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RESEARCH ARTICLE

Basic properties of a new Nd-doped laser crystal: Nd:GdNbO$_4$

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Abstract A Nd-doped GdNbO$_4$ single crystals have been grown successfully using the Czochralski technique. The chemical etching method was employed to study the defects in the structural morphology of Nd:GdNbO$_4$ crystal with phosphoric acid etchant. Mechanical properties (such as hardness, yield strength, fracture toughness, and brittle index) of the as-grown crystal were systematically estimated on the basis of the Vickers hardness test for the first time. The transmission spectrum of Nd:GdNbO$_4$ was measured in the wavelength range of 320–2400 nm at room temperature, and the absorption peaks were assigned. Results hold great significance for further research on Nd:GdNbO$_4$.

Keywords Nd:GdNbO$_4$, laser crystal, mechanical properties, chemical etching

1 Introduction

Solid-state lasers are better than free-electron and gas lasers because of their excellent performance [1]. Examples include rod, disk, and slab types of lasers which are based on rare-earth (RE)-doped laser crystals. Currently, diode-pumped solid-state lasers (DPSSLs) that depend on Nd-doped crystals have attracted considerable attention because of their high efficiency, compactness, and high stability. These lasers have been widely applied in medical treatment, industry processing, the military, and optical communication [2–5]. Many studies have been conducted to explore the novel single crystals with excellent laser performance and high quality for DPSSLs. For example, the Nd-doped vanadate series of crystals (Nd:LnVO$_4$, Ln = Y, Gd, Lu), which is designated as Nd:YVO$_4$, has been identified as a group of excellent laser materials with high chemical stability, good laser properties, and high laser damage threshold. These materials have been commercialized and broadly applied in low and moderate lasers [6].

Currently, RE-doped niobates (LnNbO$_4$; Ln = La-Lu, Y) have become a dynamic field given their extensive applications in fluorescent lamps, solid-state lasers, and cathode ray tubes [7–9]. Previous works have proven that niobates are good host lattice materials for RE ions [10–12]. Recently, our group has achieved some breakthrough research on the GdNbO$_4$ crystal. In 2014, 5 at% Yb^{3+}-doped GdNbO$_4$ laser crystal was grown successfully through the Czochralski (Cz method) for the first time, and a maximal output power of 270 mW was achieved at 1001 nm. This output power corresponds to an optical-to-optical conversion efficiency of 4.5% and a slope efficiency of 7.5% [13]. The results suggested that Yb:GdNbO$_4$ crystal was advantageous for ultra-short pulses and tunable laser. Moreover, Nd-doped GdNbO$_4$ crystal was also grown successfully, and laser characterization was performed for the first time [14]. A maximum output power of 1.076 W with 3.28 W of incident power were achieved at 1066 nm by Nd:GdNbO$_4$ crystal, corresponding to a slope efficiency of 35.3% and an optical-to-optical conversion efficiency of 32.8%. These works indicate that the GdNbO$_4$ crystal is a good laser host crystal and holds great potential for application in continuous wave and pulse lasers. The defects and mechanical properties of laser crystals usually substantially influences both crystal growth and laser performance. Therefore, in this study, a Nd-doped GdNbO$_4$ laser crystal was grown using the Cz method. The defects and fundamental physical properties including hardness, density, and basic mechanical properties are systematically studied.

2 Experimental

2.1 Crystal growth

A Nd:GdNbO$_4$ single crystal was grown by the Cz method using a JGD-60 furnace (26th Institute of CETC, China) with an automatic diameter-controlled growth system by monitoring the weight rate during growth. The oxide

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powders of Nd_2O_3 (5 N), Gd_2O_3 (5 N), and Nb_2O_5 (4 N) were used as starting materials. These powders were weighed on the basis of the stoichiometric ratio and mixed thoroughly. An *a*-oriented pure $GdTaO_4$ crystal bar was employed as seed crystal. In the crystal growth process, the pulling rate was 0.5–1 mm/h and the rotation rate was 5–10 r/min. The furnace was pumped into a vacuum and then filled with N_2 to prevent oxidation of iridium. Then, the crystal was cooled down to room temperature naturally at the end of the growth process. An as-grown Nd:$GdNbO_4$ boule is shown in Fig. 1. Under a 1 W 532 nm laser, no light-scattering points were found, indicating that the as-grown Nd:$GdNbO_4$ crystal possesses a good optical quality.

