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ACTIVE RAMAN MEDIA: $SrWO_4:Nd^{3+}$, $BaWO_4:Nd^{3+}$. GROWTH AND CHARACTERIZATION

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The $BaWO_4$ and $SrWO_4$ crystals doped with Nd^{3+} have been grown and investigated as matrices for laser active elements with nonlinear self-conversion of radiation to a new spectral range. Results on the growth technique, spectral and luminescence characteristics of Nd^{3+} ions in $BaWO_4$ and $SrWO_4$ Raman crystals are presented. Conditions were found to obtain optical homogeneous single crystals free of light scattering centers and growth striations. Values of effective segregation coefficients of active (Nd^{3+}) and compensating (Nb^{5+}, Na^{+}) ions were determined using the results of spectral emission analysis. The refraction index dispersion in the visible range was measured for both materials. The absorption and luminescence spectra are presented.

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1. Introduction

The possibility to combine laser and Raman properties in the same medium is of great interest. Barium and strontium tungstate crystals were recently demonstrated as new promising nonlinear materials for crystalline nano- and picosecond Raman lasers [1-3]. For equal values of integral Raman scattering cross section for Ca, Sr and Ba tungstates, decreasing of the line width of SRS-active mode in $BaWO_4$ (1.6 cm^{-1}) and $SrWO_4$ (2.7 cm^{-1}) results in the increase of Raman peak scattering cross section and Raman gain coefficient compared with $CaWO_4$. The peak value measured in $BaWO_4$ was as high as 64% of that in the diamond, for $SrWO_4$ – 30%. For comparison, it was 63% in $Ba(NO_3)_2$ well known as the best Raman crystal for nanosecond pump pulses and 25% in KGW the best Raman material for picosecond time scale [1]. This fact allows to consider $BaWO_4$ and $SrWO_4$ crystals as effective and perspective media for SRS and developing Raman lasers. Doping these crystals with Nd^{3+} ions could allow to use them as laser active and nonlinear Raman media simultaneously [4, 5].

2. Crystal growth

$BaWO_4$ and $SrWO_4$ crystals were grown from the melt by Czochralski method with r.f. heating. Melting point of $BaWO_4$ is 1475 °C, $SrWO_4$ – 1535 °C [6], so it is possible to use platinum crucible in the air atmosphere. Pt screen was placed above the crucible to provide the needed thermal gradients. Vertical thermal gradient for $BaWO_4$ growth was 60-100 °C/cm; thermal gradient for $SrWO_4$ was less than 50 °C/cm to avoid the crucible overheating. The starting material was synthesized from $BaCO_3$ or $SrCO_3$ (purity 5N) and WO_3 (purity 8N). The dopants were added into the melt in forms of Nd_2O_3, Nd_2O_3+Nb_2O_5 (in the ratio 1:1), Nd_2O_3+Na_2CO_3 (in the ratio 1:1). The

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crystals were grown along direction [100] perpendicular to the optical C_4 axis that corresponded to maximal Raman scattering cross-section. Rotation rate was 30 rpm and pulling rate was up to 6 mm/h. Typical defects observed in as-grown crystals were: microscopic scattering centers that cause opalescence, that is due to the evaporation of WO_3 during the growth process; cracking along [001] direction, that is cleavage plane specific for the crystals with scheelite structure, was observed in crystals grown with too high crystallization rate or wrong annealing conditions; "central defect" seems to be bubbles and dendrites and is formed due to facet growth on the convex solid-liquid interface. Growth striations are a result of slight deviations in ratio of main components or dopants because of the local variations in crystallization rate.

In our experiments it was shown that $BaWO_4$ crystals grown from the stoichiometric melt had scattering centers and introduction of some excess of WO_3 into the melt allows to decrease the number of scattering centers and under definite conditions to eliminate this defect at all. It was determined that excess of 1.5 wt. % WO_3 was optimal for growth of $BaWO_4$:Nd^{3+}:Nb^{5+} and $BaWO_4$:Nd^{3+}:Na^+ concentration series. Optimal excess of WO_3 for series $BaWO_4$:Nd_2O_3 and undoped crystals was 1wt.%.

To obtain crystals with good optical quality, the crystallization rate must not exceed 1 cm^3/h (for undoped crystals) and 0.5 cm^3/h (for doped crystals). With substantial increase of dopant concentration the rate has to be decreased to 0.1 cm^3/h. Crystals free of growth striations and optical inhomogenities with sizes 10×15×50 mm were obtained.

