Journal of Alloys and Compounds 509 (2011) 2815–2818

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Growth and spectroscopic properties of Nd^{3+}-doped $Na_2Gd_4(MoO_4)_7$ crystal

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ARTICLE INFO

Article history:
Received 29 June 2009
Received in revised form
22 November 2010
Accepted 22 November 2010
Available online 1 December 2010

PACS:
42.70.Hj
78.20.−e

Keywords:
Optical microscopy
Czochralski method
Crystal growth from melt
Molybdate
Solid-state laser materials

ABSTRACT

This paper reports the growth and spectral properties of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystals. An Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal with dimensions of Ø20 × 25 mm^3 has been grown by the Czochralski method. The spectroscopic properties of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal were investigated. The Judd–Ofelt theory was applied to calculate the spectral parameters. The polarized absorption cross-sections of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal are 4.25×10^{-20} cm^2 with full width at half maximum (FWHM) of 14.6 nm for the π-polarization and 2.87×10^{-20} cm^2 with FWHM of 16.2 nm for the σ-polarization, respectively. The emission cross-sections are 10.0×10^{-20} cm^2 at 1060 nm for π-polarization and 13.6×10^{-20} cm^2 at 1067 nm for σ-polarization, respectively. The fluorescence quantum efficiency has been estimated to be 90.0%. Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal may be considered as a potential laser gain medium for the diode laser pumping.

1. Introduction

Laser diode pumped solid-state laser plays an important role in a wide variety of applications. Recently, with the rapid development of the solid-state laser with diode laser pumping, research on more efficient new laser materials has gained much interest [1–11]. Double molybdate with general format $MT(MoO_4)_2$ (M = alkali metal; T = rare earth ion) were investigated as new laser host materials [12–14]. A molybdate with general format $M_2T_4(MoO_4)_7$ (M = alkali metal; T = rare earth ion) is another molybdate family [15,16]. $Na_2Gd_4(MoO_4)_7$ crystal is a member of $M_2T_4(MoO_4)_7$ molybdate family. In order to explore new laser materials, this paper reports the synthesis, growth and spectroscopic properties of $Na_2Gd_4(MoO_4)_7$ crystal.

2. Synthesis and crystal growth

In order to obtain the melting point of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal, Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ compound was firstly synthesized by solid state chemical reaction according to the following chemical reaction equation:

$$Na_2CO_3 + \left(2 - \frac{x}{2}\right) Gd_2O_3 + \frac{x}{2}Nd_2O_3 + 7MoO_3 = Na_2Gd_{4-x}Nd_x(MoO_4)_7 + CO_2 \uparrow \quad (1)$$

where x is the concentration of Nd^{3+} ions in Nd^{3+}:$Na_2Gd_4(MoO_4)_7$. The initial substances used were Gd_2O_3 and Nd_2O_3 with purity of 99.99%, Na_2CO_3 and MoO_3 with analytical reagent. The raw materials of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ were accurately weighted. After grinding and extruding to form chunks, the samples were placed in the crucible and heated up to 750 °C, kept at this temperature for 24 h. The process was repeated once again and held at 850 °C for 24 h to assure adequate reaction. The synthesized Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ was checked by powder X-ray diffraction (XRD) using a *D*/max-rA type diffractometer and CuKα radiation (λ = 1.54056 Å) at room temperature in a range of 2θ = 10–65°. The powder X-ray diffraction pattern of the synthesized Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ is shown in Fig. 1(a). The melting point of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ compound was determined using a NETZSCH STA 449C Simultaneous Thermal Analyzer. The result of DSC analysis shows that Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ compound melts congruently at 1194 °C, as shown in Fig. 2.

Since Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal melts congruently at 1194 °C, it was grown by the Czochralski method. Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal was grown in a 2 kHz frequency fur-

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doi:10.1016/j.jallcom.2010.11.125

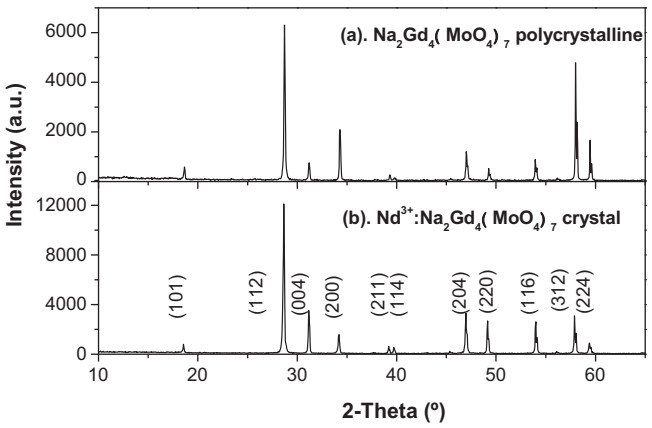

Fig. 1. Powder XRD patterns of (a) $Na_2Gd_4(MoO_4)_7$ polycrystalline and (b) as-grown Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal.