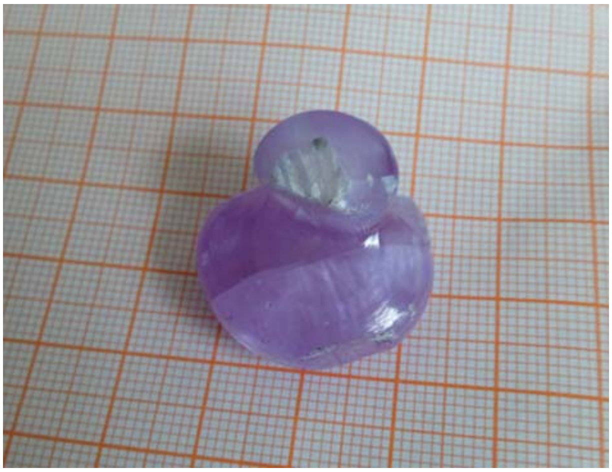

Fig. 1 As-grown Nd:$GdNbO_4$ crystal boule

2.2 Characterizations

Slices for chemical etching studies, hardness, and spectrum measurements were cut into 3 mm thick disks in three different orientations (i.e., *a*, *b*, and *c* orientations) and polished on both sides. In chemical etching research, the crystal slices were etched with phosphoric acid at approximately 423 K for 3 h. Then, the etched surfaces were washed with deionized water and dried naturally. The surface micromorphology of Nd:$GdNbO_4$ crystal was photographed using an Axio Imager A1m metalloscope. A HV-1000A microhardness tester equipped with a diamond square indenter was employed to investigate Vickers microhardness. In this work, loads ranging from 25 to 200 g were adopted for the microhardness measurement of Nd:$GdNbO_4$ with a dwell constant period of 10 s. The indentation distance between any two microhardness tests is maintained at least three times the diagonal length of the indention mark to avoid the surface effects. Other mechanical parameters (such as yield strength, fracture toughness, and brittle index) were determined by measuring the length of the indentations. The absorption spectrum was measured in the wavelength range of 320 to 2400 nm using Perkin-Elmer UV-VIS-NIR LAMBDA-950 spectrometer with an interval of 1 nm.

3 Results and discussion

3.1 Chemical etching studies

Investigating the surface morphology and microstructural imperfections of laser crystals is necessary [15]. Defective crystals may influence mechanical and optical properties and laser performance and thereby limit the crystal's application. The chemical etching method can simply and effectively identify defects in crystal structure. This method can also determine morphological features, such as etch spirals, growth hillocks, and rectangular etching pits [16]. Figure 2 shows the dislocation etching pit patterns on the (100), (010), and (001) crystallographic faces of the as-grown Nd:$GdNbO_4$ crystal. As shown, the etch pit patterns on three crystallographic faces have different features. Generally, the etch pit patterns are mainly introduced by lattice distortion and symmetry. The specific etch pit patterns are formed because the weakest and unstable chemical bonds are easily broken in the chemical etching processing [17]. Figure 3 shows the atomic arrangement of the Nd:$GdNbO_4$ crystal viewed in three different crystalline orientations using Crystalmaker 2.3. By comparison, the dislocation etch pit patterns of the Nd:$GdNbO_4$ crystal are consistent with the corresponding lattice structure. Moreover, as displayed in Fig. 2, the

