

掺钕 M'-型钽酸钪微晶荧光的温度和压力依赖性

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摘 要: M'-型 $\text{Nd}^{3+}:\text{GdTaO}_4$ 微晶被成功合成并用于变温和变压光谱测试研究。在 293~373 K 的测试温度范围内, $^3F_{3/2} \rightarrow ^4I_{9/2}$ 跃迁的光谱位置具有高热稳定性, $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_5)$ 跃迁的温度系数仅为 $0.0039 \text{ cm}^{-1} \cdot \text{K}^{-1}$, $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_2)$ 和 $^3F_{3/2}(R_1) \rightarrow ^4I_{9/2}(Z_2)$ 跃迁荧光的强度比具有高温依赖性, 在生理温度范围内的相对灵敏度为 $(0.60-0.52)(\% \cdot \text{K}^{-1})$ 。在高达 11.39 GPa 的测试压力范围内, 所有跃迁随压力呈线性移动。 $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_5)$ 跃迁的光谱位置对压力非常敏感, 其灵敏度为 $15.18 \text{ cm}^{-1} \cdot \text{GPa}^{-1}$ 。此外, 各跃迁的荧光强度和光谱宽度在升温和增压过程中的变化也被分析和讨论。与其它近红外光学传感器的对比表明, M'-型 $\text{Nd}^{3+}:\text{GdTaO}_4$ 在温度和压力传感方面具有良好性能。

关键词: 钕离子; 稀土钽酸盐; 光致发光; 温度传感; 压力传感

中图分类号: O469 文献标志码: A 文章编号: 0454-5648(2022)09-2493-08

网络出版时间: 2022-08-12



Temperature and Pressure Dependences of Luminescence from Nd-Doped M'-Type Gadolinium Tantalate Microcrystals

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Abstract: M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ microcrystals, synthesized by a molten salt synthesis method, were investigated via temperature-/pressure-dependent photoluminescence measurement. In the test temperature range 293–373 K, the spectral positions of emissions from $^3F_{3/2} \rightarrow ^4I_{9/2}$ transition exhibit high thermal stabilities. The temperature coefficient of $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_5)$ transition is only $0.0039 \text{ cm}^{-1} \cdot \text{K}^{-1}$. The intensity ratio between transitions of $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_2)$ and $^3F_{3/2}(R_1) \rightarrow ^4I_{9/2}(Z_2)$ has a large temperature dependence, and its relative sensitivity in the physiological temperature range is $(0.60-0.52)(\% \cdot \text{K}^{-1})$. In the test pressure range 10^5 Pa –11.39 GPa, all the transitions linearly shift with pressure. The spectral position of $^3F_{3/2}(R_2) \rightarrow ^4I_{9/2}(Z_5)$ transition is very sensitive to pressure, with a sensitivity of $15.18 \text{ cm}^{-1} \cdot \text{GPa}^{-1}$. The intensities and spectral widths of the transitions in the heating and compression processes were also analyzed. Compared with the other optical sensors in the near-infrared wavelength range, the good performance of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ in temperature and pressure sensing was revealed.

Keywords: neodymium ion; rare-earth tantalate; photoluminescence; temperature sensing; pressure sensing

1 Introduction

Studies on the contactless temperature and pressure sensing are recently intensified to meet the development needs in industrial and scientific fields^[1-13]. As one of the most attractive sensing systems, rare-earth ions doped

microcrystals and nanocrystals are widely investigated and applied due to their advantages of short response time, stable working and high spatial resolution,^[1,2,4,6-13] etc.. Compared with the other rare-earth activators, the thermometry and manometry performances of Nd^{3+} ions both can be excellent,^[1-13] especially in the near-infrared

收稿日期: 2022-01-02。 修订日期: 2022-01-28。

基金项目: 国家自然科学基金委青年基金(11804047)。

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Received date: 2022-01-02. Revised date: 2022-01-28.

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(NIR) wavelength range. As a result, Nd^{3+} -doped materials can be competitive for intra-tissue optical sensing^[1,2,4–9]. The most intensively studied single-band ratiometric thermometers are based on the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition of Nd^{3+} ions^[7–9]. Moreover, the emissions from the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition of Nd^{3+} ions can shift linearly with pressure, and can be more sensitive to pressure than the classic ruby sensor^[11–15].

