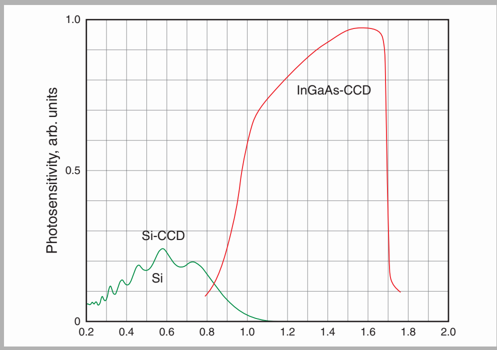
Abstract: We report on the first observation of the nonlinear cascading $\chi^{(3)} \leftrightarrow \chi^{(3)}$ effects in UV spectral range and second harmonic generation stipulated by the "defect" nonlinearity under one-micron pumping in crystalline ceramics based on cubic oxides Sc_2O_3 and Lu_2O_3. Broadband their multi-wavelength Stokes and anti-Stokes combs with the extension of 10475 cm^{-1} (for Sc_2O_3) and 8232 cm^{-1} (for Lu_2O_3) were recorded as well.



Spectral sensitivity of Si- and InGaAs-CCD linear image sensors S3923-1024Q and G9204-512D, respectively

New nonlinear-laser effects in crystalline fine-grained ceramics based on cubic Sc_2O_3 and Lu_2O_3 oxides: second and third harmonic generation, and cascaded self-sum-frequency mixing in UV spectral region

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1. Introduction

In last decade modern crystalline gain materials doped with lanthanide (Ln^{3+}) lasants are increasingly employed in the ceramic forms. A number of revolutionary fabrication methods have been developed (see, e.g. [1]) to add and replace commonly used crystal growth techniques so that laser ceramics can be obtained a lower cost and larger size. The constitution of grains and grain boundaries are fundamental difference between the crystalline ceramics and single crystals.

In spate the fact that with these ceramics allowed to get already very impressive advances, e.g. the achievement of about 100 KW output CW power ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ channel of Nd^{3+}:$Y_3Al_5O_{12}$ ceramic laser [2]) and efficient sub-100 fs ytterbium generation ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ lasing

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Ceramics	Space group [a)]	Ln^{3+} lasant	Nonlinear effect	g_{ssR}^{St1}, [b)] cm/GW
Sc_2O_3	T_h^7	Yb^{3+}	SRS, **SHG**, **THG**,**self-SFM(SRS)** [c)]	≈0.72 [8]
Y_2O_3	T_h^7	Nd^{3+}, Yb^{3+}	SRS	≈0.4 [9]
$Y_3Al_5O_{12}$	O_h^{10}	Nd^{3+}, Er^{3+}, Yb^{3+}	SRS	≈0.1 [9–11]
Ba(Sn,Zr,Mg,Ta)O_3 (*E-type*) [d)]	O_h^5	–	SRS	≈0.15 [12]
Ba(Sn,Zr,Mg,Ta)O_3 (*Z-type*) [d)]	O_h^5	–	SRS	≈0.15 [12]
Lu_2O_3	T_h^7	Nd^{3+}, Yb^{3+}	SRS, **SHG**, **THG**, **self-SFM(SRS)** [c)]	≈0.3 [13]

[a)] Grains of the ceramics are randomly oriented nano- or micro-size single crystals.
[b)] g_{ssR}^{St1} is the steady-state Raman gain coefficient for first Stokes lasing component measured under one-micron pumping radiation from picosecond Nd^{3+}:$Y_3Al_5O_{12}$ laser.
[c)] Self-SFM(SRS), i.e. self-sum frequency mixing of the arising SRS lasing components and pumping generation.
[d)] In microcrystalline grains of the Ba(Sn,Zr,Mg,Ta)O_3 ceramics the B' and B" octahedral sites statistically occupy by four unlike valency cations Mg^{2+}, Sn^{4+}, Zr^{4+}, and Ta^{5+}, i.e. in this materials is realized the second low of crystal-field disorder [14].

Table 1 Nonlinear-laser effects in highly-transparent "cubic" ceramics

in Y_2O_3 and Sc_2O_3 ceramics [3,4]), many their physical properties need more comprehensive investigation.

