

Nd:Y3ScxAl5-xO12 (x= 0.05, 0.5, 1) shaped crystals grown by the micro-pulling-down method and optical properties

Jie Xu, Qingsong Song, Jian Liu, Kaiting Bian, Wen Lu, Dongzhen Li, Peng Liu, Xiaodong Xu, Yuchong Ding, Jun Xu, et al.

► To cite this version:

Jie Xu, Qingsong Song, Jian Liu, Kaiting Bian, Wen Lu, et al.. Nd:Y3ScxAl5-xO12 (x= 0.05, 0.5, 1) shaped crystals grown by the micro-pulling-down method and optical properties. Optical Materials, 2020, 102, pp.109825. 10.1016/j.optmat.2020.109825 . hal-02613520

HAL Id: hal-02613520 https://hal.science/hal-02613520

Submitted on 11 Dec 2020 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Nd:Y₃Sc_xAl_{5-x}O₁₂ (x= 0.05, 0.5, 1) shaped crystals grown by the micro-pulling-down method and optical properties

Jie Xu^a, Qingsong Song^a, Jian Liu^a, Shidong Zhou^a, Yuxin Pan^a, Dongzhen Li^a,

Peng Liu^a, Xiaodong Xu^{a,*}, Yuchong Ding^b, Jun Xu^{c,*} Kheirreddine Lebbou^d

^a Jiangsu Key Laboratory of Advanced Laser Materials and Devices, School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, China

^b Research & Development Center of Material and Equipment, China Electronics Technology Group Corporation No.26 Research Institute, Chongqing 400060, China

^c School of Physics Science and Engineering, Institute for Advanced Study, Tongji University, Shanghai 200092, China

^d Institut Lumière Matière, UMR5306 Université Lyon1-CNRS, Université de Lyon, Lyon 69622, Villeurbanne Cedex, France

Corresponding author: Email address: <u>xdxu79@jsnu.edu.cn</u> (X. Xu), <u>xujun@mail.shcnc.ac.cn</u> (J. Xu), Tel: +86-13916443810

Abstract:

Nd³⁺ doped Y₃Sc_xAl_{5-x}O₁₂ (x= 0.05, 0.5, 1) single crystals were successfully grown by the micro-pulling-down (µ-PD) technique. The effect of compositional parameter x on the structure, absorption, emission and fluorescence lifetime of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals was studied. The Nd³⁺ concentration in the core increased with increasing of compositional parameter x. The full width at half maximum (FWHM) of the emission band centered at 1064 nm was calculated to be 6.1, 7.1, and 7.3 nm for x= 0.05, 0.5 and 1, respectively. The fluorescence lifetime of ⁴F_{3/2} levels are 259.3, 269.6, and 276.9 µs for x= 0.05, 0.5, and 1, respectively. The results indicate that the Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals are promising materials for laser output.

Keywords: Nd:Y₃Sc_xAl_{5-x}O₁₂, Micro-pulling-down method, Spectral property

1. Introduction

Nd:YAG single crystal has been proved to be excellent laser material for diode-pumped solid-state lasers owning to its high thermal conductivity, good chemical and mechanical properties [1]. One major shortcoming of Nd:YAG crystal is its narrow emission bandwidth, which limits the pulse width when used for mode locking lasers [2]. Nd³⁺-doped yttrium scandium aluminum (Nd:Y₃Sc_xAl_{5-x}O₁₂) compositions are considered as solid solution of Nd:YAG and Nd:Y₃Sc₂Al₃O₁₂ (Nd:YSAG) [3]. These crystals have some advantages in comparison to Nd:YAG crystal [4-8]. In the lattice, Sc³⁺ and Al³⁺ ions are randomly distributed on the octahedral positions. The disordered structure will result in inhomogeneous broadening of absorption and emission spectra, which is better for efficient Q-switched and mode-locked laser pulse operations. Moreover, replacing Al³⁺ ions with larger Sc³⁺ ions increases the distance between dodecahedral lattice sites that Nd³⁺ ions substitute, which decreases the concentration quenching of Nd³⁺ fluorescence.

In $Nd:Y_3Sc_xAl_{5-x}O_{12}$, the Nd3+ electronic structure dependence on structural changes with composition evolution and can strongly affect the local symmetry. The multicenter structure and inhomogeneous broadening of Nd3+ lines is attributed to crystal field distributions determined by the random occupancy of the octahedral sites by Sc3+ and Al3+ (Aurelia Lupei et al <u>Optical Materials</u> 47:465-472 · September 2015). So it is very important to investigate the impact of the substitution of Al3+ by Sc3+ in the system Nd-YSAG where the Nd is the activator.