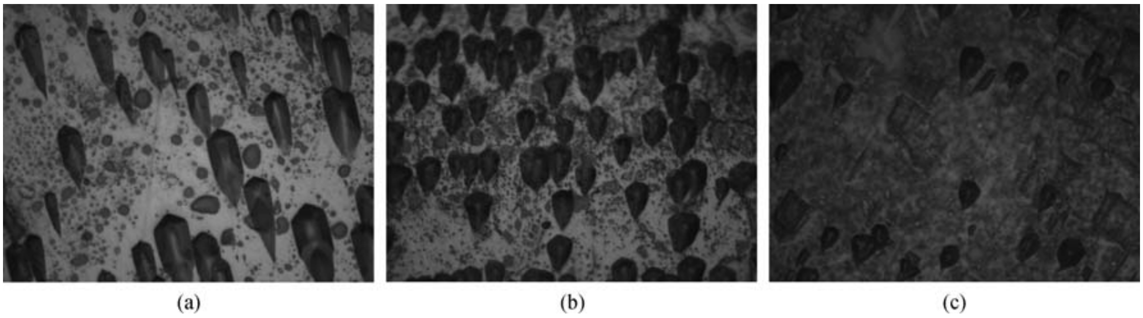

Fig. 2 Dislocation etch pit patterns of the Nd:$GdNbO_4$ crystal on three different crystallographic faces. (a) (100); (b) (010); and (c) (001)

defect density on the c-oriented crystal is lower than that on the a- and b-oriented crystals. This result means that the c-oriented crystal may possess a higher crystalline quality.

3.2 Mechanical properties

The mechanical properties of laser crystal are important for the stability and fabrication of optical devices [18]. Therefore, the mechanical properties of Nd:GdNbO$_4$ crystal were systematically investigated using Vickers hardness tests in this study. Hardness indentations were performed on three crystallographic faces at room temperature with an applied load of 100 g and a dwell time of 10 s. The Vickers hardness measurement was repeated five times, and the average was obtained. The Vickers indentation marks on the Nd:GdNbO$_4$ crystal at different loads of (100), (010), and (001) faces are shown in Fig. 4.

The Vickers hardness value H_v was calculated using the following equation:

$$H_v = 1.8544\left(\frac{P}{d^2}\right)\text{kg/mm}^2, \tag{1}$$

where d is the diagonal length of the indentation mark, 1.8544 is a geometrical constant factor for diamond pyramid, and P is the applied load. The hardness of Nd:GdNbO$_4$ exhibited strong anisotropy. Besides, the crystal is hardest along the a-orientation and cracks easily along the c-orientation. The Vickers hardness (H_v) values of Nd:GdNbO$_4$ versus the applied load P is shown in Fig. 5. As shown, the hardness value increases gradually with the increase in applied load. This trend indicates that the crystal exhibits a reverse indentation size effect [19].

Meyer's index can be estimated using Meyer's law [20]:

$$P = K_1 d^n, \tag{2}$$

$$\log P = \log K_1 + n \log d, \tag{3}$$

where P is the applied load, K_1 is the material constant, d is the diagonal length of impression, and n is the Meyer's index, also known as work hardening coefficient. The values of n were 2.017, 2.037, and 2.030, respectively, obtained by fitting the slope of $\log P$ and $\log d$ plot (Fig. 6). Onitsch and Hanneman [21] pointed out that the value of n is between 1 and 1.6 for hard materials and more than 1.6 for soft materials. Thus, Nd:GdNbO$_4$ crystal is regarded as a soft material and suitable for device fabrication.