In the first place this concerns the grain boundary properties which play a key role in the determination of main characteristics of crystalline laser ceramics and different types of laser on their basis. Recently, it was found that the grain boundaries in these laser-host ceramics improved mechanical toughness and micro-hardness to the same name laser-host crystals [5]. Comparative experiments with the same names of laser single crystals and ceramics have shown that grain boundaries in the latter do not contribute to reducing the optical damage limit [6]. Review paper on the influence of the grain boundaries on the heat transfer in laser ceramics on the base of cubic oxides is given in [7]. The walls of micro-size grains in ceramics on the base of oxide, in particular Sc_2O_3 and Lu_2O_3, are surface defects where the centrosymmetric cubic crystallographic nature (their space group is $T_h^7 - Ia3$) is broken. Therefore, in these bulk crystalline ceramics with high concentration of grain-boundary walls should be manifested both cubic $\chi^{(3)}$- and quadratic $\chi^{(2)}$- nonlinearities under high peak-power of laser excitation, as stimulated Raman scattering (SRS), low-intensity non-phase-matched third and second harmonic generation (THG and SHG)), as well as multi-wave parametric mixing processes. The main goal of this work was the discovery of all these possible nonlinear-laser effects under one-micron picosecond pumping in highly-transparent Sc_2O_3 and Lu_2O_3 ceramics which were fabricated in Konoshima Chemical Co. Ltd. Incidentally, in this experiments was the task to significant widen of Stokes and anti-Stokes wings in their SRS spectra. The Table 1 summarized of observed nonlinear-laser interactions in crystalline ceramics on the base of cubic oxides.

2. Multi-wavelength nonlinear lasing from UV till mid-IR region

For more detail investigation of single-pass Raman induced nonlinear lasing processes in crystalline host-

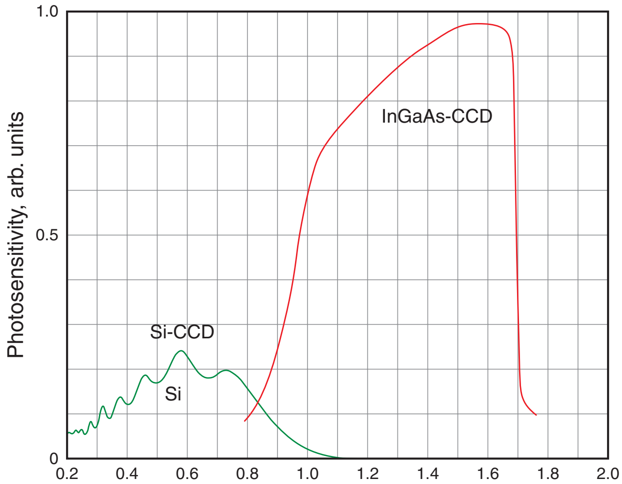

Figure 1 (online color at www.lphys.org) Spectral sensitivity of Si- and InGaAs-CCD linear image sensors S3923-1024Q and G9204-512D, respectively (data from Hamamatsu catalog)

ceramics Sc_2O_3 and Lu_2O_3 for Ln^{3+} lasants we used a home-made Xe-flashlamp-pumped picosecond (≈100 ps) Nd^{3+}:$Y_3Al_5O_{12}$ laser emitted at a fundamental wavelength $\lambda_f = 1.06415$ μm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ generation channel of Nd^{3+} activator ions). The nearly Gaussian profile of its beam was focused into about 15-mm long ceramic samples with a lens (f = 25 cm), resulting in beam-waist diameter of about 160 μm. The spectral composition of the SRS and Raman-induced multi-wave mixing was analyzed with a grating monochromator (McPherson Model 270 in Cherny-Turned arrangement) combined with spectrometric system (CSMA) equipped with two Hamamatsu linear image sensors Si-CCD (3923-1024Q) and CCD-InGaAs (G9204-512D) offering good enough spectral sensitivity from UV till ≈1.7 μm (see Fig. 1). In consequence of more careful matching of an excitation scheme and new IR detector compared to our earlier SRS-measurements [8,13] we significant widened Stokes and anti-Stokes wings for