According to the previous researches^[1–15], the spectral properties and sensing performance of Nd^{3+} ions rely on the choice of host material. Among the candidate hosts, gadolinium tantalate with the form of GdTaO_4 can be rather attractive due to its promising properties^[15–22], such as high chemical and biological inertness, high thermal stability, low symmetry crystal field and large solid solubility for rare-earth ions. Under the normal condition, GdTaO_4 has two different monoclinic structures, namely M-type and M'-type^[17–21]. The main difference between the M-type and the M'-type structures lies in the coordination environment of Ta atoms^[17–21]. In the M-type structure, each Ta atom is coordinated by four O atoms, while in the M'-type structure, each Ta atom is coordinated by six O atoms. The luminescent properties of M-type $\text{Nd}^{3+}:\text{GdTaO}_4$ are already investigated^[15–16]. However, little work on M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ has been reported. Compared with M-type GdTaO_4 (with a synthesis temperature $\geq 1\,300\text{ }^\circ\text{C}$ ^[17,18,20–22]), an apparent advantage for M'-type GdTaO_4 as a host is its lower synthesis temperature (*i.e.*, $1\,000\text{ }^\circ\text{C}$ ^[17,19]) and easier to manufacture.

This paper was to study the photoluminescence (PL) of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ as a function of temperature and pressure for the promising application potentials of this material in thermometry and manometry.

2 Experimental

2.1 Materials and synthesis procedure

M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ microcrystals were prepared by a molten salt synthesis method. The starting materials are Nd_2O_3 (4N), Gd_2O_3 (4N), Ta_2O_5 (4N) and Na_2SO_4 (AG) powders in a molar ratio of 1:199:200:2 000. These powders were mixed with acetone, and the mixed slurry was then totally dried at $80\text{ }^\circ\text{C}$. The dried mixture was sintered in a model KSL-1700X-A2-W furnace (HF-Kejing Co., Ltd., China) in the presence of Na_2SO_4 flux at $1\,200\text{ }^\circ\text{C}$ for 6 h. The sintered product was cooled to room temperature and then washed with deionized water to remove the residual flux.