Fracture toughness (K_c) plays an important role in selecting laser crystals for device fabrication and applications. This parameter can also accurately evaluate the fracture resistance of brittle crystals [22]. In this work, $c/a \geqslant 2.5$, where c is the crack length (measured from center of the indentation mark to tip of the crack) and a is the half diagonal length of the indentation mark. Hence,

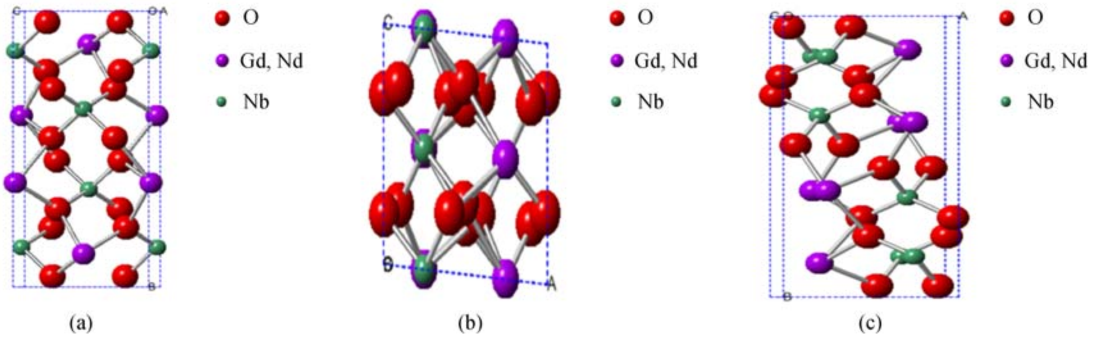

Fig. 3 Atomic arrangement diagrams viewed along the three different crystalline orientations for the Nd:GdNbO$_4$ crystal. (a) (100); (b) (010); and (c) (001)

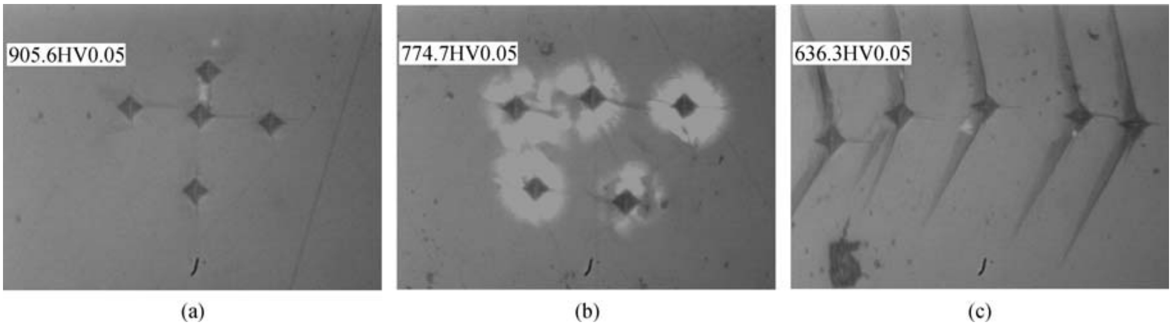

Fig. 4 Vickers indentation mark on the Nd:GdNbO$_4$ crystal along three different crystallographic faces. (a) (100); (b) (010); and (c) (001)

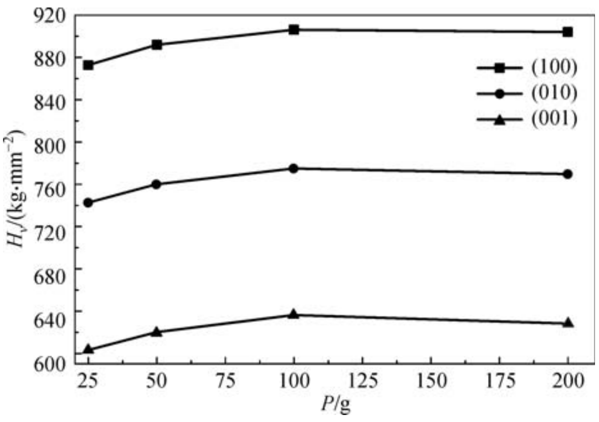

Fig. 5 Dependence of Vickers hardness H_v on the indentation load P on (100), (010), and (001) crystallographic faces of Nd:GYNO crystal