Nominally pure $SrWO_4$ and series of $SrWO_4$:Nd^{3+}:Na^+ crystals with good optical quality were grown without any excess of WO_3. Optimal WO_3 excess for $SrWO_4$:Nd^{3+}:Nb^{5+} was 1.5wt.%. Crystals grown without charge compensation were doped by $Nd_2(WO_4)_3$. The crystallization rate must not exceed 1.2 cm^3/h (for undoped crystals) and 0.5 cm^3/h (for heavy-doped crystals). The crystals obtained had good optical quality and sizes 12×16×80 mm.

$BaWO_4$ and $SrWO_4$ single crystals are shown in Fig. 1.

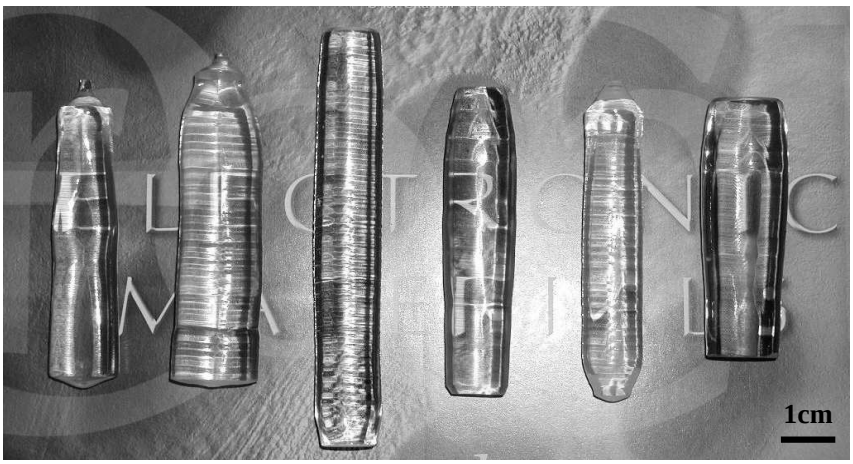

Fig.1. Single crystals of $BaWO_4$ and $SrWO_4$ grown by Czochralski method.

3. Crystal composition

Elemental analyses of $BaWO_4$ and $SrWO_4$ samples were carried out using the spectral emission technique. Crystals grown from the melts with different compositions were investigated. Content of the main components Ba (Sr), W and O in the investigated samples corresponded to the stoichiometric ratio within the experimental error. The values of effective segregation coefficient K_{eff}^{Nd3+} for $BaWO_4$ crystals, grown from the melt compositions: $BaWO_4$+$NdNbO_4$; $BaWO_4$+ Nd_2O_3; $BaWO_4$+Nd_2O_3+Na_2CO_3, were calculated and are presented in Table 1. The highest value of K_{eff}^{Nd3+} was estimated in case of charge compensation by Na^+ ions. Crystals grown from the melt composition $BaWO_4$:Nd_2O_3:Na_2CO_3 had no optical quality. Nd^{3+} income with K_{eff}^{Nd3+} = 0.3 can be achieved with

Nb^{5+} charge compensation. In this case Nb^{5+} content in the crystal corresponded to stoichiometric Nd/Nb ratio; $BaWO_4$ of good optical quality can be obtained.

Values of K_{eff}^{Nd3+} in $SrWO_4$ are higher than in $BaWO_4$ due to proximity of the ionic radii of Sr^{2+} and Nd^{3+}. K_{eff}^{Nd3+} was found to be equal to 0.8 in $SrWO_4$:$NdNbO_4$ series and 0.3 without charge compensation (Table 2).

Table 1. Nd^{3+}-doped $BaWO_4$ crystals.