2.2 Characterizations

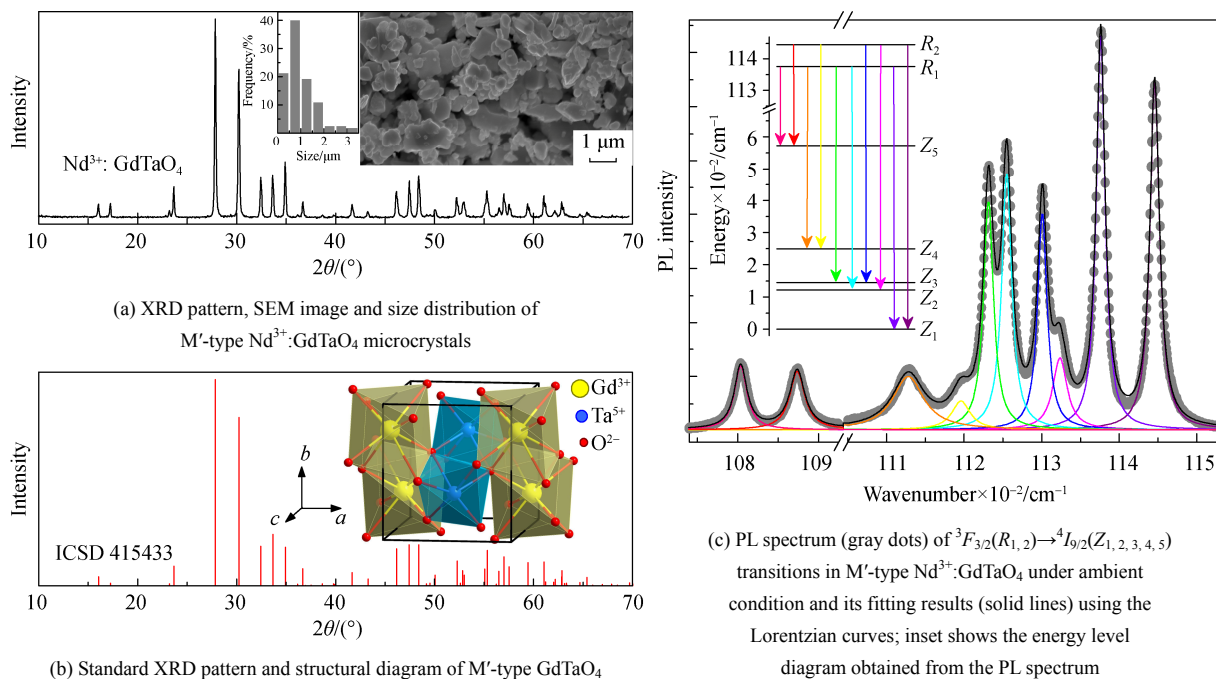
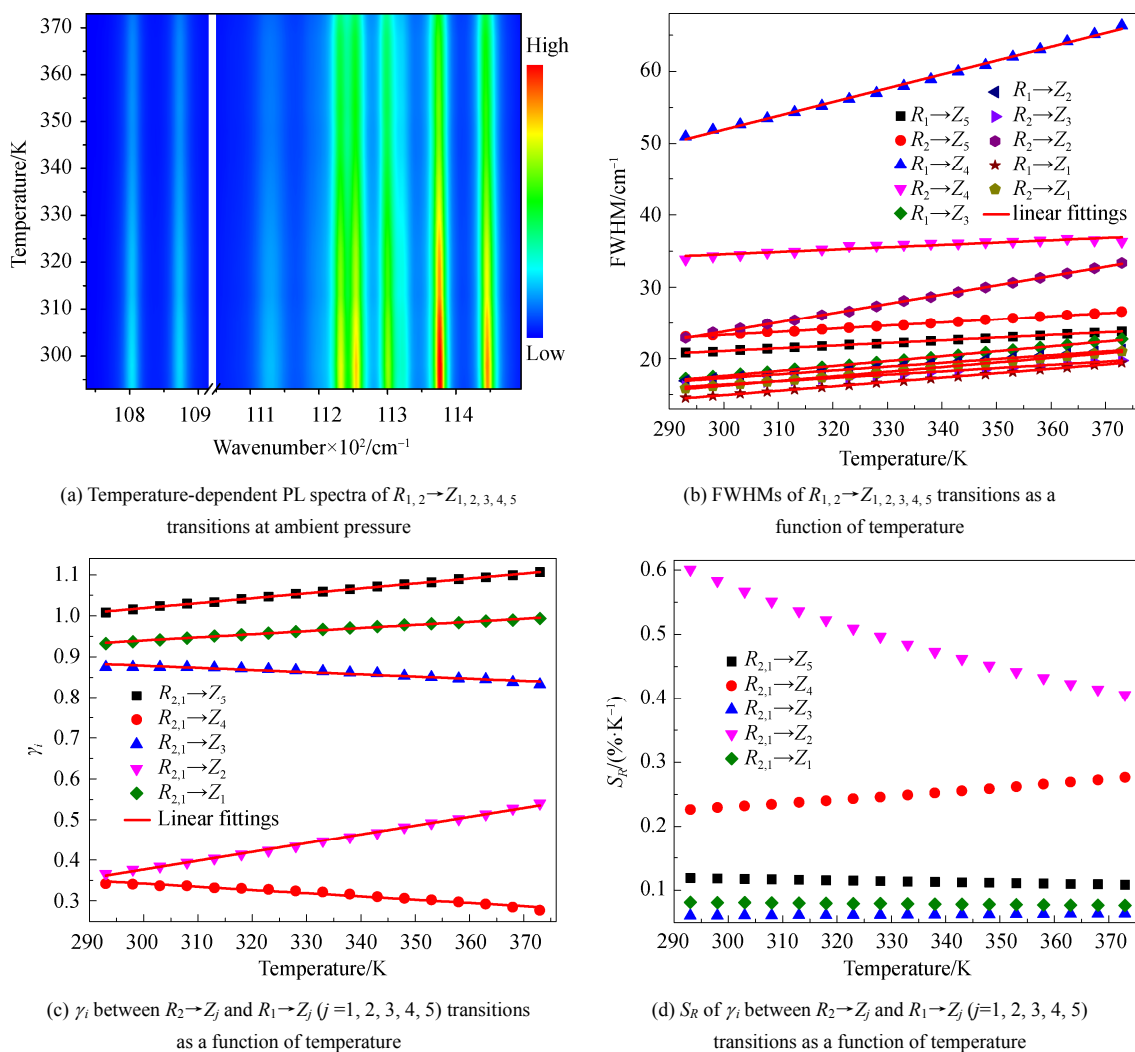
The structure of the sample was identified with X-ray diffraction (XRD), using a model DX-2700B X-ray diffractometer (Haoyuan Instrument Co., Ltd., China) with Cu K_α radiation. The morphology was observed by a model JSM-7900 scanning electron microscope (SEM, JEOL Co., Ltd., Japan). A 532 nm diode laser was used as an excitation source, and the

luminescence from the sample was determined using a model HRS-500MS-NI 0.5 m focal length monochromator (Princeton Instruments Co., Ltd., USA) equipped with a model PIX-400BRX Peltier-cooled silicon charge-coupled device (Princeton Instruments Co., Ltd., USA). A temperature-controlled stage with a resolution value of 0.1 K was used to regulate the sample temperature. A diamond anvil cell (DAC) was used to apply pressure on the sample. The sample chamber was a hole (with a diameter of about $150\text{ }\mu\text{m}$) of a stainless-steel flake, which was sealed by two diamond anvils. The pressure-transmitting medium inside was a 4:1 methanol–ethanol mixture. The pressure value was determined *in situ* from the shift of the *R* lines of a ruby chip^[23], loaded in the DAC.