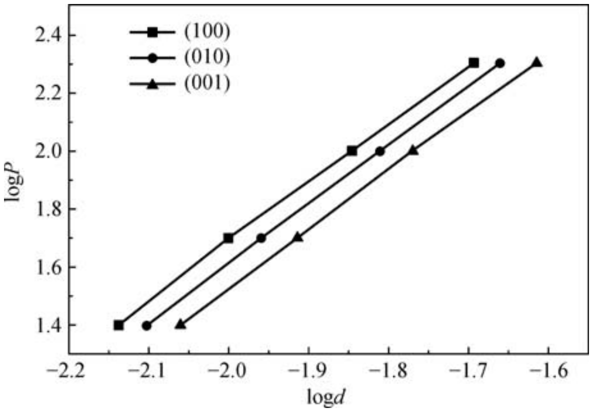

Fig. 6 Variation of log$P$ with log$d$ on (100), (010), and (001) crystallographic faces of Nd:GYNO crystal

the fracture toughness K_c can be given by [23]

$$K_c = \frac{P}{\beta c^{3/2}}, \tag{4}$$

where P is the load and β (= 7) is a constant for Vickers indenter. The calculated K_c values are given in Table 1.

Given the hardness value, the yield strength σ_v of the Nd:GdNbO$_4$ crystal can be calculated using [24]

$$\sigma_v = \frac{H_v}{3} \text{ (For Meyer's index } n<2). \tag{5}$$

Therefore, the yield strength σ_v for the (100), (010), and (001) faces were 3.02, 2.58, and 2.12 GPa, respectively. Hence, the as-grown Nd:GdNbO$_4$ crystal possesses a relatively high mechanical strength.

The brittleness index is a key parameter for laser crystal, which reveals crystal fracture without any appreciable deformation. The brittleness index value (B_i) can be estimated using the equation [25] as follows:

$$B_i = \frac{H_v}{K_c}. \tag{6}$$

The calculated B_i values are also given in Table 1.

3.3 Optical properties

The transmission spectrum of the Nd:GdNbO$_4$ crystal from 320 to 2400 nm at room temperature is shown in Fig. 7. Eight absorption bands correspond to the typical transitions of Nd^{3+} from the ground state, namely, $^4I_{9/2}$ to $^4F_{3/2}$, $^4F_{5/2}$ + $^2H_{9/2}$, $^4H_{7/2}$ + $^4S_{3/2}$, $^4G_{5/2}$ + $^2G_{7/2}$, $^4G_{7/2}$ + $^4G_{9/2}$, $^2G_{9/2}$ + $^2D_{3/2}$ + $^2P_{3/2}$ + $^4D_{11/2}$, $^2P_{1/2}$, and $^4D_{3/2}$ + $^4D_{5/2}$ + $^2I_{11/2}$ + $^2L_{15/2}$ + $^4D_{1/2}$, respectively. All the absorption bands are assigned and marked in Fig. 7. The strongest absorption peak is located at 808 nm, indicating that the crystal can be well matched with the commercially high-power AlGaAs diode laser.

4 Conclusions

Our group developed a good-quality single crystal of Nd:GdNbO$_4$ using the Cz method. Its mechanical properties, such as Vickers hardness, yield strength, fracture toughness, and brittle index were systematically studied using Vickers diamond pyramid indenter. The chemical etching result reveals that the etch pit patterns possesses a close relationship with the crystal structure and lattice symmetry of Nd:GdNbO$_4$. The spectral properties of the as-grown crystal were investigated by measuring the absorption spectrum at room temperature, and the eight absorption peak groups were assigned in the wavelength range of

Table 1 Mechanical parameters of Nd:GdNbO$_4$ crystal

mechanical parameters	values (P = 100 g)		
	(100) face	(010) face	(001) face
hardness number H_v/(kg·mm^{-2})	906	775	636
Meyer's index n	2.017	2.037	2.030
fracture toughness K_c/(kg·mm$^{-3/2}$)	8.36	7.40	6.44
yield strength σ_v/GPa	3.02	2.58	2.12
brittleness index B_i/mm$^{-1/2}$	108.5	107.7	98.7

