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Stimulated Raman scattering of 0.3-ps 515 nm laser pulses in $Ca_3(VO_4)_2$ and $Ca_{0.27}Sr_{0.3}(VO_4)_2$

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The prospects of SRS-active calcium/strontium orthovanadate crystals, ($Ca_3(VO_4)_2$ and $Ca_{2.7}Sr_{0.3}(VO_4)_2$), for spectral conversion of ultrashort visible-range laser pulses evaluated in a single-pass scheme with pump focusing into the samples. For the 3 μJ incident laser pulses of 0.3 ps duration at wavelength of 515 nm the energy conversion efficiency of up to $\sim 3.5\%$ to the Stokes component shifted in frequency by $\sim 850\,cm^{-1}$ obtained in a 1.3 cm long sample of $Ca_{2.7}Sr_{0.3}(VO_4)_2$ crystal. Simultaneously, in the transmitted radiation spectrum the amplitude of Stokes component reached 1/3 of the amplitude at the pump wavelength. Under the same conditions, SRS in a $Ca_3(VO_4)_2$ crystal was not detected at all. It was shown that the observed differences can be explained by the attenuation of pump pulse due to difference in two-photon absorption in these crystals.

Keywords: stimulated Raman scattering, two-photon absorption, $Ca_3(VO_4)_2$; femtosecond pulses.

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Introduction

The problem of spectral broadening of ultrashort (subpicosecond) laser pulses is still essential due to continuously growing range of various laser applications in different fields: physics, photochemistry, biology, medicine, etc. Stimulated Raman scattering (SRS) is one of the efficient methods for laser pulse spectrum conversion. Despite a rather long research and development history in this area, the problem is still at its extensive study stage due to multiple phenomena and factors influencing the SRS conversion efficiency (see, for example, recent publications [1–4]). This is due to the fact that phase relaxation time T_2 of applicable vibrational modes in the majority of SRS-active materials is generally ≥ 1 ps [5]. As a consequence, SRS interaction has a considerably transient regime and, therefore, the pumping emission intensity required for efficient SRS conversion grows and, thus, the contribution of accompanying nonlinear effects increases.

$Ca_{3-x}Sr_x(VO_4)_2$ ($x = 0 - 3$) (CSVO) crystals characterized by uniquely wide ($\Delta\nu \approx 50\,cm^{-1}$ ($x = 0$)) SRS-active vibration line with frequency $\nu_1 = 854\,cm^{-1}$ [6–8] are of interest for implementation of SRS-ultrashort laser pulses since $T_2 \simeq 0.2$ ps could correspond to such line width (in case of homogeneous broadening). However, this line is inhomogeneously broadened and there is no valid data about T_2 in the literature.

The phenomena significantly influencing SRS interaction efficiency include the effects caused by Kerr nonlinearity of the material (nonlinear refraction index n_2) such as self-focusing, self-phase modulation (SPM), cross-phase modulation, etc. In accordance with [9], contribution of nonlinear effects caused by cubic nonlinear response of bound electrons may be considerably reduced and even completely suppressed when the ratio of photon energy to material bandgap is $h\nu/E_g \approx 0.7$. Since E_g in CSVO ($x = 0$) is (3.55 ± 0.2) eV [10], then the effect predicted in [9] shall appear for laser emission in the range of 500 ± 20 nm. This range exactly includes second harmonic emission of a widely used ytterbium fiber laser (emission wavelength 515 nm, $h_\nu/E_g \approx 2.4\,eV/3.55\,eV \approx 0.68$). Therefore, it may be expected that the influence of effects associated with cubic electron nonlinearity in these crystals will be negligible. This, in its turn, suggests that SRS of 515 nm subpicosecond laser pulses will appear in its classical (similar to steady-state) regime.

However, in this case, nonlinear two-photon absorption (TPA) of such emission in CSVO may considerably influence SRS efficiency. It is not possible to assess in advance the degree of TPA influence on SRS in these crystals due to the lack of appropriate data in the literature.

Previously, SRS in $Ca_3(VO_4)_2$ crystal was studied using fundamental frequency pulses of neodymium laser ($\lambda = 1.06\,\mu m$) with duration of dozens picoseconds and more [7,8]. Features of SRS conversion in this material for visible range subpicosecond laser pulses are studied experimentally herein.

Experiment setup.

Experiments were carried out using second harmonic emission of Satsuma (Amplitude Systems) ytterbium fiber

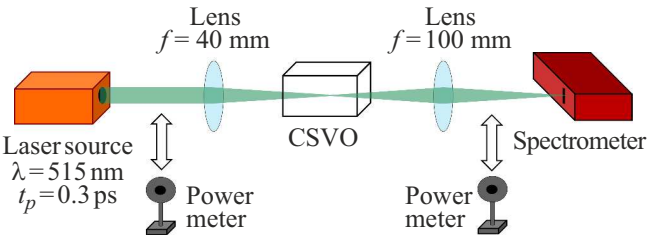

Figure 1. Optical diagram of the experiment.