3 Results and discussion

The structure and PL characterization results of the synthesized $\text{Nd}^{3+}:\text{GdTaO}_4$ microcrystals under ambient condition are summarized in Fig. 1. As the SEM image in Fig. 1(a) shows, the as-obtained microcrystals are inhomogeneous and irregular, possibly due to the high-temperature reaction and the low lattice symmetry of the host. Their sizes mainly range from 0.5 to $2.0\text{ }\mu\text{m}$, with a mean value of about $1\text{ }\mu\text{m}$. The XRD pattern of $\text{Nd}^{3+}:\text{GdTaO}_4$ (see Fig. 1(a)) is in a good agreement with the ICSD file 415 433 (see Fig. 1(b)), indicating its structure is M'-type. The inset of Fig. 1(b) exhibits the M'-type structure in detail. In M'-type GdTaO_4 , each Gd atom is coordinated by eight O atoms, forming a GdO_8 dodecahedron, while each Ta atom is coordinated by six O atoms, forming a TaO_6 octahedron. The polyhedrons of a same type share edges each other and compose the layers parallel to the *b*–*c* plane. TaO_6 and GdO_8 layers are alternately packed along the *a*-axis. Neighboring TaO_6 and GdO_8 polyhedrons are also edge-linked. The lattice parameters of M'-type GdTaO_4 are:^[24] $a=5.169(6)\text{ }\text{\AA}$, $b=5.517(6)\text{ }\text{\AA}$, $c=5.355(2)\text{ }\text{\AA}$, $\alpha=\gamma=90^\circ$, and $\beta=96.664(0)^\circ$. Ten emission lines from the $^3F_{3/2} \rightarrow ^4I_{9/2}$ transition of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ appear under the 532 nm laser excitation (see Fig. 1(c)), since the $^4F_{3/2}$ state has two Stark levels (R_1 , R_2) and the $^4I_{9/2}$ state has 5 Stark levels (Z_1 , Z_2 , Z_3 , Z_4 , Z_5)^[10–13]. According to the spectrum, a diagram of these Stark levels under ambient condition was obtained (see the inset of Fig. 1(c)).

The temperature-dependent PL of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ was determined in a temperature range of 293–373 K and at ambient pressure. The intensities of $R_{2,1} \rightarrow Z_{1,2,3,4,5}$ transitions decrease with increasing temperature (see Fig. 2(a)), due to the thermal quenching effect^[25]. The $R_{2,1} \rightarrow Z_{1,2,3,4}$ transitions red-shift with increasing temperature (with total energy decrements of $0.7\text{--}3.8\text{ cm}^{-1}$), which can be due to the stationary effect of ion-phonon interaction^[26–27]. However, the $R_{2,1} \rightarrow Z_5$ transitions blue-shift with increasing temperature (with total energy increments of 0.3 and 0.8 cm^{-1}), which is just contrary to the theoretical expectation, indicating the Z_5 level can be

Fig. 1 Structure and PL characterizations of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ under ambient conditionFig. 2 PL of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ as a function of temperature at ambient pressure

more sensitive to temperature than the other Stark levels. The full width at half maximum (FWHM) for each transition increases with increasing temperature (see Fig. 2(b)). This could be due to the thermal enhancements of Raman photon scattering and direct one-phonon processes^[5,26–27]. The FWHM of $R_1 \rightarrow Z_4$ transition is more sensitive to temperature with a temperature coefficient (TC) of $0.19 \text{ cm}^{-1} \cdot \text{K}^{-1}$, while the FWHMs of $R_{2,1} \rightarrow Z_5$ transitions are insensitive to temperature with a similar TC of $0.04 \text{ cm}^{-1} \cdot \text{K}^{-1}$.

To evaluate the applicability of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ for luminescent intensity ratio (γ_i) thermometry, thermal evolution of γ_i of any two transitions with a same lower energy level was analyzed (see Fig. 2(c)). The γ_i values change almost linearly with temperature, indicating the convenience of using M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ to determine the temperature. According to the Boltzmann distribution law, the population ratio of the thermally coupled $R_{2,1}$ levels as well as the γ_i of two transitions with $R_{2,1}$ as the upper levels can vary with temperature as follows:^[1–9]

$$\gamma_i = A \exp\left(-\frac{\Delta E}{k_0 T}\right) \quad (1)$$

where ΔE is an energy difference between R_2 and R_1 levels, k_0 is the Boltzmann constant, T is absolute temperature, A is a constant. For M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$, the measured ΔE is 70.5 cm^{-1} . The calculated γ_i at 373 K is 1.08 times greater than that at 293 K. However, only the thermal evolutions of γ_i values of $R_{2,1} \rightarrow Z_j$ ($j = 1, 5$) transitions (see Fig. 2(c)) are consistent with this theoretical expectation. The deviations from the Boltzmann distribution law for the evolutions of γ_i values of $R_{2,1} \rightarrow Z_j$ ($j = 2, 3, 4$) transitions indicate that the spectrally overlapped transitions could be involved with

some non-radiation energy transfer processes, dependent on the lattice vibration variation by temperature, such as resonant energy transfer,^[28–29] non-resonant energy transfer,^[28–29] cross-relaxation,^[30] etc..