Nonlinear generation		
Wavelength, μm [a]	Line [b]	Lasing component attribution
Sc_2O_3, $\omega_{SRS} \approx 419$ cm^{-1} (see Fig. 2)		
0.3344	$ASt_2\lambda_{THG}$	$3\omega_f + 2\omega_{SRS}$
0.3495	$ASt_1\lambda_{THG}$	$3\omega_f + \omega_{SRS}$
0.3547	λ_{THG}	$3\omega_f$
0.3600	$St_1\lambda_{THG}$	$3\omega_f - \omega_{SRS}$ [c]
0.3656	$St_2\lambda_{THG}$	$3\omega_f - 2\omega_{SRS}$ [c]
0.3712	$St_3\lambda_{THG}$	$3\omega_f - 3\omega_{SRS}$ [c]
0.3771	$St_4\lambda_{THG}$	$3\omega_f - 4\omega_{SRS}$ [c]
0.3832	$St_5\lambda_{THG}$	$3\omega_f - 5\omega_{SRS}$ [c]
0.3894	$St_6\lambda_{THG}$	$3\omega_f - 6\omega_{SRS}$ [c]
0.53207	λ_{SHG}	$2\omega_f$
0.5761	ASt_{19}	$\omega_f - 2\omega_{SRS}$
0.5903	ASt_{18}	$\omega_f - 3\omega_{SRS}$
0.6053	ASt_{17}	$\omega_f - 4\omega_{SRS}$
0.6211	ASt_{16}	$\omega_f - 5\omega_{SRS}$
0.6377	ASt_{15}	$\omega_f + 15\omega_{SRS}$
0.6552	ASt_{14}	$\omega_f + 14\omega_{SRS}$
0.6737	ASt_{13}	$\omega_f + 13\omega_{SRS}$
0.6932	ASt_{12}	$\omega_f + 12\omega_{SRS}$
0.7140	ASt_{11}	$\omega_f + 11\omega_{SRS}$
0.7360	ASt_{10}	$\omega_f + 10\omega_{SRS}$
0.7594	ASt_9	$\omega_f + 9\omega_{SRS}$
0.7844	ASt_8	$\omega_f + 8\omega_{SRS}$
0.8110	ASt_7	$\omega_f + 7\omega_{SRS}$
0.8396	ASt_6	$\omega_f + 6\omega_{SRS}$
0.8702	ASt_5	$\omega_f + 5\omega_{SRS}$
0.9031	ASt_4	$\omega_f + 4\omega_{SRS}$
0.9386	ASt_3	$\omega_f + 3\omega_{SRS}$
0.9770	ASt_2	$\omega_f + 2\omega_{SRS}$
1.0187	ASt_1	$\omega_f + \omega_{SRS}$
1.06415	λ_f	ω_f
1.1138	St_1	$\omega_f - \omega_{SRS}$
1.1684	St_2	$\omega_f - 2\omega_{SRS}$
1.2285	St_3	$\omega_f - 3\omega_{SRS}$
1.2952	St_4	$\omega_f - 4\omega_{SRS}$
1.3695	St_5	$\omega_f - 5\omega_{SRS}$
1.4528	St_6	$\omega_f - 6\omega_{SRS}$
Lu_2O_3, $\omega_{SRS} \approx 392$ cm^{-1} (see Fig. 3)		
0.3498	$ASt_1\lambda_{THG}$	$3\omega_f + \omega_{SRS}$
0.3547	λ_{THG}	$3\omega_f$
0.3597	$St_1\lambda_{THG}$	$3\omega_f - \omega_{SRS}$ [c]
0.3648	$St_2\lambda_{THG}$	$3\omega_f - 2\omega_{SRS}$ [c]
0.3701	$St_3\lambda_{THG}$	$3\omega_f - 3\omega_{SRS}$ [c]
0.3756	$St_4\lambda_{THG}$	$3\omega_f - 4\omega_{SRS}$ [c]
0.53207	λ_{SHG}	$2\omega_f$
0.6382	ASt_{16}	$\omega_f + 16\omega_{SRS}$
0.6546	ASt_{15}	$\omega_f + 15\omega_{SRS}$
0.6718	ASt_{14}	$\omega_f + 14\omega_{SRS}$
0.6900	ASt_{13}	$\omega_f + 13\omega_{SRS}$
0.7092	ASt_{12}	$\omega_f + 12\omega_{SRS}$
0.7294	ASt_{11}	$\omega_f + 11\omega_{SRS}$
0.7509	ASt_{10}	$\omega_f + 10\omega_{SRS}$
0.7737	ASt_9	$\omega_f + 9\omega_{SRS}$
0.7979	ASt_8	$\omega_f + 8\omega_{SRS}$
0.8236	ASt_7	$\omega_f + 7\omega_{SRS}$
0.8511	ASt_6	$\omega_f + 6\omega_{SRS}$
0.8805	ASt_5	$\omega_f + 5\omega_{SRS}$
0.9120	ASt_4	$\omega_f + 4\omega_{SRS}$
0.9458	ASt_3	$\omega_f + 3\omega_{SRS}$
0.9822	ASt_2	$\omega_f + 2\omega_{SRS}$
1.0215	ASt_1	$\omega_f + \omega_{SRS}$
1.06415	λ_f	ω_f
1.1105	St_1	$\omega_f - \omega_{SRS}$
1.1610	St_2	$\omega_f - 2\omega_{SRS}$
1.2114	St_3	$\omega_f - 3\omega_{SRS}$
1.2773	St_4	$\omega_f - 4\omega_{SRS}$
1.3446	St_5	$\omega_f - 5\omega_{SRS}$