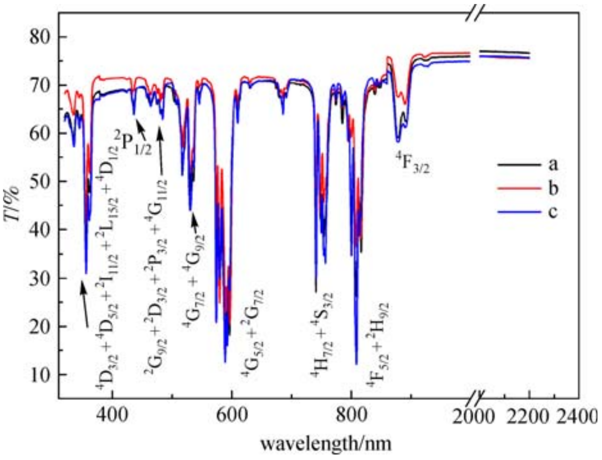

Fig. 7 Transmission spectra of Nd:GdNbO$_4$ at room temperature

320–2400 nm. The obtained results play an important role for further investigation of the Nd:GdNbO$_4$ laser crystal.

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References

1. Sanghera J, Kim W, Villalobos G, Shaw B, Baker C, Frantz J, Sadowski B, Aggarwal I. Ceramic laser materials. Materials (Basel), 2012, 5(12): 258–277
2. Zhang H J, Meng X L, Zhu L, Wang C Q, Wang P, Zhang H Z, Chow Y T, Dawes J. Growth and laser properties of laser crystal Nd: Gd$_{0.8}$La$_{0.2}$VO$_4$. Journal of Crystal Growth, 1998, 193(3): 370–373
3. Lee M C, Chang C S, Huang Y L, Chang S L, Chang C H, Lin Y F, Hu S. Treatment of melasma with mixed parameters of 1064-nm *Q*-switched Nd:YAG laser toning and an enhanced effect of ultrasonic application of vitamin C: a split-face study. Lasers in Medical Science, 2015, 30(1): 159–163
4. Kane T J, Kozlovsky W J, Byer R L, Byvik C E. Coherent laser radar at 1.06 μm using Nd:YAG lasers. Optics Letters, 1987, 12(4): 239–241
5. Rodin A M, Grishin M, Michailovas A. Picosecond laser with 11 W output power at 1342 nm based on composite multiple doping level Nd:YVO$_4$ crystal. Optics & Laser Technology, 2016, 76: 46–52
6. Yu H H, Liu J H, Zhang H J, Kaminskii A A, Wang Z P, Wang J Y. Advances in vanadate laser crystals at a lasing wavelength of 1 micrometer. Laser & Photonics Reviews, 2014, 8(6): 847–864
7. Nazarov M, Kim Y J, Lee E Y, Min K, Jeong M S, Lee S W, Noh D Y. Luminescence and Raman studies of YNbO$_4$ phosphors doped by Eu^{3+}, Ga^{3+}, and Al^{3+}. Journal of Applied Physics, 2010, 107 (10): 103104
8. Wang Y Z, Zhang L L, Cao R P, Miao Q, Qiu J Q. Structure and properties of CaNb$_2$O$_6$:Sm^{3+} thin films by pulsed laser deposition. Applied Physics A, 2014, 115(4): 1365–1370
9. Ding S J, Peng F, Zhang Q L, Luo J Q, Liu W P, Sun D L, Dou R Q, Sun G H. Structure, spectroscopic properties and laser performance of Nd:YNbO$_4$ at 1066 nm. Optical Materials, 2016, 62: 7–11
10. Fang X, Roushan M, Zhang R, Peng J, Zeng H, Li J. Tuning and enhancing white light emission of II–VI based inorganic–organic hybrid semiconductors as single-phased phosphors. Chemistry of Materials, 2012, 24(10): 1710–1717
11. Jüstel T, Nikol H, Ronda C. New developments in the field of luminescent materials for lighting and displays. Angewandte Chemie International Edition, 1998, 37(22): 3084–3103
12. Huang C, Liu W, Chen T. Single-phased white-light phosphors Ca$_9$Gd(PO$_4$)$_7$:Eu^{2+}, Mn^{2+} under near-ultraviolet excitation. Journal of Physical Chemistry C, 2010, 114(43): 18698–18701
13. Dou R Q, Zhang Q L, Luo J Q, Chen J K, Yang H J, Liu W P, Sun G H, Sun D L. Growth, structure, and spectroscopic properties of 5 at.% Yb:GdNbO$_4$ laser crystal. Optical Materials, 2015, 42: 56–61