The temperature dependence of the γ_i values for M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ was analyzed using linear fitting. Fig. 2(c) and Table 1 show the results. By comparison, the γ_i of $R_{2,1} \rightarrow Z_2$ transitions has the maximum absolute temperature sensitivity, which is $(21.7 \pm 0.3) \times 10^{-4} \text{ K}^{-1}$. According to the fitting results, the relative sensitivities for the γ_i values were calculated by^[1–9]

$$S_R = \left| \frac{1}{\gamma_i} \cdot \frac{\partial \gamma_i}{\partial T} \right| \quad (2)$$

Fig. 2(d) shows the calculation results. Clearly, the S_R of γ_i of $R_{2,1} \rightarrow Z_4$ transitions increases, while the others decrease when temperature increases. The S_R of γ_i of $R_{2,1} \rightarrow Z_2$ transitions is larger than the others in the test temperature range. Moreover, in the physiological temperature range of 290–320 K, the S_R of γ_i of $R_{2,1} \rightarrow Z_2$ transitions is $(0.60\text{--}0.52)(\% \cdot \text{K}^{-1})$, which is superior to most of the Nd^{3+} -based single-band temperature sensors reported previously (see Table 2).

Table 1 Linear fitting results for the γ_i data shown in Fig. 2(c)

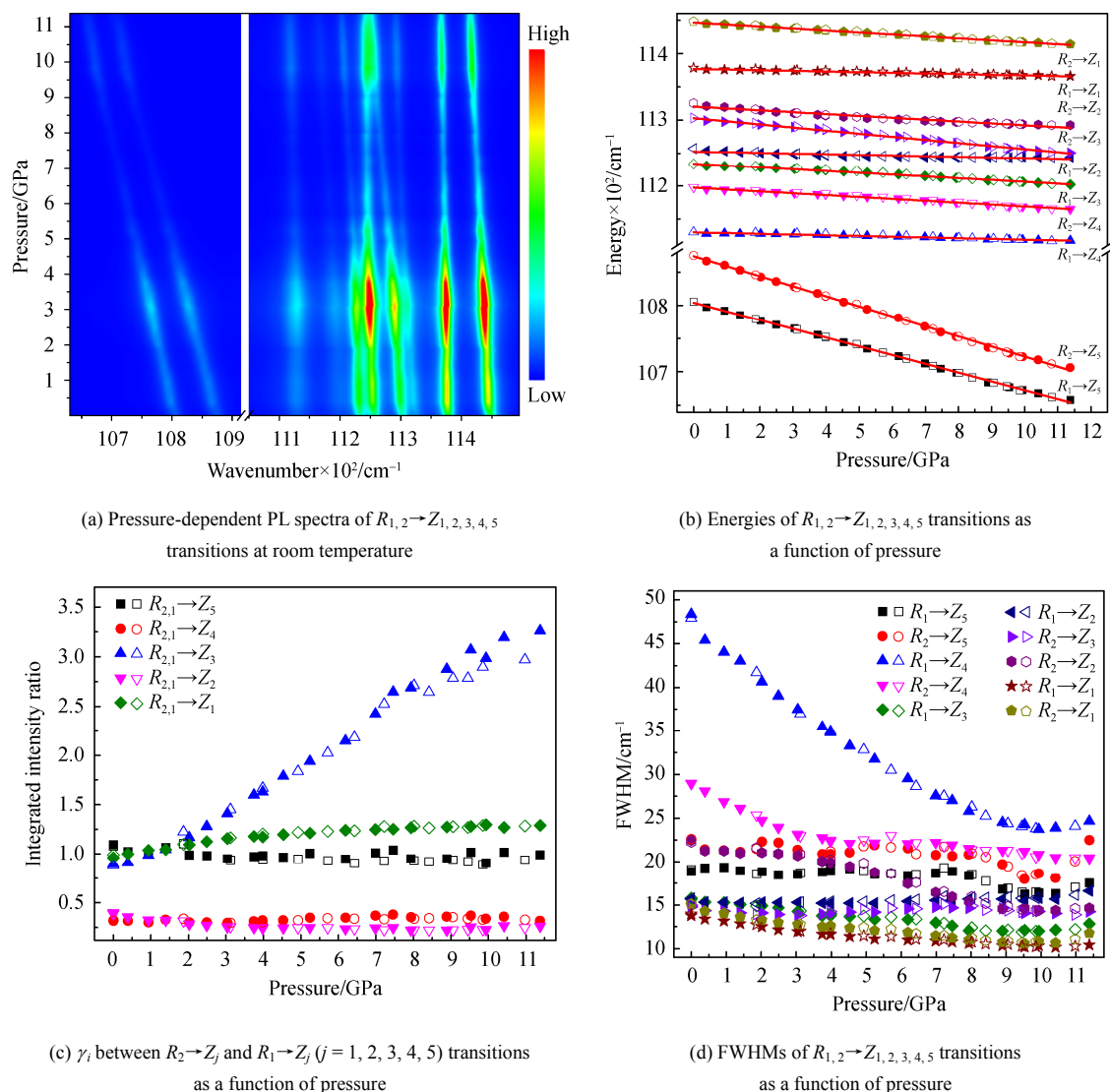
Transitions for calculating γ_i	Intercept	Slope $\times 10^{-4} / \text{K}^{-1}$
$R_{2,1} \rightarrow Z_1$	0.71 ± 0.01	7.6 ± 0.1
$R_{2,1} \rightarrow Z_2$	-0.28 ± 0.01	21.7 ± 0.3
$R_{2,1} \rightarrow Z_3$	1.03 ± 0.01	-5.3 ± 0.4
$R_{2,1} \rightarrow Z_4$	0.58 ± 0.01	-7.9 ± 0.4
$R_{2,1} \rightarrow Z_5$	0.66 ± 0.01	12.0 ± 0.1