[a] Measurement accuracy is 0.0003 μm.
[b] For example, the condition notation of cascaded generation $ASt_1\lambda_{THG}$ is defined as the first anti-Stokes component connected with THG of fundamental pump emission.
[c] One of possible five-wave parametric interaction involving pump and Stokes lasing emission.

Table 2 Room-temperature spectral composition of nonlinear-laser generation in crystalline ceramics based on cubic oxides Sc_2O_3 and Lu_2O_3 under picosecond Nd^{3+}:$Y_3Al_5O_{12}$-laser excitation at its fundamental wavelength $\lambda_f = 1.06415$ μm

both studied ceramics, from 0.5761 μm to 1.4528 μm for Sc_2O_3 and from 0.6382 μm to 1.3446 μm wavelengths for Lu_2O_3. These results are shown in Figs. 2a,b and Figs. 3a,b and listed in Table 2.

In an effort to investigate of our second problem in Sc_2O_3 and Lu_2O_3 ceramics connected with exacting supervision their possible SHG, THG, and $\chi^{(3)}$-nonlinear multi-wave parametric lasing using filters and other standard experimental contrivances. By this we significant decreased unwanted (saturated) influence of strong one-micron pump radiation and intensive Stokes and anti-Stokes bands emission on the Si-CCD sensor and thus significantly enhanced its sensitivity in the visible and UV spectral regions. The results of these measurements are shown in Fig. 2c and Fig. 3c. As seen, in both ceramics under picoscond one-micron pumping we recorded relatively low-intensity signals of SHG at $\lambda_{SHG} = 0.53207$ μm and THG at $\lambda_{THG} = 0.3547$ μm wavelengths, as well as in the neighbourhood of latter several cascaded five-wave mix-