In 1990, Allik et al. reported the laser operation of $Nd:Y_3Sc_2Al_3O_{12}$ crystal under diode array pumping for the first time [4]. In 2017, Feng et al. demonstrated diode pumped continuous wave and mode-locked laser of a $Nd:Y_3ScAl_4O_{12}$ crystal. The maximum continuous wave output power was 2.0 W with a slope efficiency of 53.1%. The pulse width of the mode-locked laser was as short as 3.8 ps and the mode-locked laser exhibited dual-wavelength operation at 1060.8 nm and 1063.2 nm [5].

Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals has been grown by the Czochralski method [6], floating zone method [7] and micro-pulling-down method [8]. The μ -PD method has the capability to produce under stationary stable regime single crystalline materials quickly, relatively inexpensively and the grown samples are of sufficient dimensions for the microscopic and macroscopic characterization [9-12]. Cornacchia et al. reported the μ -PD growth and optical properties of Nd:Y₃Sc₂Al₃O₁₂ crystal [8]. But the Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals with different Sc³⁺ content (*x*) have not been investigated yet. In this work, we demonstrated the growth of Nd:Y₃Sc_xAl_{5-x}O₁₂ (*x*= 0.05, 0.5, 1) crystals by the μ -PD method. The structure and spectroscopic properties were discussed in detail.

2. Experimental

2.1 Crystal growth and structure

 Nd^{3+} -doped $Y_3Sc_xAl_{5-x}O_{12}$ single crystals have been grown by the μ -PD method, simply shown in Fig. 1. The growth process was described previously [13-15]. We use RF heating source. It consist of iridium conical crucible with capillary die of diameter 2mm and hole of 1 mm, which

contains starting charge to be crystalized and induction heating to heat crucible up to melting temperature of the raw material. High density and high purity (99,8%) alumina was used as ceramic construction around the crucible for the thermal insulation. The program heating and cooling is automatically controlled using special software. The starting materials were 99.999% grade Nd₂O₃, Sc₂O₃, Y₂O₃ and Al₂O₃ powder. They were weighed according to the formula $Nd_{0.006}Y_{2.994}Sc_{0.05}Al_{4.95}O_{12},\ Nd_{0.006}Y_{2.994}Sc_{0.5}Al_{4.5}O_{12}\ and\ Nd_{0.006}Y_{2.994}ScAl_{4}O_{12},\ respectively.\ The$ mixed powders were pressed into rod under a hydrostatic pressure of 160 MPa for 2 min and sintered in air at 1300 °C for 20 h. During the growth process, the <111> oriented YAG crystal was used as the seed, pulling rate was 0.30 mm/min and the growth atmosphere was flowing argon. The seed is dipped in the melt at the bottom of the crucible in the capillary die and the melt temperature through the power is adjusted until a meniscus is supported. The molten zone and meniscus lenrth are controlled by careful adjustment of the heater power. The whole assembly is maintained in the chamber, which permits control of the ambient gas and enables visualization of The as-grown 0.2 at.% Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals with a the grown crystal by CCD camera. diameter of about 2 mm close to diameter of the crucible opening are shown in Fig. 2. Whatever the scandium concentration, all the crystals are constant in diameter, transparent, colorless and have a smooth surface. We had not seen any composition variation resulting in a second phase apparition Disconnection of the crystal growing from the molten zone was never observed even in the case of changing growth parameters such as pulling rate. The structure of Nd3+ requires a careful design during the preparation step. It was not necessary to grow crystal with high Nd3+ concentration larger than 1at%. The crystal grown from 0.2at% doped YSAG along <111> direction. Using this concentration, the longitudinal composition is homogeneous and we didn't observed any composition variation along the growth direction. The composition distribution of Nd through the analysis by X-ray diffraction (lattice parameters measurement) on different fraction of the crystal was found to be of high uniformity and effective distribution coefficients Keff is close to 1.

Phase composition of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals was examined with room temperature X-ray powder diff raction (XRD, Bruker-D2, Germany). Fig. 3. illustrates the powder XRD patterns of the as-grown crystals. The diffraction peaks of the samples are well indexed to the YAG phase (ICSD 79-1892) and there are no additional impurity peaks in the X-ray diagram, which confirms their cubic system with space group Ia3d. The lattice constants of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals were shown in Table 1. With the increasing of compositional parameter *x*, the calculated lattice constant increased, which is due to the substitution of Al³⁺ ions with larger Sc³⁺ ions. It also can be observed that the diffraction peaks shift toward lower 2-Theta angles in respect with the increase of the Sc³⁺ content. So, this behavior is very interested for the properties of this crystal. The substitution of Al³⁺ by Sc³⁺ ions is a good way to increase the distance between the dodecahedral lattice sites (comfortable sites for Nd³⁺ ions) allowing to decrease the strong Nd³⁺ ion-ion interaction encountered in YAG crystal connected with the concentration quenching of Nd³⁺ fluorescence.