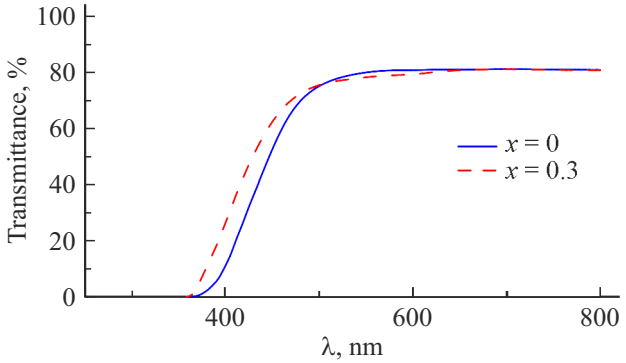

Figure 2. transmittance of CSVO crystals with $x = 0$ (solid curve) and $x = 0.3$ (dashed curve).

laser operating on the fundamental TEM_{00} mode. Emission wavelength was $\lambda = 515$ nm, FWHM pulse duration was $t_p = 0.3$ ps, pulse energy E_p was up to $3.2\,\mu$J at pulse repetition rate 1 kHz. Optical scheme of the expirement is shown in Figure 1.

Laser beam was focused into the center of a sample by a lens with the focal lenght 40 mm. Focal waist radius in the samples was equal to $\omega_0 \approx 10\,\mu$m, waist length was about 2.4 mm and was considerably lower than the sample length. The passed emission was sent to Avesta-150 spectrometer entrance slit (spectral resolution 0.3 nm) using a lens with the focal lenght of 100 mm. To avoid a spectrometer saturation, the emission passed through the sample was also passed through a neutral attenuator (a pair of wedge-shaped quartz plates, not shown in Figure 1). Energy efficiency of SRS conversion was estimated as the ratio of stokes emission pulse energy at sample exit to pump pulse energy at the sample entrance measured by OPHIR-3A calorimeters. In this case, the stokes component in the passing emission was extracted using a 1200 groves/mm diffraction grating.

The experiment investigated 1.3 cm long CSVO crystal with $x = 0$ and $x = 0.3$ ($Ca_3(VO_4)_2$ and $Ca_{2.7}Sr_{0.3}(VO_4)_2$) grown by the Department of Laser Materials and Photonics, GPI RAS. Optical axis of the samples was perpendicular to the incident beam propagation and polarization direction. Sample transmittance spectra are shown in Figure 2.

Shortwave transmission edge for CSVO sample ($x = 0.3$) appeared to be shifted into the UV range which demonstrates a wider (by $\sim 3\%$) band gap. In this case it should be noted that no considerable difference in the spontaneous Raman scattering spectra of crystals at $x = 0$ and $x = 0.3$ was detected [11], i.e. the crystals having similar properties in terms of Raman scattering have different bandgap.

Experimental results

Spectra of pulses passing through CSVO crystal samples with $x = 0$ and $x = 0.3$ at maximum laser system energy $E_p = 3.2\,\mu$J are shown in Figure 3.

First of all, the spectra of emission that has passed through the crystal are considerably broadened in both samples compared with the pump pulse spectrum, and their asymmetry with prevailing broadening into the stokes region is clearly seen. The fact of spectral broadening of pumping, despite the met condition $h\nu/E_g \approx 0.7$ [9], demonstrates that the Kerr nonlinearity responsible for broadening is not of electronic type. In combination with broadening asymmetry, this fact may indicate that the Kerr nonlinearity in CSVO has a „slow“ (for example, orientational type) component similar to that detected in $BaWO_4$ [12,13] earlier. Spectral broadening at $E_p = 1\,\mu$J in CSVO crystals was equal to $\sim 700 \pm 200\,\text{cm}^{-1}$, which was ~ 1.5 times greater than in $BaWO_4$ [12,13] crystal in similar experimental conditions.

In addition to the broadened pump spectrum, a clearly pronounced peak is observed at 537.5 ± 1.5 nm in CSVO crystal ($x = 0.3$) at $E_p > 0.6\,\mu$J (Figure 3, *b*). Its frequency shit relative to the pump pulse ($\sim 850\,\text{cm}^{-1}$) corresponds to SRS in CSVO crystal at vibrational mode $\nu_1 = 854\,\text{cm}^{-1}$ [11]. Amplitude of this peak reached $\sim 30\%$ from the pumping pulse spectrum amplitude at 515 nm, with decrease of E_p, the peak amplitude decreased and achieved $\sim 3\%$ and 1% of the pump pulse spectrum amplitude at $E_p = 1.6$ and $0.8\,\mu$J, respectively.