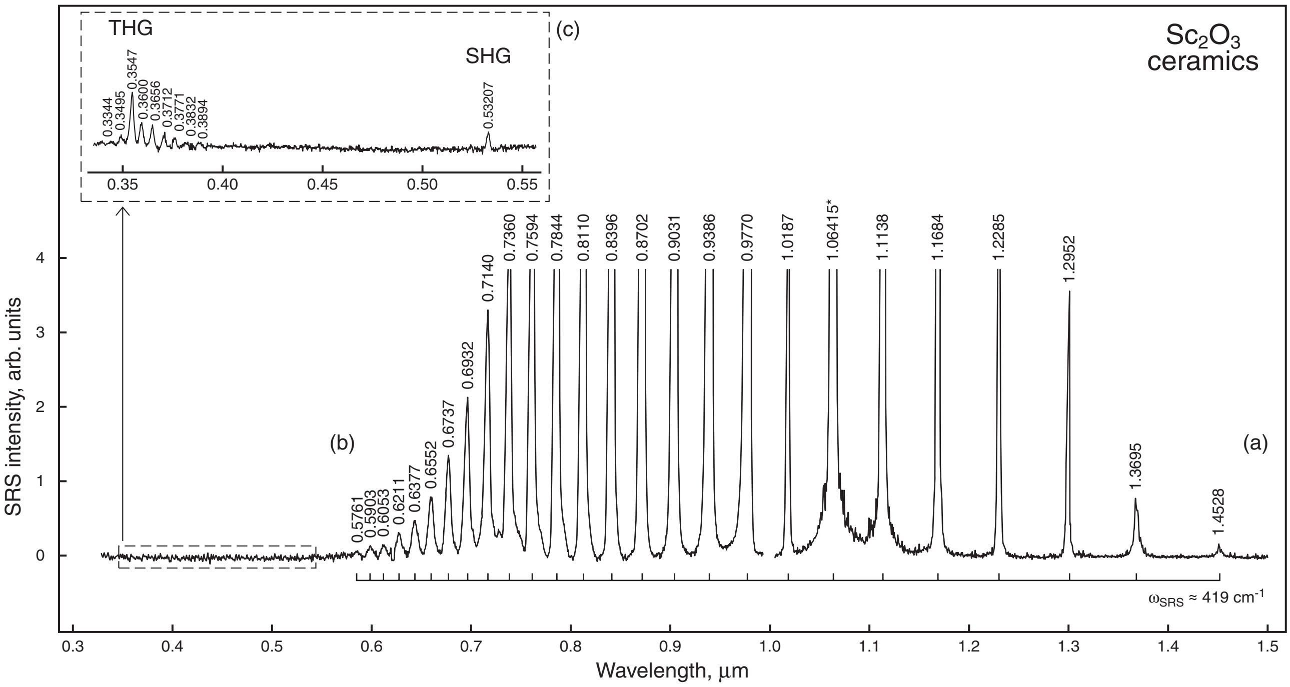

Figure 2 Room-temperature spectra of nonlinear self-frequency lasing in fine-grained Sc_2O_3 ceramics obtained with excitation of one-micron generation of picosecond Nd^{3+}:$Y_3Al_5O_{12}$-laser recorded: (a) and (b) with InGaAs-CCD and Si-CCD sensors, respectively; (c) with Si-CCD sensor and under strong attenuation of pump and its intensive Stokes and anti-Stokes signals (see inset). The wavelength of all lasing lines given in μm (pump line is marked by an asterisk). Stokes and anti-Stokes lines (see spectra (a) and (b)) related to SRS-promoting vibration modes ω_{SRS} $\approx$419 cm^{-1} are indicated by horizontal scale brackets