Fig. 1. Schematic illustration of $Nd:Y_3Sc_xAl_{5-x}O_{12}$ crystals grown by the μ -PD method



Fig. 2. Photograph of Nd: $Y_3Sc_xAl_{5-x}O_{12}$ crystals grown by the μ -PD method. x=0.05 (a), 0.5 (b), 1 (c).



Fig. 3. Room temperature XRD patterns of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals compared with a standard pattern of YAG (ICSD 79-1892).

Table 1 Lattice parameters for Nd:Y ₃ Sc _x Al _{5-x} O ₁₂ crystals	
$Nd:Y_3Sc_xAl_{5-x}O_{12}$	a (Å)
$Nd:Y_3Sc_{0.05}Al_{4.95}O_{12}$	12.0134
$Nd:Y_{3}Sc_{0.5}Al_{4.5}O_{12}$	12.0390
$Nd:Y_3ScAl_4O_{12}$	12.1299

2.2 Spectral measurement

The samples were cut from the as-grown crystals and two surfaces perpendicular to the <111>-growth axis were polished for spectral measurements. The spectral measurements were detected in the core (diameter of 0.5 mm) of the samples. The room temperature absorption spectra of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals were measured in a range of 320-1000 nm by a UV–VIS–NIR spectrophotometer (Lambda 900, Perkin -Elmer UV-VIS-NIR) in. The room temperature emission spectra, as well as the decay curves of the ⁴F_{3/2} multiplet, were recorded by an Edinburgh Instruments FLS980 spectrophotometer under 807 nm excitation.

3. Spectral properties

The room temperature absorption spectra of $Nd:Y_3Sc_xAl_{5-x}O_{12}$ crystals in a range from 300 to 1000 nm are shown in Fig. 1. It can be observed that there are 5 prominent absorption bands in the measured range, corresponding to the transitions of Nd^{3+} from the ${}^{4}I_{9/2}$ ground state to the

excited states, as marked in the Fig. 4. by introducing Sc^{3+} will generate a modification of the surrounding of the optical center Nd3+ and so the nergy level structure would be altered. We have shown the absorption bands around 808 nm corresponding to the ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2} + {}^{2}H_{9/2}$ in the inset of Fig. 4, which could be pumped by commercially high-power AlGaAs laser diodes. The absorption coefficient at 808 nm was 0.29, 0.39 and 1.39 cm⁻¹ for x= 0.05, 0.5 and 1, respectively. During the micro-pulling-down growth of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals, the pulling rate is high and there is no mixing in the capillary, the diffusion length $\beta = D/\nu$ (*D*: diffusion rate, *v*:pulling rate) is smaller than the inner length of the crucible capillary (2.5 mm). Therefore the Nd³⁺ distribution along the growth axis was practically constant, but the Nd³⁺ concentration is lower in the core than at the rim due to the small distribution coefficient of Nd³⁺ in Y₃Sc_xAl_{5-x}O₁₂ crystals. The similar results were reported on (Mg_{1-x}Fe_x)₂SiO₄ [16], Ga:Al₂O₃ [17] and Ce:LuAG [18] crystals grown by the μ -PD method. With the increasing of compositional parameter *x* in Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals, the transversal distribution coefficient of Nd³⁺ increased, which induced the increase of Nd³⁺ concentration in the core and the increase of absorption coefficient of Nd³⁺ at 808 nm.



Fig. 4. Absorption spectra of $Nd: Y_3Sc_xAl_{5-x}O_{12}$ crystals. The inset presents the absorption spectra around 808 nm.

Fig.5 presents the room temperature emission spectra of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals in the wavelength range of 850-1500 nm under 807 nm excitation. With the increasing of compositional parameter *x* in Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals, the emission spectra show a blue shift, which was attributed to the different crystal field environment for Nd³⁺. For each spectrum, three emission bands corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$, ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$, and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ transitions are observed at 850-960, 1040-1140, and 1300-1460, respectively. This shift can be connected to changes of the Nd³⁺ electronic level structure affected by the modification of the lattice in the vicinity of the

doping ion. The FWHM of the emission band centered at 1064 nm was calculated to be 6.1, 7.1, and 7.3 nm for x= 0.05, 0.5 and 1, respectively, which is larger than that of Nd:YSGG (1.0 nm) [19], Nd:YGAG (3.5 nm) [20], and Nd:YSAG (5.5 nm) [21]. Thus Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals are promising laser gain media for tunable laser and/or ultrashort laser system.