Table 2 Comparison for performances of Nd^{3+} -based single-band temperature sensors in the physiological temperature range

Material	Emission lines used for γ_i thermometry	$(S_R)_{\text{max}} / (\% \cdot \text{K}^{-1})$
M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ (this work)	11 324 and 11 255 cm^{-1}	0.60
$\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ^[1]	10 661 and 10 571 cm^{-1}	0.15
$\text{Nd}^{3+}:\text{LaF}_3$ ^[2]	11 614 and 11 587 cm^{-1}	0.40
$\text{Nd}^{3+}:\text{YVO}_4$ ^[3]	9 391 and 9 378 cm^{-1}	0.35
$\text{Nd}^{3+}:\text{Y}_2\text{O}_3$ ^[4]	9 497 and 9 302 cm^{-1}	0.43
$\text{Nd}^{3+}:\text{LiYF}_4$ ^[5]	9 557 and 9 463 cm^{-1}	0.22
$\text{Nd}^{3+}:\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ ^[6]	10 684 and 10 571 cm^{-1}	0.20
$\text{Nd}^{3+}:\text{LiLuF}_4$ ^[7]	11 274 and 10 953 cm^{-1}	0.58
$\text{Nd}^{3+}:\text{LiBaPO}_4$ ^[8]	11 340 and 11 450 cm^{-1}	0.16
$\text{Nd}^{3+}:\text{Bi}_2\text{SiO}_5$ ^[9]	11 521 and 11 130 cm^{-1}	0.34
M'-type $\text{Nd}^{3+}:\text{YTbO}_4$ ^[14]	10 838 and 10 762 cm^{-1}	0.13
M-type $\text{Nd}^{3+}:\text{GdTaO}_4$ ^[16]	10 869 and 10 783 cm^{-1}	0.14

The pressure dependence of the transitions in M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ was investigated in a range up to 11.39 GPa and at room temperature. Fig. 3(a) shows the

pressure-dependent PL spectra. All the transitions shift with pressure linearly. Their pressure sensitivities were evaluated by linear fitting (see Fig. 3(b) and Table 3).



Solid dots represent the data recorded in the compression process; hollow dots represent the data recorded in the decompression process

Fig. 3 PL of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ as a function of pressure at room temperature

Table 3 Zero-pressure energies and PCs of the transitions of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ at room temperature

Transition	Zero-pressure energy/ cm^{-1}	Pressure coefficients/ $(\text{cm}^{-1} \cdot \text{GPa}^{-1})$
$R_2 \rightarrow Z_1$	$11\,446.6 \pm 0.2$	-2.94 ± 0.03
$R_1 \rightarrow Z_1$	$11\,377.3 \pm 0.2$	-0.99 ± 0.03
$R_2 \rightarrow Z_2$	$11\,320.1 \pm 0.7$	-2.80 ± 0.10
$R_2 \rightarrow Z_3$	$11\,303.6 \pm 0.4$	-4.74 ± 0.06
$R_1 \rightarrow Z_2$	$11\,252.3 \pm 0.6$	-0.94 ± 0.09
$R_1 \rightarrow Z_3$	$11\,234.6 \pm 0.4$	-2.80 ± 0.06
$R_2 \rightarrow Z_4$	$11\,198.3 \pm 0.4$	-2.92 ± 0.05
$R_1 \rightarrow Z_4$	$11\,130.3 \pm 0.3$	-1.14 ± 0.04
$R_2 \rightarrow Z_5$	$10\,874.3 \pm 0.5$	-15.18 ± 0.08
$R_1 \rightarrow Z_5$	$10\,804.2 \pm 0.5$	-13.20 ± 0.07