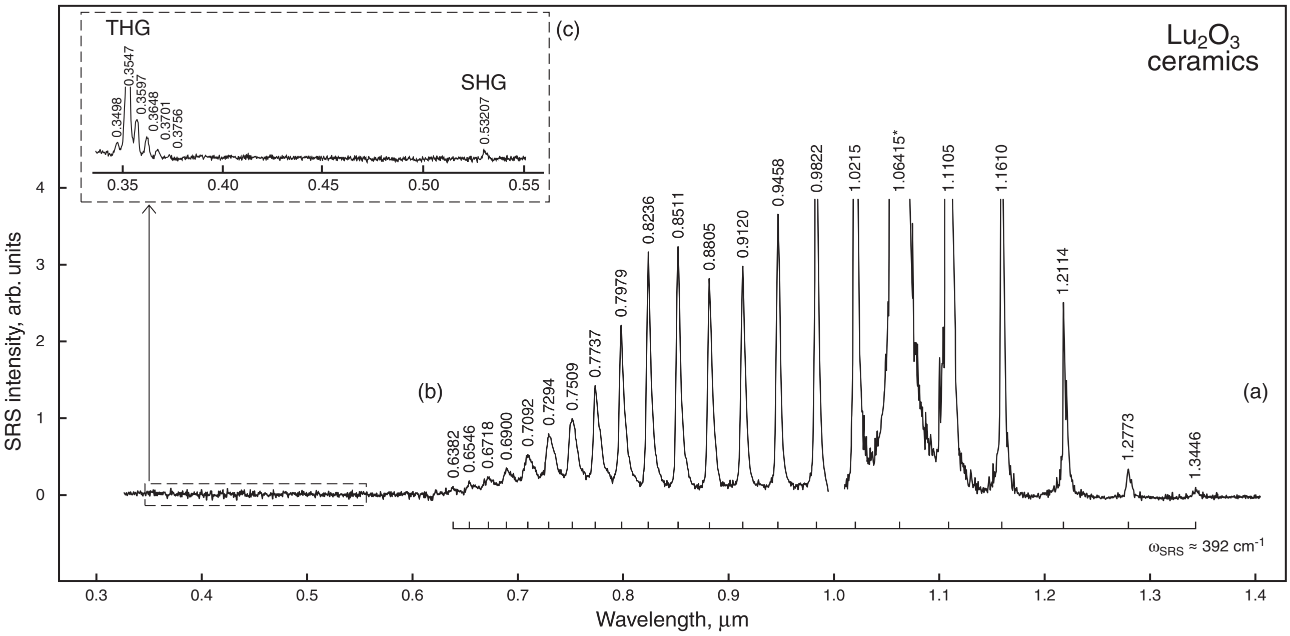

Figure 3 Room-temperature spectra of nonlinear self-frequency lasing in fine-grained Lu_2O_3 ceramics obtained with excitation of one-micron generation of picosecond Nd^{3+}:$Y_3Al_5O_{12}$-laser recorded: (a) and (b) with InGaAs-CCD and Si-CCD sensors, respectively; (c) with Si-CCD sensor and under strong attenuation of pump and its intensive Stokes and anti-Stokes signals (see inset). Stokes and anti-Stokes lines (see spectra (a) and (b)) related to SRS-promoting vibration modes ω_{SRS} $\approx$392 cm^{-1} are indicated by horizontal scale brackets. Other notation as in Fig. 2

ing UV components. Whereas all observed $\chi^{(3)}$-nonlinear components in Sc_2O_3 and Lu_2O_3 ceramics are sufficiently understandable and in a great part agrees with the data on measurements of nonlinear refractive indices n_2 (which directly related to $\chi^{(3)}$-susceptibility) [15], as well as with recently achieved efficient sub-100 fs Kerr-lens mode-locked lasing in Yb^{3+}:Sc_2O_3 ceramics [4], while the expected and observed SHG need be investigated with great care. The case is that the efficiency of recorded self-frequency doubling was very low in both ceramics studied. It should be noted here, that week SHG could be associated also with induced $\chi^{(2)}$-nonlinearity (local mechanical stress) and with arising plasma in micro-interstices (babbles or pores) in centrosymmetric crystalline materials under focusing strong laser excitation. But, these possible reasons are not likely to take place in our case.

3. Conclusion

We have discovered several new nonlinear-laser effects in highly transparent crystalline host-ceramics (for Ln^{3+} lasants) based on cubic oxides Sc_2O_3 and Lu_2O_3, namely: the non-phase-matched THG and nonlinear cascaded $\chi^{(3)} \leftrightarrow \chi^{(3)}$ lasing in UV spectral area arising from one-micron picosecond laser excitation and Raman induced Stokes and anti-Stokes lasing fields in near-IR, as well as SHG arising from induced $\chi^{(2)}$-nonlinearity related to fundamental property of fine-grained nature of ceramics studied. It is worth noting that nonlinear laser cascading in crystalline materials has been observed up to now only of the $\chi^{(2)} \leftrightarrow \chi^{(3)}$ type (see, e.g. [16-18]). Thanks to the improvement of the excitation and recorded condition we also significantly widened of SRS and Raman induced four wave mixing lasing wings. So, we recorded 25 Stokes and anti-Stokes lasing sidebands covered spectral region from 0.5761 μm to 1.4528 μm for Sc_2O_3 and 21 lines within 0.6382 μm and 1.3446 μm wavelengths for Lu_2O_3 ceramics.

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