Fig. 5. Emission spectra of Nd: Y₃Sc_xAl_{5-x}O₁₂ crystals under 807 nm excitation.

The decay curves of the ${}^{4}F_{3/2}$ multiplet of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals under 807 nm excitation are shown in Fig. 6. The fluorescence lifetime was calculated to be 259.3, 269.6, and 276.9 µs for x= 0.05, 0.5 and 1, respectively, by a single exponential fitting. The lifetime matches perfectly with the results found in the literature corresponding to Nd:YGAG (270 µs) [20], Nd:LuGdAG (262 µs) [22], Nd:LuYAG (263 µs) [23]. As can be seen, with the increasing of compositional parameter *x* in Y₃Sc_xAl_{5-x}O₁₂ crystals, the Nd³⁺ concentration in the core increased, but no concentration quenching was observed. The results indicated that Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals are promising laser gain media.



Fig. 6. Decay curves of the ${}^{4}F_{3/2}$ level of Nd: $Y_{3}Sc_{x}Al_{5-x}O_{12}$ crystals

4. Conclusions

In this work, Nd:Y₃Sc_xAl_{5-x}O₁₂ (x= 0.05, 0.5, 1) single crystals were successfully grown by the μ -PD technique. Under stable growth conditions, the obtained crystals was of high quality. The Sc³⁺ is substituted to Al³⁺ with homogeneous distribution along the growth axis. The effect of Sc³⁺ content on the structure, absorption, emission and fluorescence lifetime of Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals was studied. The crystals crystallized in the cubic system with space group Ia3d and the calculated lattice constant increased with the increase of *x*. With the increasing of compositional parameter *x*, the distribution coefficient of Nd³⁺ increased and the absorption coefficient of Nd³⁺ at 808 nm in the core increased. The full width at half maximum (FWHM) of the emission band centered at 1064 nm was calculated to be 6.1, 7.1, and 7.3 nm for *x*= 0.05, 0.5 and 1, respectively. The fluorescence lifetime of ⁴F_{3/2} levels are 259.3, 269.6, and 276.9 µs for *x*= 0.05, 0.5, and 1, respectively. The results indicate that the Nd:Y₃Sc_xAl_{5-x}O₁₂ crystals are promising laser gain media.

Acknowledgements

This work is partially supported by the National Natural Science Foundation of China (No. 61621001).

References:

[1] A.A. Kaminskii, Laser crystals and ceramics: recent advances, Laser Photon. Rev. 1 (2007) 93-177.

[2] E. Sorokin, M.H. Ober, I. Sorokina, E. Wintner, A.J. Schmidt, Femtosecond solid-state lasers

using Nd³⁺-doped mixed scandium garnets, J. Opt. Soc. Am. B 10 (1993) 1436-1442

[3] Y. Sato, T. Taira, A. Ikesue, Spectral parameters of Nd^{3+} -ions in the polycrystalline solid-solution composed of $Y_3Al_5O_{12}$ and $Y_3Sc_2Al_3O_{12}$, Jpn. J. Appl. Phys. 42 (2003) 5071-5074 [4] T.H. Allik, C.A. Morrison, J.B. Cruber, M.R. Kokta, Crystallography, spectroscopic analysis,

and lasing properties of Nd³⁺:Y₃Sc₂Al₃O₁₂, Phys. Rev. B 41 (1990) 21-30.

[5] C. Feng, H. Zhang, Q. Wang, J. Fang, Dual-wavelength synchronously mode-locked laser of a Nd:Y₃ScAl₄O₁₂ disordered crystal, Laser Phys. Lett. 14 (2017) 045804

[6] S. Ding, Q. Zhang, W. Lu, J. Xu, W. Liu, J. Luo, X. Wang, D. Sun, Growth, defects, mechanical and optical properties of Nd:GSAG and Nd:YSAG laser crystal, Optik 148 (2017) 136-141

[7] G.B. Lutts, A.L. Denisov, E.V. Zharikov, A.I. Zagumennyi, S.N. Kozlikin, S.V. Lavrishchev, S.A. Samoylova, GSAG and YSAG: a study on isomorphism and crystal growth, Opt. Quantum Electron. 22 (1990) S269-S281