Compared with the other transitions, the $R_{2,1} \rightarrow Z_5$ transitions are more sensitive to pressure, which have pressure coefficients of -15.18 ± 0.08 and $-13.20 \pm 0.07 \text{ cm}^{-1} \cdot \text{GPa}^{-1}$, respectively. The pressure sensitivity (or absolute PC value) of $R_2 \rightarrow Z_5$ transition of M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ is less than those of M'-type $\text{Nd}^{3+}:\text{YTaO}_4$ and M-type $\text{Nd}^{3+}:\text{GdTaO}_4$, but larger than those of the other rare-earth NIR pressure sensors (see Table 4) and ruby ($7.56 \text{ cm}^{-1} \cdot \text{GPa}^{-1}$ [11]). Moreover, the estimated temperature sensitivity of $R_2 \rightarrow Z_5$ transition in M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ is $0.0039 \text{ cm}^{-1} \cdot \text{K}^{-1}$ (or $-0.0004 \text{ nm} \cdot \text{K}^{-1}$), which is less than those of M'-type $\text{Nd}^{3+}:\text{YTaO}_4$ ($0.011 \text{ cm}^{-1} \cdot \text{K}^{-1}$ [14]), M-type $\text{Nd}^{3+}:\text{GdTaO}_4$ ($0.009 \text{ cm}^{-1} \cdot \text{K}^{-1}$ [16]), $\text{Nd}^{3+}:\text{YAlO}_3$ ($0.001 \text{ nm} \cdot \text{K}^{-1}$ [31]) and ruby ($0.0068 \text{ nm} \cdot \text{K}^{-1}$ [31]). This indicates that M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ has a higher anti-interference capability for the ambient temperature fluctuation, which can be another advantage for its application in pressure sensing.

Table 4 Comparison for performances of pressure sensors based on shifts of NIR emissions from rare-earth ions

Material	Transition	Energy at ambient condition/cm ⁻¹	Pressure coefficients/(cm ⁻¹ ·GPa ⁻¹)
M'-type Nd ³⁺ :GdTaO ₄ (this work)	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 874	-15.18
Nd ³⁺ :YAlO ₃ ^[10]	³ F _{3/2} (R ₁)→ ⁴ I _{9/2} (Z ₅)	10 753	-4.7
Nd ³⁺ :Ca ₃ Ga ₂ Ge ₃ O ₁₂ ^[11]	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 743	-10.8
Nd ³⁺ :Y ₃ Al ₅ O ₁₂ ^[12]	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 661	-9.9
Nd ³⁺ :Gd ₃ Sc ₂ Ga ₃ O ₁₂ ^[13]	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 741	-11.3
M'-type Nd ³⁺ :YTbO ₄ ^[14]	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 838	-16.44
M-type Nd ³⁺ :GdTaO ₄ ^[16]	³ F _{3/2} (R ₂)→ ⁴ I _{9/2} (Z ₅)	10 869	-15.6
Nd ³⁺ :LaVO ₄ ^[32]	³ F _{3/2} (R ₁)→ ⁴ I _{9/2} (Z ₅)	10 977	-15.1
Tm ³⁺ /Yb ³⁺ :YPO ₄ ^[33]	³ H ₄ → ³ H ₆	12 531	-13.8
Nd ³⁺ :YVO ₄ ^[34]	³ F _{3/2} (R ₁)→ ⁴ I _{9/2} (Z ₅)	10 927	-13.59
Er ³⁺ /Yb ³⁺ :NaBiF ₄ ^[35]	⁴ I _{13/2} → ⁴ I _{15/2}	6 653	3.54

The linear shifts of the transitions with pressure indicate that the Stark levels of ⁴F_{3/2} and ⁴I_{9/2} states shift with pressure linearly. The energies of the Stark levels at different pressures were calculated from the spectral position data in Fig. 3(b), and analyzed by linear fitting. The fitting results in Table 5 show that the PCs of R₂, 1 and Z₂ levels are negative, while the others are positive. By comparison, the Z₅ level is much more sensitive to pressure, which can be helpful for understanding the thermal blue-shifts of R₂, 1→Z₅ transitions. Specifically, the expansion of the host during the heating process may be similar to the expansion during the decompression process, which may accelerate the downward movement of Z₅ level, resulting in the thermal blue-shifts of R₂, 1→Z₅ transitions. The PCs of the Stark levels indicate that the ⁴I_{9/2} state splitting increases, while the ⁴F_{3/2} state splitting decreases with increasing pressure. The estimated PCs of splittings of ⁴I_{9/2} and ⁴F_{3/2} states for M'-type Nd³⁺:GdTaO₄ are 12.22 and -1.95 cm⁻¹·GPa⁻¹, respectively. The increase of ⁴I_{9/2} state splitting can be due to the enhancement of crystal field around Nd³⁺ ions induced by the host lattice shrinking under pressure^[10–11]. In contrast, the reason for the variation of ⁴F_{3/2} state splitting under pressure is more complicated, involving with the symmetry variation of crystal field^[10–12,32,34].