Melt composition	V, cm^3/h	At.% Nd in the melt	At.% Nd in the crystal	K_{eff}	Crystal quality
$BaWO_4$: 1.0 wt.%$NdNbO_4$ +1.0 wt.%WO_3	0.75	0.21	0.06	0.27	Cracked. Opalescence
$BaWO_4$: 1.0 wt.%$NdNbO_4$ +1.5 wt.%WO_3	0.33	0.21			Optical quality
$BaWO_4$: 1.0 wt.%$NdNbO_4$ +1.5 wt.%WO_3	0.66	0.21	0.11	0.53	Optical quality. Grown by modified Stepanov technique
$BaWO_4$: 2.0 wt.%$NdNbO_4$ +1.0 wt.% WO_3	0.48	0.40	0.15	0.36	Cracked along [001]. Weak scattering
$BaWO_4$: 4.0 wt.%$NdNbO_4$ +4.0 wt.% WO_3	0.12	0.74	0.18	0.24	Cracked
$BaWO_4$: 1.0 wt.% Nd_2O_3 +1.0 wt.% WO_3	0.36	0.45	0.05	0.14	Optical quality
$BaWO_4$: 2.0 wt.%Nd_2O_3 +1.0 wt.WO_3	0.98	0.88	0.12	0.16	Cracked along [001]. Weak scattering
$BaWO_4$: 1.0 wt.% Nd_2O_3 +0.1 wt.%Na_2CO_3	0.33	0.45	0.18	0.40	Central defect.
$BaWO_4$: 2.0 wt.% Nd_2O_3 +0.63 wt.%Na_2CO_3 +2.76 wt.%WO_3	0.33	0.85	0.36	0.42	Central defect. Cracked along [001].

Table 2. Nd^{3+}-doped $SrWO_4$ crystals.

Melt composition	V, cm^3/h	Ат.% Nd in the melt	Ат.% Nd in the crystal	K_{eff}	Crystal quality
$SrWO_4$:1.0 wt.% $NdNbO_4$	1.11	0.18	0.11	0.61	Weak scattering
$SrWO_4$: 1.0 wt.% $NdNbO_4$ +1.0 wt.%WO_3	1.36	0.18	0.15	0.82	Optical quality
$Sr_{0.91}Ba_{0.09}WO_4$:0.67 wt.%$NdNbO_4$+1.0 wt.%WO_3	0.44	0.122	0.11	0.86	Strong scattering
$SrWO_4$:0.36 wt.%$Nd_2(WO_4)_3$	1.3	0.042	0.01	0.28	Optical quality
$SrWO_4$:1.43 wt.%$Nd_2(WO_4)_3$	1.00	0.076	0.035	0.22	Weak scattering
$SrWO_4$:2.50 wt.%$Nd_2(WO_4)_3$	1.26	0.13	0.09	0.33	Central defect.
$SrWO_4$:3.57 wt.%$Nd_2(WO_4)_3$	0.93	0.19	0.093	0.25	Central defect. Cracked
$SrWO_4$:0.25 wt.%Nd_2O_3 + 0.08 wt.%Na_2CO_3	0.52	0.10			Optical quality
$SrWO_4$:0.5 wt.%Nd_2O_3 + 0.16 wt.%Na_2CO_3	0.38	0.20			Optical quality
$SrWO_4$:1.0 wt.%Nd_2O_3 + 0.32 wt. %Na_2CO_3	0.63	0.39			Optical inhomogeneities
$SrWO_4$:2.0 wt.%Nd_2O_3 + 0.64 wt.% Na_2CO_3	0.23	0.77			Optical inhomogeneities. Weak scattering

4. Optical properties

Measurements of refractive indices dispersion were carried out using goniometer GS-2. The room-temperature dispersion curves of refractive indices of ordinary (n_o) and extraordinary (n_e) waves between 400 and 700 nm for $SrWO_4$ and $BaWO_4$ are presented in Fig.2 and Fig.3, respectively. It was shown that $SrWO_4$ is optically positive crystal and $BaWO_4$ is optically negative crystal (Fig.2). The natural room-temperature birefringence (n_e-n_o) for $SrWO_4$ is 0.01087, for $BaWO_4$ is -0.00189.