Compared with SRS efficiency estimated from the spectra, stokes component generation energy efficiency K_{SRS} in CSVO crystal ($x = 0.3$) was considerably lower. K_{SRS} vs. E_p is shown in Figure 4. Here, conversion efficiency at 1% level was achieved at $E_p \approx 2\,\mu$J, grew up to 3.5% at $E_p \approx 2.8\,\mu$J and stopped growing with further increase (up to $3.2\,\mu$J).

Such conversion efficiency is ~ 9 times lower than the SRS efficiency estimated by the spectra. It should be noted that, compared with CSVO ($x = 0.3$), we have failed to record any peak in the region of ~ 538 nm in the CSVO crystal ($x = 0$) experiments even at maximum pump pulse energy (Figure 3, *a*). Analysis of possible causes of such differences has shown that they may be a consequence of pump energy decrease due to nonlinear absorption in the sample.

Transmittance of CSVO crystal sample with $x = 0$ and $x = 0.3$ vs. incident pulse energy measured in the same interaction geometry is shown in Figure 5. The dashed and solid curves in Figure 5 represent the best interpolation of the experimental data.

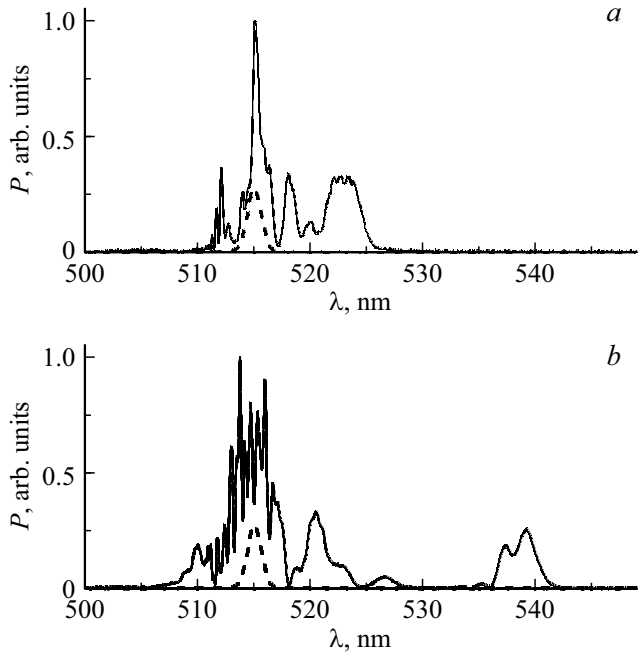

Figure 3. Pump pulse spectra (dashed lines) and spectra of the pulse that has passed through CSVO crystal with $x = 0$ (a) and with $x = 0.3$ (b) (solid lines).

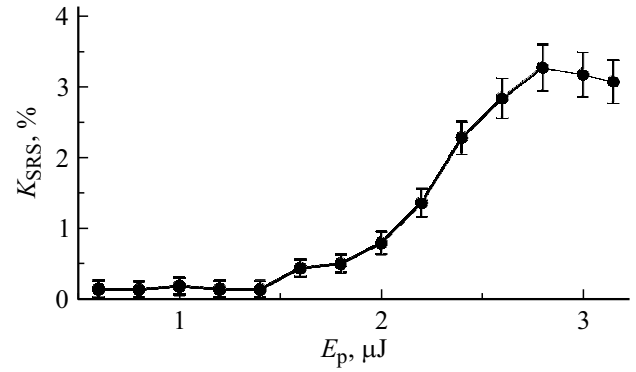

Figure 4. SRS conversion energy efficiency in CSVO crystal ($x = 0.3$) vs. pump pulse energy E_p.

Figure 5 shows that, as early as at $E_p \approx 0.1\,\mu$J, transmittance of the studied samples becomes lower than 80%, i.e. the value caused only by the loss due to Fresnel reflection from their uncoated factes (see transmittance in Figure 1). With E_p growth, their transmittance decreases and achieves 8 and 14% at $E_p \approx 3\,\mu$J for CSVO with $x = 0$ and $x = 0.3$, respectively. Such type of obtained dependences is typical of nonlinear absorption in samples. Since the photon energy vs. bandgap $h\nu/E_g \approx 0.7 > 0.5$ in our experiment, then it is reasonable to correlate the nonlinear absorption to the two-photon process. Two-photon absorption coefficients β in the studied samples, which were estimated taking into account that laser emission with Gaussian transverse distribution was focused inside the samples by the lens so that the waist center was in the middle of the sample, were equal to 50 ± 14 and 25 ± 7 cm/TW in CSVO with $x = 0$ and $x = 0.3$, respectively.