[8] F. Cornacchia, R. Simura, A. Toncelli, M. Tonelli, A. Yoshikawa, T. Fukuda, Spectroscopic properties of $Y_3Sc_2Al_3O_{12}$ (YSAG) single crystals grown by μ -PD technique, Opt. Mater. 30 (2007) 135-138

[9] Y.M. Yu, V.I. Chani, K. Shimamura, T. Fukuda, Growth of Ca₃(Li,Nb,Ga)₅O₁₂ garent crystals from stoichiometric melts, J. Cryst. Growth 171 (1997) 463-471

[10] K. Lebbou, Single crystals fiber technology design. Where we are today? Opt. Mater. 63 (2017) 13-18

[11] J. Didierjean, M. Castaing, F. Balembois, P. Georges, D. Perrodin, J.M. Fourmigue, K. Lebbou, A. Brenier, O. Tillement, High-power laser with Nd:YAG single-crystal fiber grown by the micro-pulling-down technique, Opt. Lett. 31 (2006) 3468-3470

[12] A. Yoshikawa, M. Nikl, G. Boulon, T. Fukuda, Challenge and study for developing of novel single crystalline optical materials using micro-pulling-down method, Opt. Mater. 30 (2007) 6-10

[13] J. Wang, Q. Song, Y. Sun, Y. Zhao, W. Zhou, D.Z Li, X. Xu, C. Shen, W. Yao, L. Wang, J. Xu,D. Shen, High-performance Ho:YAG single-crystal fiber laser in-band pumped by a Tm-doped all-fiber laser, Opt. Lett. 44 (2019) 455-459

[14] Q. Song, X. Xu, Z. Zhou, B. Xu, D. Li, P. Liu, J. Xu, K. Lebbou, Laser operation in a Tm:LuAG crystal grown by the micro-pulling-down technique, IEEE Photon. Technol. Lett. 30 (2018) 1913-1916

[15] N. Li, Y. Xue, D. Wang, B. Liu, C. Guo. Q. Song, X. Xu, J. Liu, D. Li, J. Xu, Z. Xu, J. Xu, Optical properties of Nd:Bi₄Ge₃O₁₂ crystals grown by the micro-pulling-down method, J. Lumin. 206 (2019) 412-416

[16] S. Ganschow, D. Klimm, Growth of olivine single crystals by the micro-pulling-down method, Cryst. Res. Technol. 40 (2005) 359-362

[17] D. Maier, D. Rhede, R. Bertram, D. Klimm, R. Fornari, Dopant segregations in oxide single-crystal fibers grown by the micro-pulling-down method, Opt. Mater. 30 (2007) 11-14

[18] X. Xu, K. Lebbou. F. Moretti, K. Pauwels, P. Lecoq, E. Auffray, C. Dujardin, Ce-doped LuAG single-crystal fibers grown from the melt for high-energy physics, Acta Mater. 67 (2014) 232-238

[19] E. Sorokin, M.H. Ober, I. Sorokina, E. Wintner, A.J. Schmidt, Femtosecond solid-state lasers using Nd³⁺-doped mixed scandium garnets, J. Opt. Soc. Am. B. 10 (1993) 1436-1442.

[20] D. Zhou, X. Xu, J. Meng, D. Li, J. Di, C. Xia, F. Wu, J. Xu, Spectroscopic analysis and lasing properties of Nd:Y_{2.5}Gd_{0.5}Al₅O₁₂ crystals, Laser Phys. Lett. 8 (2011) 201-204.

[21] Y. Sato, J. Saikawa, T. Taira, Characteristics of Nd^{3+} -doped $Y_3ScAl_4O_{12}$ ceramic laser, Opt. Mater. 29 (2007) 1277-1282.

[22] J. Di, X. Xu, S. Cheng, D. Li, D. Zhou, F. Wu, Z. Zhao, J. Xu, Crystal growth, spectroscopic and CW laser properties of Nd_{0.03}Lu_{2.871}Gd_{0.099}Al₅O₁₂,crystal, Laser Phys. 21 (2011) 1891-1894.

[23] X. Xu, S. Cheng, J. Meng, D. Li, D. Zhou, L. Zheng, J. Xu, W. Ryba-Romanowski, R. Lisiecki, Spectral characterization and laser performance of a mixed crystal $Nd:(Lu_xY_{1-x})_3A_{15}O_{12}$, Opt. Express. 18 (2010) 21370-21375.