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Monoclinic $LaBWO_6$: A new SRS-active crystal

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Abstract. **We have synthesised a new SRS-active $LaBWO_6$ tungstate crystal with a high steady-state Raman gain (less than 2.8 cm GW^{-1}) and ability to generate a multicomponent Stokes and anti-Stokes comb in the visible and near-IR spectral regions, with a length of $\sim$13010 cm^{-1}. The newly found photon – phonon nonlinear $\chi^{(3)}$ processes in known SRS- and laser-active tungstate crystals are briefly described in tables.**

Keywords: *$LaBWO_6$ tungstate crystal, $\chi^{(3)}$ nonlinearity, stimulated Raman scattering, frequency comb.*

1. Introduction

The role of tungstate laser crystals in the development of quantum electronics is very important. In particular, $CaWO_4:Nd^{3+}$ [1] became the third laser crystal after $Al_2O_3:Cr^{3+}$ [2] and $CaF_2:U^{3+}$ [3], $CaF_2:Sm^{2+}$ [4] and the first crystal base for trivalent lanthanide lasant ions Ln^{3+} (Pr^{3+} [5], Ho^{3+} [6], Er^{3+} [7], and Tm^{3+} [8]). The later achievements in the excitation of stimulated emission (SE) from Ln^{3+} lasant ions in tungstate crystals under different experimental conditions were reported in several reviews (see, e.g., [9 – 12]).

A new stage in the study of the fundamental physical properties of tungstate laser crystals is related to the excitation of efficient stimulated Raman scattering (SRS) in them, which is due to their $\chi^{(3)}$ nonlinearity. The combination of lasing activity (Ln^{3+}) and SRS activity has extended the application potential of laser tungstates. The intracavity generation of SE by Ln^{3+} ions in SRS lasers due to the $\chi^{(3)}$ nonlinearity is coherently transformed into Stokes generation at other frequencies with participation of Raman-active vibrational modes of tungstates. The characteristics of known SRS lasers are briefly reviewed in Table 1, which contains also the description of other nonlinear $\chi^{(3)}$ processes revealed in SRS-active tungstates. Of fundamental interest is that some of the aforementioned crystals can generate multioctave Stokes and anti-Stokes $\chi^{(3)}$ combs, which are promising for Fourier synthesis of ultrashort pulses.

The presented data, which indicate the importance of searching for new SRS-active tungstates, stimulated this study, as a result of which a new SRS-active $LaBWO_6$ crystal was synthesised. Some of its physical properties are listed in Table 2.

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2. $LaBWO_6$ tungstate crystal and SRS generation in it

The experiments with excitation of stationary nonlinear $\chi^{(3)}$ generation in the $LaBWO_6$ crystal were performed at room temperature under conditions similar to those applied for some known SRS tungstates [18, 21]), using a picosecond $Nd^{3+}:Y_3Al_5O_{12}$ laser for pumping in the near-IR (λ_{ex} = 1.06415 μm) and visible (second harmonic with λ_{ex} = 0.53207 μm) ranges.

One of the recorded spectra of nonlinear $\chi^{(3)}$ generation in the $LaBWO_6$ crystal is shown in Fig. 1, and its Stokes and anti-Stokes lines are identified in Table 3.

3. Conclusions

The synthesis of orthorhombic $LaBWO_6$ crystal and study of the nonlinear $\chi^{(3)}$ generation in it extended the range of SRS tungstates that are widely used in experimental quantum electronics (many of these crystals become laser-active after doping with Ln^{3+} ions). The crystal under study has a relatively high steady-state Raman gain (less than 2.8 cm GW^{-1}) in the visible wavelength range and can generate a 1.5-octave ($\sim$13010 cm^{-1} wide) 15-component Stokes and anti-Stokes $\chi^{(3)}$ comb.

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Table 1. Known SRS tungstate crystals and their properties.