nace in air. The synthesized raw materials of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ with 3 at.% Nd^{3+} were molted in a platinum crucible with dimensions of Ø45 × 40 mm^3, where 1 wt.% excess amount of MoO_3 was added to the raw materials to compensate for the evaporation of MoO_3 during crystal growth. The fully charged crucible was heated up to 1300 °C. After adjusting the growing temperature, the crystal was grown at a pulling rate of 0.5–2.0 mm/h and rotating rate of 10–30 r/min. When the growth process ended, the grown crystal was cooled down to the room temperature at an annealing rate of 10–30 °C/h. Finally, A transparent Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal with dimensions of Ø20 × 25 mm^3 and free crack was obtained, as shown in Fig. 3.

The powder XRD pattern of the grown crystal is shown in Fig. 1(b), which agrees with that of synthesized Nd^{3+}:$Na_2Gd_4(MoO_4)_7$. The lattice parameters of the grown crystal were determined to be: $a = b = 5.2365$ Å, $c = 11.4573$ Å and $\alpha = \beta = \gamma = 90°$ by the Rigaku AFC7R diffractometer. The single XRD shows that Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal is of isomorphism of $Li_2Gd_4(MoO_4)_7$ crystal with tetragonal system and lattice parameters: $a = b = 5.192$ Å, $c = 11.30$ Å [15]. According to the lattice parameters of the grown crystal, all XRD lines can be indexed (see Fig. 1). The XRD results confirm that the grown crystal belong to Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal.

3. Spectroscopic properties

Nd^{3+} concentrations in Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal were measured to be 1.96 at.%, i.e. 1.43×10^{20} cm^{-3} by the inductively

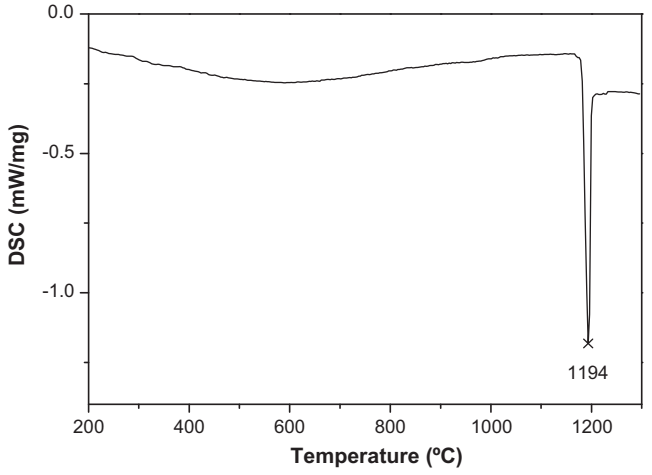

Fig. 2. DSC curve of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ compound.

Fig. 3. Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal grown by the Czochralski method (where white color is reflecting light).

coupled plasma and atomic emission spectrometry (ICP-AES). A plate sample with dimensions of 9 × 5 × 1 mm^3 cut from the as-grown crystal along the *c*-axis was used for the spectral measurement. The σ- and π-polarization were defined in terms of the *E*-vector being perpendicular or parallel to the *c*-axis, respectively. The polarized absorption spectrum of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal was measured using a Perkin-Elmer UV–VIS–NIR Spectrometer (Lambda-900) in a range of 350–950 nm at room temperature. The polarized fluorescence spectrum and fluorescence lifetime were determined using an Edinburgh Analytical Instruments FLS92 Fluorescence Spectrophotometer with a continuous Xe-flash lamp.