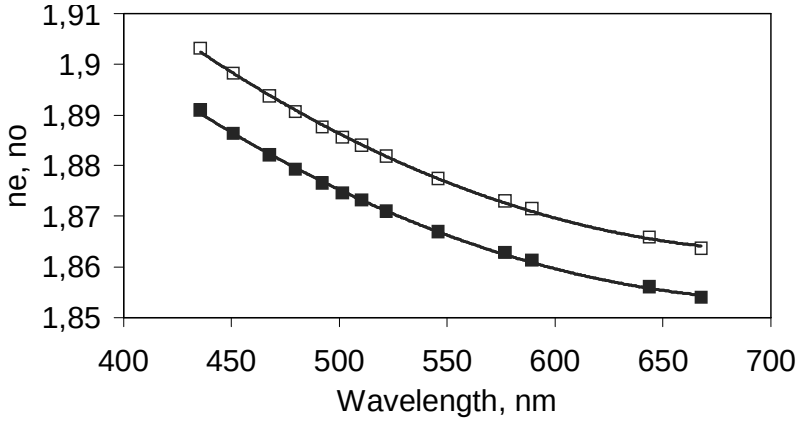

Fig. 2. Dispersion of the refractive indices in $SrWO_4$: □ - experimental data for n_e, ■ - experimental data for n_o.

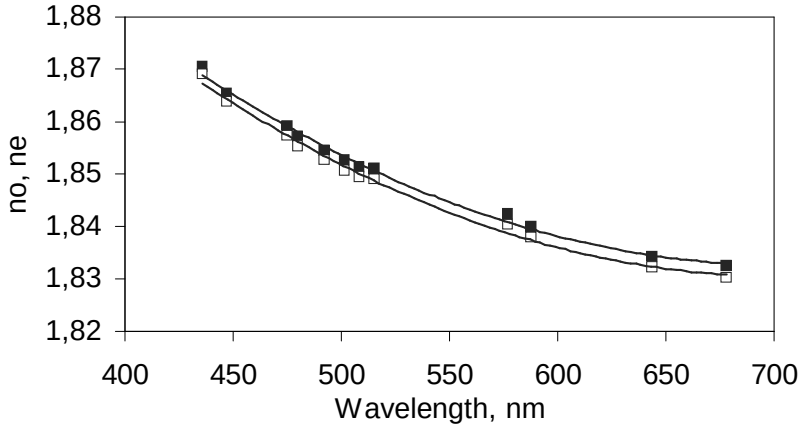

Fig. 3. Dispersion of the refractive indices in $BaWO_4$: □ - experimental data for n_e, ■ - experimental data for n_o.

The dispersion curves in $SrWO_4$ crystal can be described by the following Sellmeier equation (λ in micrometers), [7]:

$$n_o^2(\lambda) = 3.3219 + \frac{0.04538}{\lambda^2 - 0.007226} + 0.02657\lambda^2 \quad (1)$$

$$n_e^2(\lambda) = 3.3490 + \frac{0.04825}{\lambda^2 - 0.0090808} + 0.03085\lambda^2 \quad (2)$$

The dispersion curves in $BaWO_4$ crystal can be described by the following Sellmeier equations (λ in micrometers):

$$n_o^2(\lambda) = 3.3550 + \frac{0.01738}{\lambda^2 - 0.08176} - 0.0965\lambda^2 \quad (3)$$

$$n_e^2(\lambda) = 3.3460 + \frac{0.01770}{\lambda^2 - 0.08197} - 0.09620\lambda^2 \quad (4)$$

Absorption spectra for $BaWO_4:Nd^{3+}$ and $SrWO_4:Nd^{3+}$ crystals at 300 K were obtained using photoelectronic multiplier (UV and visible range) and a photodiode (IR range). Polished samples with thickness ~3 mm along the [100] direction shows peaks typical for Nd^{3+} ion (Figs. 4, 5). The absorption line $^4I_{9/2} \rightarrow {}^2H_{9/2} + {}^4F_{5/2}$ consists of a narrow peak (centered at 802 nm) and a broad band which can be convenient for temperature independent diode laser pumping (λ = 810 nm).