Table 5 Zero-pressure energies and pressure coefficient of the energy levels of M'-type Nd³⁺:GdTaO₄ at room temperature

Energy level	Zero-pressure energy/cm ⁻¹	Pressure coefficient/(cm ⁻¹ ·GPa ⁻¹)
R ₂	11 446.6±0.2	-2.94±0.03
R ₁	11 377.3±0.2	-0.99±0.03
Z ₅	572.7±0.4	12.22±0.06
Z ₄	247.7±0.2	0.07±0.03
Z ₃	142.9±0.3	1.81±0.04
Z ₂	125.7±0.6	-0.12±0.09
Z ₁		

The PL spectra in Fig. 2(a) indicate that the PL intensity of M'-type Nd³⁺:GdTaO₄ evolves non-monotonically with pressure. All the transitions are gradually strengthened in the ranges 100 KPa–3 GPa and 7–10 GPa, while are gradually weakened in the ranges 3–7 GPa and >10 GPa. The spectrum recorded at 3 GPa has the maximum intensity, which is about twice greater than the initial intensity. The phenomenon of pressure-enhancing PL intensity could be due to the enhancement of 4f→4f transition induced by the symmetry degradation of the crystal field around rare-earth ions^[36]. The possible reasons for the PL intensity decreasing processes could be the increases of cross-relaxation^[35–37], phonon-assisted non-radiative relaxation and crystal defects^[33,35–36] for the host under pressure. Furthermore, the cross-relaxation and phonon-assisted non-radiative relaxation are correlated to the energies of transitions, so the transitions with different PCs could weaken with pressure in different degrees, and may cause variations for the γ_i values. Accordingly, the γ_i values of R₂, 1→Z_j (j = 1, 2, 3, 4, 5) transitions at different pressures were calculated (see Fig. 3(c)). By comparison, the γ_i of R₂, 1→Z₃ transitions is more sensitive to pressure, which evolves monotonically within a finite fluctuation at a rate of 0.232 GPa⁻¹. Moreover, the γ_i values of R₂, 1→Z_j (j = 2, 4, 5) transitions vary little in the pressure range, indicating that they may even be good parameters for temperature determination in a pressure varying environment.

Pressure can also change FWHM of a luminescent transition by changing the crystal strain inhomogeneity, direct single-phonon process and Raman phonon scattering process^[26–27]. Fig. 3(d) shows the FWHM values of the transitions of M'-type Nd³⁺:GdTaO₄ at different pressures. By comparison, the variation of the FWHM of R₂→Z₅ transition is insignificant, indicating that the pressure measurement precision based on its spectral position can be stable at different pressures. Moreover, the FWHM of R₁→Z₄ transition exhibits a larger pressure dependence in a range up to 9 GPa, which evolves with pressure almost linearly at a rate of

$-2.64\text{ cm}^{-1}\cdot\text{GPa}^{-1}$. Compared to the spectral position of $R_2\rightarrow Z_5$ transition, the FWHM of $R_1\rightarrow Z_4$ transition and the γ_i of $R_{2,1}\rightarrow Z_3$ transitions are less sensitive to pressure, but still can be auxiliary parameters for pressure determination, because of their self-referencing sensing properties and regular relations with pressure. Moreover, the corresponding results reveal that rare-earth tantalates may have various application potentials in pressure sensing, which needs to be further investigated.

4 Conclusions

M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ was synthesized by a molten salt synthesis method. The variations of spectral positions, FWHMs, intensities and γ_i values of the $R_{2,1}\rightarrow Z_{1,2,3,4,5}$ transitions with temperature and pressure were investigated. Their attractive potentials for sensing applications were revealed. The γ_i of $R_{2,1}\rightarrow Z_2$ transitions had a linear relation with temperature in the range of 293–373 K, and with a maximum S_R value of $0.6\%\cdot\text{K}^{-1}$, which is superior to the other reported Nd^{3+} -based single-band temperature sensors. The γ_i of $R_{2,1}\rightarrow Z_2$ transitions varied little with pressure at room temperature, indicating that it could also be a good parameter for temperature sensing at different pressures. The spectral position of $R_2\rightarrow Z_5$ transition was rather sensitive to pressure, with a sensitivity of $15.18\text{ cm}^{-1}\cdot\text{GPa}^{-1}$ that was twice greater than that of ruby. Furthermore, the thermal shift of $R_2\rightarrow Z_5$ transition was rather small, indicating that it has a high anti-interference capability for the environmental temperature fluctuation, which was beneficial for its use in pressure sensing. Besides, the FWHM of $R_1\rightarrow Z_4$ transition and the γ_i of $R_{2,1}\rightarrow Z_3$ transitions also had a large pressure dependence, and could be auxiliary parameters for pressure determination. The experimental results indicated that M'-type $\text{Nd}^{3+}:\text{GdTaO}_4$ could be a bifunctional optical sensor of temperature and pressure with competitive advantages.

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