Crystal	SRS implementation year [a]	Space group	Non-linearity	Lasant ions [b]	SRS-phonon frequencies/cm^{-1}	Observed nonlinear $\chi^{(3)}$ processes
α-$KY(WO_4)_2$	1985 [13]	C^6_{2h}–C2/c	$\chi^{(3)}$	Pr^{3+}, Nd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}	~905, ~765, ~87	SRS, SRS + SE (Nd^{3+}[13], Tm^{3+} [24], Yb^{3+}[25])[c], combined mode[d], $\chi^{(3)}$ cross-cascade[e], $\chi^{(3)}$ comb[f]
α-$KCd(WO_4)_2$	1985 [13, 14]	C^6_{2h}–C2/c	$\chi^{(3)}$	Pr^{3+}, Nd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}	~901, ~768,~84	SRS, SRS + SE (Nd^{3+}[13, 14], Yb^{3+}[26]), $\chi^{(3)}$ cross-cascade, $\chi^{(3)}$ comb
$NaBi(WO_4)_2$	1995 [15]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Nd^{3+}	~910	SRS
$NaY(WO_4)_2$	1998 [16]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Nd^{3+}	~914, ~328	SRS, $\chi^{(3}$ comb
α-$KDy(WO_4)_2$	1998 [17]	C^6_{2h}–C2/c	$\chi^{(3)}$	–	~899, ~760	SRS
α-$KLu(WO_4)_2$	1998 [17]	C^6_{2h}–C2/c	$\chi^{(3)}$	Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}	~907, ~757	SRS, SRS + SE (Nd^{3+}[27], Yb^{3+}[28])
$CaWO_4$	1999 [18]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}	~908	SRS
$ZnWO_4$	1999 [18]	C^4_{2h}	$\chi^{(3)}$	Cr^{3+}	~907	SRS
$CdWO_4$	1999 [18]	C^4_{2h}	$\chi^{(3)}$	–	~890	SRS
$La_2(WO_4)_3$	1999 [19]	C^6_{2h}	$\chi^{(3)}$	–	~940	SRS
$PbWO_4$	1999 [18]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Nd^{3+}	~901, ~328	SRS, SRS + SE (Nd^{3+}[18])
$BaWO_4$	2000 [20]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	–	~925, ~332	SRS
$SrWO_4$	2002 [21]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Nd^{3+}	~927	SRS
$NaLa(WO_4)_2$	2007 [22]	C^6_{4h}–$I4_1$/a	$\chi^{(3)}$	Nd^{3+}	~923, ~912, ~326	SRS
$CsLa(WO_4)_2$	2017 [23]	D^4_{2d}	$\chi^{(3)}$	Nd^{3+}	~956	SRS, $\chi^{(3)}$ comb
$LaBWO_4$	2019 this study	D^1_2–P222	$\chi^{(2)} + \chi^{(3)}$	–	~930	SRS, $\chi^{(3)}$ comb

[a] Only pioneer journal papers are cited. [b] Data from [3, 4]. [c] Laser converter: simultaneous generation of radiation from Ln^{3+} ions and SRS generation in tungstate crystals excited in optical cavity. [d] Result of interaction of coherently excited SRS-active modes. [e] Cascade Stokes (anti-Stokes) generation with participation of dissimilar SRS-active modes. [f] Generation of a multioctave (high order) Stokes and anti-Stokes frequency comb.

Table 2. Properties of orthorhombic SRS $LaBWO_6$ tungstate.

Space group	Unit-cell parameters/Å	Non-linearity	Melting point/°C	Transparency range/μm	SRS-promoting phonon mode frequency/cm^{-1}	Raman gain for the first Stokes component/cm GW^{-1} [a]	Spectral width of the Stokes and anti-Stokes $\chi^{(3)}$ comb/cm^{-1} [b]
D^1_2–P222 [29]	$a = 4.10$, $b = 10.31$, $c = 21.71$[30]	$\chi^{(2)} + \chi^{(3)}$	1078 [30]	0.293 [30]–6.1	~930	< 2.8 (for the line with $\lambda_{St1} = 0.5598$ μm)	~13010

[a] Estimated from comparative gain measurements in the $PbWO_4$ crystal [31]. [b] Measured using a McPherson Model 370 diffraction monochromator with linear Si CCD and InGaAs detectors (Hamamatsu S3924-1924Q and G9204-512D, respectively) in the visible and mid-IR spectral regions upon excitation of $LaBWO_6$ crystal by fundamental radiation of picosecond $Nd^{3+}:Y_3Al_5O_{12}$-laser ($\lambda_{ex} = 1.06415$ μm, $\tau_{ex} \approx 80$ ps). The parameters of the recorded 15-component $\chi^{(3)}$ comb are as follows: $\omega_{ASt11} \approx 19617$ cm^{-1} ($\lambda_{ASt11} \approx 0.5095$ μm) – $\omega_{St3} \approx 6607$ cm^{-1} ($\lambda_{St3} \approx 1.5135$ μm) = $\omega_{comb} \approx 13010$ cm^{-1}.