The polarized absorption spectrum of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal at room temperature is shown in Fig. 4. All the absorption bands are attributed to the transitions of Nd^{3+} ions from the ground state $^4I_{9/2}$ to the excited state J' manifolds, which are marked in Fig. 4. The absorption band at 807 nm has an absorption cross-section of 2.87×10^{-20} cm^2 with full width at half maximum (FWHM) of 16.2 nm for the σ-polarization, and has an absorption cross-section of 4.25×10^{-20} cm^2 with FWHM of 14.6 nm for the π-polarization, which is closed to the laser output wavelength of AlGaAs diode laser (λ ≈ 808 nm). Since the emission wavelength of the diode laser is increased at 0.2–0.3 nm/°C with the operating temperature of the laser device, the temperature stability of the output wavelength of the diode laser needs to be crucially controlled. Thus, such broad absorption band is suitable for diode laser

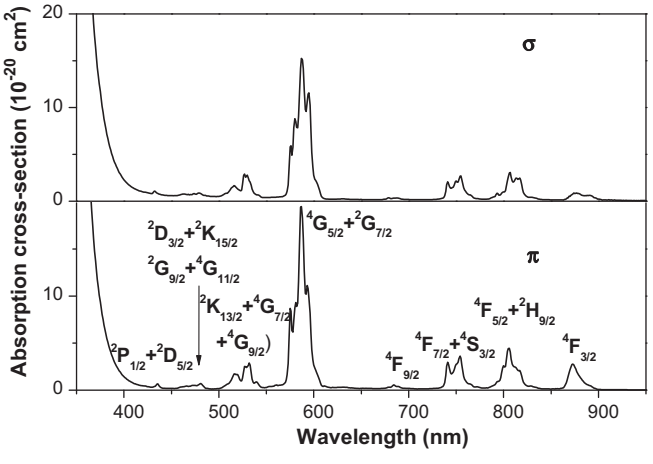

Fig. 4. Polarized absorption spectra of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal at room temperature.

Table 1
Calculated spontaneous-emission probabilities A, radiative branching ratios β and radiative lifetime τ_{rad} of $^4F_{3/2}$ Nd^{3+} multiplet in Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal.

Transition	π-Polarization		σ-Polarization		τ_{rad} (μs)
	A (S^{-1})	β	A (S^{-1})	β	
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	4768.3	0.548	2935.6	0.492	145.3
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	3371.5	0.388	2551.5	0.427	
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	532.02	0.061	460.59	0.077	
$^4F_{3/2} \rightarrow {}^4I_{15/2}$	27.66	0.003	28.83	0.004	

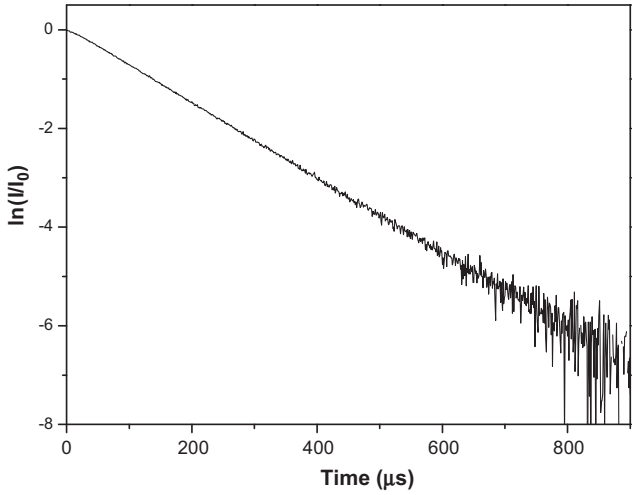

Fig. 5. Fluorescence decay curve of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal at room temperature.

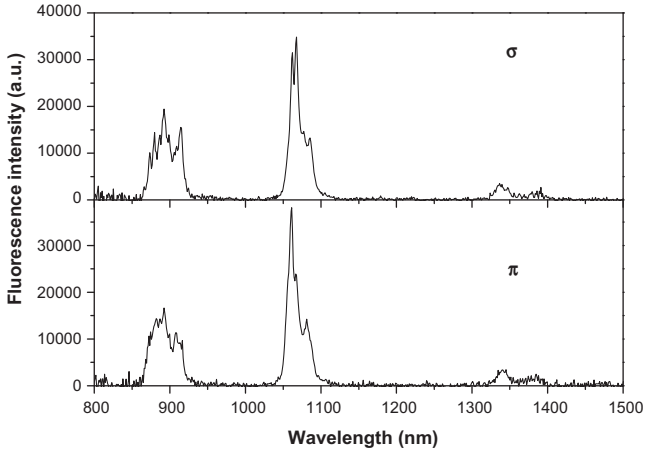

Fig. 6. Polarized fluorescence spectra of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal excited with 807 nm radiation at room temperature.

pumping, since it is not crucial to temperature stability of the output wavelengths of diode laser.

Based on the Judd–Ofelt theory [17,18], the data of the absorption spectrum can be used to calculate the line oscillator strength, radiative lifetime and the branching ratio. The calculating procedures follow those of Ref. [19]. The calculated results are listed in Tables 1 and 2. In Table 2 the Ω_4/Ω_6 is defined as spectroscopic quality factor. The spectroscopic quality factor, which was firstly introduced by Kaminskii, is an important predictor of stimulated emission in a laser active medium [28].

