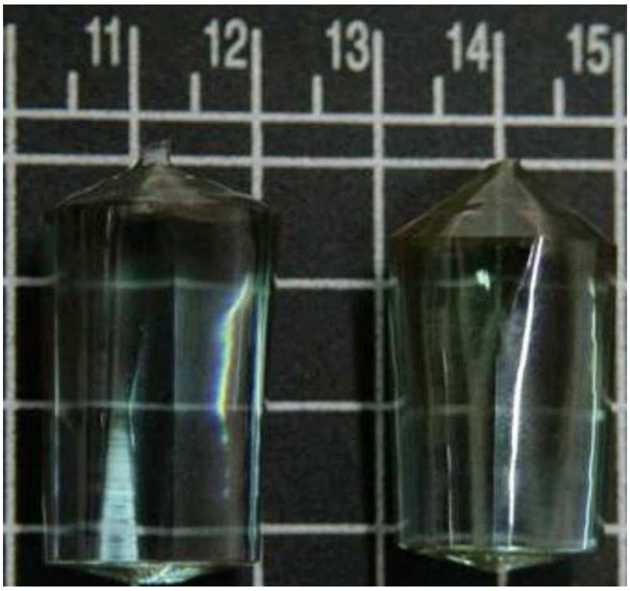

Fig. 3. Photos of as-grown $Nd:GdVO_4$ crystals with the doping concentration of 1.56 at.%.

The basic properties of $Nd:GdVO_4$ crystal is also shown in Table and the as grown crystal is presented in Fig. 3. Compared with $Nd:YVO_4$, $Nd:GdVO_4$ has much higher thermal conductivity which is comparable with Nd:YAG crystals and higher effective segregation coefficient of Nd^{3+} ions (0.78) [8]. Its emission cross-section is larger than Nd:YAG, therefore, this crystal was considered as a gain medium for the generation of efficient moderate and even high power lasers.

2.3. $Nd:LuVO_4$ crystals

From 1996, Terada et al. have investigated $LuVO_4$ crystals as optical materials [20]. Until 2002, Maunier et al. grew and studied the optical and laser properties of $Nd:LuVO_4$ [21] with the flux method. In 2003, we reported the growth of large-size $Nd:LuVO_4$ crystals with the Czochralski method for the first time to our knowledge [22]. The as-grown $Nd:LuVO_4$ crystals with different doping concentrations (0–3 at.%) are shown in Fig. 4. The basic properties of the $Nd:LuVO_4$ crystal is also summarized in Table. Its thermal conductivity is a bit smaller than $Nd:GdVO_4$ and Nd:YAG, but much larger than $Nd:YVO_4$. The higher effective segregation coefficient of Nd^{3+} ions in $Nd:LuVO_4$ crystal is 0.91. The emission cross-section of $Nd:LuVO_4$ is about twice of that for $Nd:GdVO_4$, which indicates that the $Nd:LuVO_4$ should be an excellent laser material for the generation of high efficient lasers at about 1.06 μm. The maximum continuous-wave output power is 17.2 W [23] and the shortest Q-switched pulse is 12 ns and the shortest mode--locked pulse is 7.1 ps [24]. The maximum output power of 3.5 W yellow laser was achieved with $Nd:LuVO_4$ as the gain and Raman material [25]. However, this crystal has strong up-conversion at the wavelength of 1.3 μm, which determines the relative low efficient lasers at this wavelength.

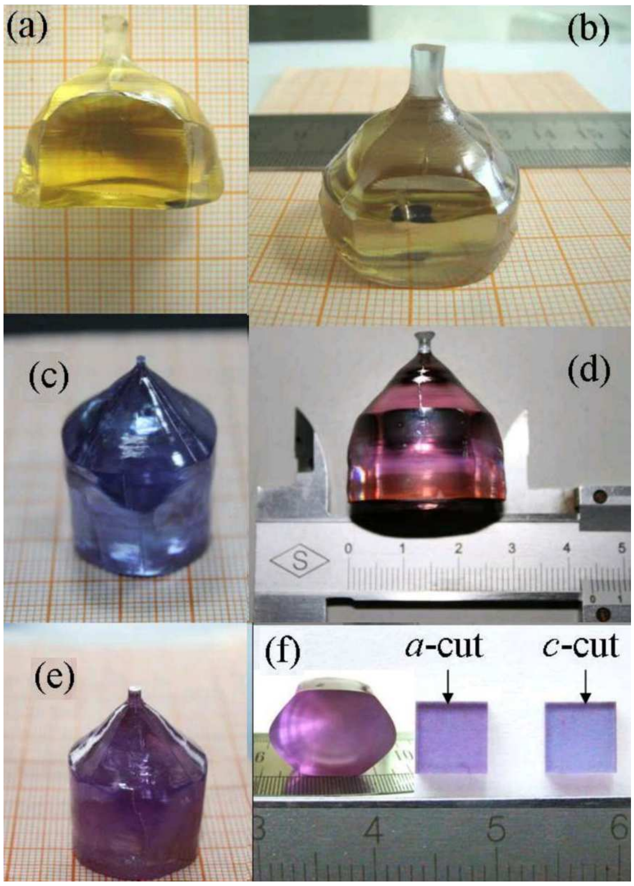

Fig. 4. $Nd:LuVO_4$ crystals with doping concentrations from 0 to 3 at.%.

3. Conclusion

The neodymium doped vanadate crystals have been widely studied and identified as excellent laser gain materials. As the development of solid-state lasers, it can be proposed that these crystals would play more and more important roles. As possible future prospects, the novel vanadate laser crystals with smaller cations such as Sc^{3+} and larger cations such as La^{3+} should be paid more attentions, because Sc^{3+} has the smallest radius which determines the atypical crystal growing property [26], and La^{3+} has the largest radius which induces the different crystal symmetry [27].

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