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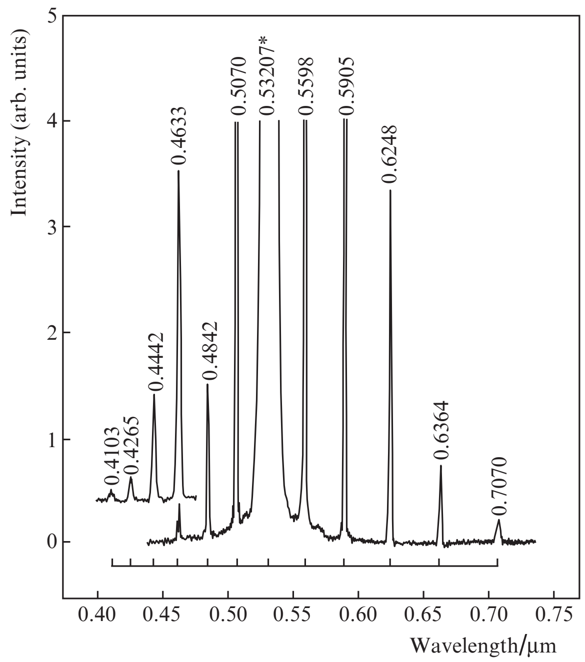

Figure 1. Spectrum of nonlinear steady-state $\chi^{(3)}$ generation in a sample of orthorhombic $LaBWO_6$ crystal with sizes of 24 (along the *a* axis) $\times$ 6 $\times$ 5 mm in the *a*(*c*,*c*)*a* excitation geometry under pumping by a picosecond $Nd^{3+}:Y_3Al_5O_{12}$ laser (λ_{ex} = 0.53207 μm, $\tau_{ex} \approx$ 60 ps), recorded on a McPherson Model 370 diffraction monochromator with a linear Hamamatsu S3924-1924Q Si CCD detector. The wavelength lines (the pump line is indicated by an asterisk) are given in μm, and the equidistant frequency intervals between them (indicated by scale brackets) are equal to the frequency of SRS-promoting phonon mode $\omega_{SRS} \approx 930$ cm^{-1}.

Table 3. Spectral composition of nonlinear $\chi^{(3)}$ generation in orthorhombic $LaBWO_6$ crystal [Stokes (St) and anti-Stokes (ASt) lines].

Wavelength/μm[a]	Line	Process of $\chi^{(3)}$ generation[c]
0.4103	ASt6	$*\omega_{ex} + 6\omega_{SRS} = \omega_{ASt6}$
0.4265	ASt5	$*\omega_{ex} + 5\omega_{SRS} = \omega_{ASt5}$
0.4442	ASt4	$*\omega_{ex} + 4\omega_{SRS} = \omega_{ASt4}$
0.4633	ASt3	$*\omega_{ex} + 3\omega_{SRS} = \omega_{ASt3}$
0.4842	ASt2	$*\omega_{ex} + 2\omega_{SRS} = \omega_{ASt2}$
0.5070	ASt1	$*\omega_{ex} + \omega_{SRS} = \omega_{ASt4}$[c]
0.53207	λ_{ex}	ω_{ex}
0.5598	St1	$\omega_{ex} - \omega_{SRS} = \omega_{St1}$
0.5905	St2	$*\omega_{ex} - 2\omega_{SRS} = \omega_{St2}$
0.6248	St3	$*\omega_{ex} - 3\omega_{SRS} = \omega_{St3}$
0.6634	St4	$*\omega_{ex} - 4\omega_{SRS} = \omega_{St4}$
0.7070	St5	$*\omega_{ex} - 5\omega_{SRS} = \omega_{St5}$

[a] Measurement error: ±0.0003 μm. [b] Cascade processes are indicated by asterisks. [c] As an example, the complete process of $\chi^{(3)}$ generation for the ASt1 line (λ = 0.5070 μm) is recorded as $\omega_{ex} + \omega_{SRS} = [\omega_{ex} + \omega_{ex} - (\omega_{ex} - \omega_{SRS})] = [\omega_{ex} + \omega_{ex} - \omega_{St1}] = \omega_{ASt1}$. The three most likely components, providing parametric four-wave generation, are given in square brackets.

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