The radiative lifetime τ_{rad} of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal was calculated to be 145.3 μs. The fluorescence lifetime τ_f was determined to be 130.8 μs, as shown in Fig. 5. Then the fluorescence quantum efficiency η of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal was calculated to be 90.0%, where η is defined as

$$\eta = \frac{\tau_f}{\tau_{rad}} \times 100\% \quad (2)$$

The calculated result shown that Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal has a high fluorescence quantum efficiency. It is generally believed that the high fluorescence quantum efficiency of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal is due to the low phonon energy of the $(MoO_4)^{2-}$ group [29].

Fig. 6 shows the fluorescence spectrum of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal at room temperature. Three emission bands were obtained, corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ transitions, respectively. The emission cross-section σ_e can be calculated by the following formula

$$\sigma_e(\lambda) = \frac{A\lambda^2}{4\pi^2 n^2 \Delta\nu} \quad (3)$$

where A is the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ radiative transition rate (see Table 1), λ is the emission wavelength, $\Delta\nu$ is the frequency full width at half-maximum, and n is the value of the refractive index estimated to be 2 in agreement with the value of the similar crystal $Li_2Gd_4(MoO_4)_7$ [29]. Thus, the emission cross-sections were calculated to be 10.0×10^{-20} cm^2 at 1060 nm for π-polarization and 13.6×10^{-20} cm^2 at 1067 nm for σ-polarization, respectively.

Table 2
Comparison of spectrum parameters of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal with other Nd^{3+}-doped crystals (Ω_t is in unit of 10^{-20} cm^2).

Crystals	Polarization	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6	FWHM (nm)	σ_a (10^{-20} cm^2)	σ_{em} (10^{-20} cm^2)	τ_f (μs)	η (%)	Ref.
Nd^{3+}:YAG	un	0.20	2.70	5.00	0.54	0.9	7.0	34.0	240	91.0	[20,21]
Nd^{3+}:YVO_4	π	5.88	4.08	5.11	0.80	2.0	27.0	100.0	98	46.8	[22]
Nd^{3+}:$BaGd_2(MoO_4)_4$	un	14.96	5.04	3.58	1.41	5.0	3.42	22.1	130	83.3	[23]
Nd^{3+}:β′-$Gd_2(MoO_4)_3$	σ	6.15	6.79	6.21	1.09	–	≈4.5	11.0	165	95.0	[24]
Nd^{3+}:$KLa(MoO_4)_2$	π	18.50	4.66	4.49	1.04	5.0	11.4	9.7	158	93.0	[14]
Nd^{3+}:$NaGd(MoO_4)_2$	π	26.68	13.36	10.44	1.28	9.0	15.92	1.7	93.3	93.3	[13,25]
	σ	23.82	4.29	5.24	0.82	17.0	3.66	1.9			
Nd^{3+}:$LiGd(MoO_4)_2$	π	23.04	7.14	5.81	0.91	7.1	4.51	11.2	136	87.7	[26]
	σ	22.17	6.96	4.61	1.51	8.9	1.35	7.1			
Nd^{3+}:$Li_2Gd_4(MoO_4)_7$	π	23.80	13.30	9.10	1.46	7.0	16.6	12.4	124	–	[27]
	σ	20.90	5.90	4.50	1.31	16.0	3.8	6.4			
Nd^{3+}:$Na_2Gd_4(MoO_4)_7$	π	18.51	9.14	4.34	2.11	14.6	4.3	10.0	131	90.0	This work
	σ	18.44	5.44	3.74	1.45	16.2	2.9	13.6			

4. Conclusions

An Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal with dimensions of $Ø20 \times 25\,mm^3$ has been successfully grown by the Czochralski method. In comparison with other Nd^{3+}-doped crystals (see Table 2), Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal has a broad absorption band at 807 nm, which is suitable for laser diode pumping. Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal has a larger value of Ω_4/Ω_6. Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal has high fluorescence quantum efficiency as well as Nd:YAG and all molybdate crystals which is caused by the low phonon energy of the $(MoO_4)^{2-}$ group. To sum up the growth and spectroscopic properties of Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal, it suggests Nd^{3+}:$Na_2Gd_4(MoO_4)_7$ crystal as a potential laser gain medium for the laser diode pumping.

Acknowledgement

This project was supported by the National Natural Science Foundation of China (No. 60778035).

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