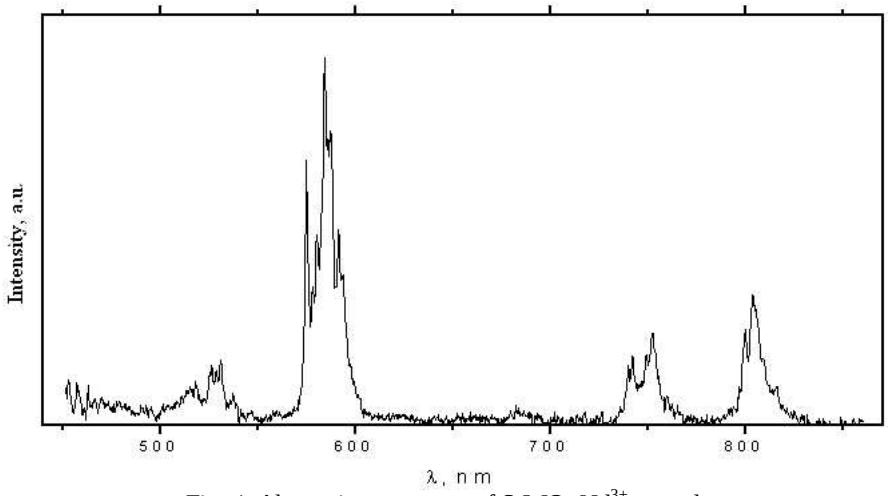

Fig. 4. Absorption spectrum of $SrWO_4:Nd^{3+}$ crystal.

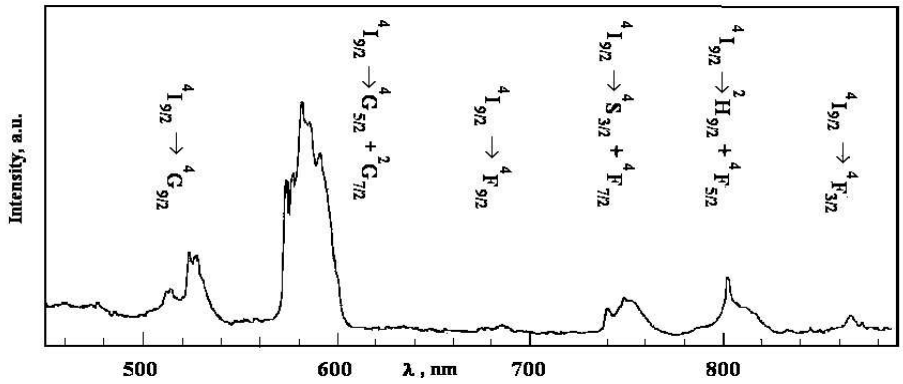

Fig. 5. Absorption spectrum of $BaWO_4:Nd^{3+}$ crystal.

Luminescence spectrum of the crystal $BaWO_4$: 2wt.%$NdNbO_4$:1.5wt.%WO_3 at 300 K was obtained with diode laser pumping with λ = 810 nm. (Fig.6). Peak intensities of the main laser transitions of Nd ions, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, are centered on 1056 nm and 1327 nm, respectively.

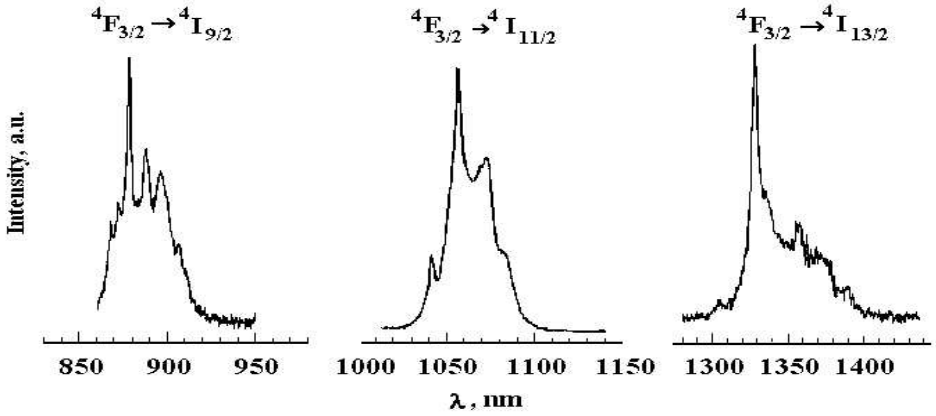

Fig. 6. Luminescence spectrum of $BaWO_4:Nd^{3+}$ crystal at T = 300 K under 810 nm diode laser excitation.

The fluorescence decay was measured for the crystals with different Nd^{3+} concentration under green laser pumping (λ = 532 nm, pulse duration = 20 ns). The lifetime at room temperature is 234 μs in $BaWO_4:Nd^{3+}$ and 195 μs in $SrWO_4:Nd^{3+}$.

5. Conclusion

Our results show that $BaWO_4$ and $SrWO_4$ crystals doped with Nd^{3+} are prospective materials for developing laser with self-Raman conversion of radiation inside the active medium.

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