Based on $\beta = 25 \pm 7$ cm/TW in CSVO ($x = 0.3$), effective decrement of pump emission absorption $\alpha_{\text{eff}} l = \beta I_p l$ at a distance from the sample entrance to the waist ($l/2 \approx 0.64$ cm) and at the waist length ($l_c = 0.24$ cm) was equal to 0.46 and 0.5 at $E_p = 0.8\,\mu$J, and 0.3 and 0.44 at $E_p = 1.6\,\mu$J, respectively. Finally, in these cases, the pump emission intensities in the waist region (I_{pc}) which provide SRS conversion coefficient ~ 1 and 3% were equal to 0.11 and 0.13 TW/cm^2, and $\alpha_{ef} \approx 3$ cm^{-1}. According to [14], SRS amplification increment in the light absorbing medium is as follows

$$G = [-\alpha l + g_{SRS} I_p (1 - e^{\alpha l})/\alpha],$$

where α is the absorption coefficient, l is the medium length and g_{SRS} is the SRS amplification coefficient. The data provided above allowed to estimate the effective (for this experiment) SRS gain coefficient in CSVO crystal ($x = 0.3$) as $g_{SRS} = 0.9 \pm 0.3$ cm/GW and, respectively, SRS amplification threshold increment $G_{th} \approx 17$.

In CSVO ($x = 0$), even at maximum $E_p = 3.2\,\mu$J in our experiments due to a doubled two-photon absorption coefficient ($\beta = 50 \pm 14$ cm/TW), pump emission intensity in the waist region is by $\sim 40\%$ lower, while the effective emission absorption coefficient is by $\sim 40\%$ higher. As a result, despite g_{SRS} of these crystals are identical [11], in CSVO ($x = 0$) $G \approx 10$, i.e. are considerably lower than G_{th}. This circumstance explains the fact that no SRS peak was detected in CSVO ($x = 0$) near 537 nm even at maximum E_p.

Findings and conclusion

The experiments included investigation of laser pulse spectrum conversion with duration 0.3 ps, wavelength 515 nm and energy up to $3.2\,\mu$J in CSVO crystals with $x = 0$ and $x = 0.3$ in the optical setup with one focused beam passage through a 1.3 cm long sample. Spectra of laser pulses that had passed through the crystal samples were broadened due to the self-phase modulation effect. In this

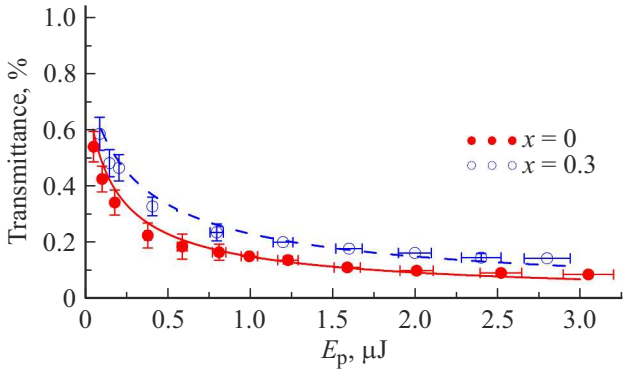

Figure 5. transmittance of CSVO crystal samples with $x = 0$ and $x = 0.3$ vs. laser pulse energy.

case, in the spectrum of emission that had passed through CSVO crystal with $x = 0.3$ at $E_p > 0.8\,\mu$J, a peak was observed at 537.5 ± 1.5 nm (frequency shift $\sim 850\,\text{cm}^{-1}$) corresponding to SRS at the strongest mode $\nu_1 = 854\,\text{cm}^{-1}$. At $E_p \approx 2.8\,\mu$J, SRS peak amplitude reached 1/3 of the pump emission amplitude, while the energy efficiency reached 3.5%. In the same conditions, no SRS peak was recorded in CSVO crystal with $x = 0$.

It has been found that the difference in SRS efficiency in crystals is a sequence of difference in pump emission two-photon absorption coefficients. The corresponding values for CSVO were equal to 50 ± 14 cm/TW ($x = 0$) and 25 ± 7 cm/TW ($x = 0.3$). When taking into account the two-photon absorption, an effective SRS amplification coefficient was calculated for the first time for laser emission pulses with 515 nm and 0.3 ps $g_{SRS} = 0.9 \pm 0.3$ cm/GW.

Thus, CSVO crystal with $x = 0.3$ seems promising for SRS conversion of subpicosecond laser pulses and may be used, for example, in a mid-IR solid-state laser system as in [15].

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Conflict of interest

The authors declare that they have no conflict of interest.

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