14. Ding S J, Peng F, Zhang Q L, Luo J Q, Liu W P, Sun D L, Dou R Q, Gao J Y, Sun G H, Cheng M J. Crystal growth, spectral properties, and continuous wave laser operation of Nd:GdNbO$_4$. Journal of Alloys and Compounds, 2017, 693: 339–343
15. Zhong D G, Teng B, Cao L F, Fei Y, Zhang S M, Li Y Y, Wang C, He L X, Huang W X. Characterization of dislocations and sub-grain boundaries in mixed rare earth orthovanadate of Yb:Y$_x$Lu$_{1-x}$VO$_4$. Optical Materials, 2014, 36(12): 2034–2038
16. Dou R Q, Zhang Q L, Liu W P, Luo J Q, Wang X F, Ding S J, Sun D L. Growth, structure, chemical etching, and spectroscopic properties of a 2.9 μm Tm,Ho:GdYTaO$_4$ laser crystal. Optical Materials, 2015, 48: 80–85
17. Ding S J, Liu W P, Zhang Q L, Peng F, Luo J Q, Dou R Q, Sun G H, Sun D L. Crystal growth, defects, and mechanical and spectral properties of a novel mixed laser crystal Nd:GdYNbO$_4$. Applied Physics A, 2017, 123: 70
18. Thirumurugan R, Babu B, Anitha K, Chandrasekaran J. Structural, optical, thermal, mechanical, dielectric and laser damage threshold studies of a succinate salt of creatinine for nonlinear optical applications. Materials Letters, 2016, 185: 214–217
19. Mythili P, Kanagasekaran T, Sharma S N, Gopalakrishnan R. Growth and characterization of sodium sulfanilate dihydrate (SSDH) crystals for NLO applications. Journal of Crystal Growth, 2007, 306(2): 344–350
20. Hanumantha Rao R, Kalainathan S. Microhardness, chemical etching, SEM, AFM and SHG studies of novel nonlinear optical crystal–l-threonine formate. Materials Research Bulletin, 2012, 47 (4): 987–992
21. Singh P, Hasmuddin M, Shakir M, Vijayan N, Abdullah M M, Ganesh V, Wahab M A. Investigation on structural, optical, thermal, mechanical and dielectric properties of l-proline cadmium chloride monohydrate single crystals: an efficient NLO material. Materials Chemistry and Physics, 2013, 142(1): 154–164
22. Gupta V, Bamzai K K, Kotru P N, Wanklyn B M. Mechanical characteristics of flux-grown calcium titanate and nickel titanate crystals. Materials Chemistry and Physics, 2005, 89(1): 64–71
23. Jain A, Razdan A K, Kotru P N, Wanklyn B M. Load and directional effects on microhardness and estimation of toughness and brittleness for flux-grown LaBO$_3$ crystals. Journal of Materials Science, 1994, 29(14): 3847–3856
24. Cahoon J P, Broughton W H, Kutzuk A R. The determination of

yield strength from hardness measurements. Metallurgical and Materials Transactions B, Process Metallurgy and Materials Processing Science, 1971, 2(7): 1979–1983

25. Townsend D, Field J E. Fracture toughness and hardness of zinc sulphide as a function of grain size. Journal of Materials Science, 1990, 25(2): 1347–1352

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