

The first observation of SRS in a trigonal LiCaAlF_6 crystal

A A Kaminskii, H J Eichler, K Ueda, P Reiche, G M Gad

Abstract. The Raman parametric generation is excited for the first time in a trigonal LiCaAlF_6 fluoride crystal pumped by picosecond pulses. The energy of the $\chi^{(3)}$ -active vibrational mode is determined and all Stokes and anti-Stokes components of SRS are detected for this crystal in the visible region.

The $\text{LiMe}^{2+}\text{Me}^{3+}\text{F}_6$ crystals (where Me^{2+} is Ca^{2+} and Sr^{2+} ; and Me^{3+} is Al^{3+} , Ga^{3+} , and Cr^{3+}) doped with Cr^{3+} and Ce^{3+} ions play a special role in modern optics and laser physics [1, 2]. They are used in ultrashort-pulse lasers emitting in the UV and near IR spectral ranges, in particular, in tunable femtosecond lasers. A first laser fluoride among these crystals was a $\text{LiCaAlF}_6:\text{Cr}^{3+}$ crystal [3]. A LiCaAlF_6 crystal doped with Nd^{3+} ions is considered now as a promising optical material for VUV lithography [4]. In this paper, we excited for the first time multiwave Stokes and anti-Stokes Raman parametric generation in a LiCaAlF_6 crystal pumped by picosecond pulses at 300 K, identified all its components, determined the SRS-active vibrational mode, and estimated the steady-state Raman gain. As far as we know, SRS has not been observed so far in fluoride crystals.

The LiCaAlF_6 single crystals were grown by the Czochralski method using a platinum crucible and high-frequency heating from a stoichiometric melt of LiF , CaF_2 , and AlF_3 (of chemical purity 0.9999) in the atmosphere of pure nitrogen (0.9999) at a rate of 0.5 mm/h [4]. We fabricated for our experiments the samples of size $35 \times 10 \times 8$ mm, which were cut along the [100] crystallographic direction of the crystal and had plane-parallel ($\sim 30''$) ends without antireflection coating. The Raman parametric generation of a LiCaAlF_6 crystal was excited in a single-pass scheme without a cavity by picosecond pulses from a $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ laser with two amplifying cascades and a KTiOPO_4 frequency doubler ($\lambda_p = 0.53207 \mu\text{m}$, $\tau_p \approx 85$ ps, and $E_p \leq 3$ mJ). The laser pump beam with a Gaussian spa-

tial profile was focused on a sample by a lens with the focal length $f = 250$ mm, providing the beam diameter of about $50 \mu\text{m}$ at the waist.

The spectra of Stokes and anti-Stokes generation were measured with a McPherson-218 monochromator equipped with a Hamamatsu S3423-1024Q CCD detector. One of the emission spectra of a LiCaAlF_6 crystal and the results of analysis of Stokes and anti-Stokes components are presented in Fig. 1. It follows from the spectrum that the frequency of the SRS-active vibrational mode of this fluoride is $\omega_{\text{SRS}} = 560 \pm 3 \text{ cm}^{-1}$.

The LiCaAlF_6 fluoride is crystallised in the trigonal syngony and is isostructural to the mineral calacruite [6, 7]. Cations L^+ , Ca^{2+} and Al^{3+} of different valence are locate

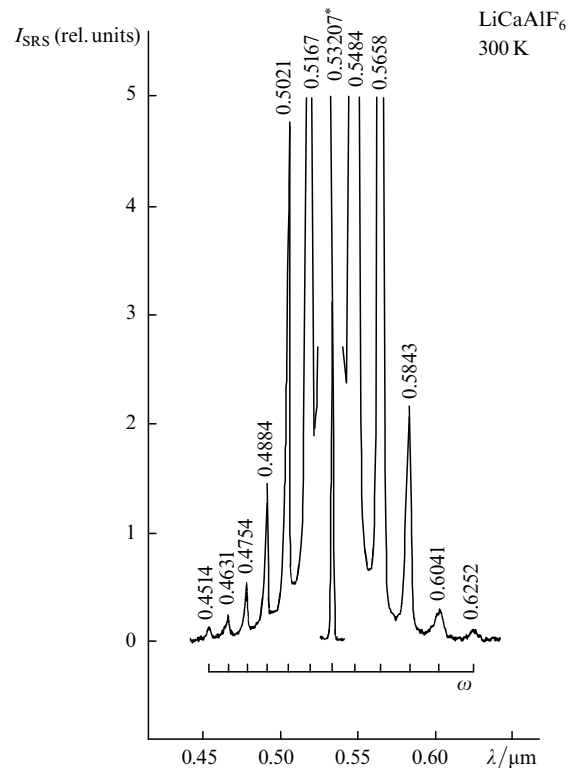


Figure 1. Orientation SRS spectrum of a trigonal LiCaAlF_6 fluoride excited at $0.53207 \mu\text{m}$ (indicated by asterisk) in the a(cc)a excitation geometry at 300 K. The spectral sensitivity of a silicon CCD array was not taken into account; the linewidths are given in micrometers. The scale division on the axis ω is 560 cm^{-1} .

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in three types of fluoride octahedrons in its unit cell with three formula units; 18 atoms in the unit cell produce $3N = 54$ degrees of freedom, resulting, according to the factor-group concepts [8] and the symmetry degeneracy, in the appearance of 36 vibrational modes (for $k = 0$) in this crystal,

$$\Gamma_N = 3A_{1g} + 8E_g + 5A_{2g} + 6A_{2u} + 10E_u + 4A_{1u},$$

of which 11 ($3A_{1g} + 8E_g$) modes are SRS-active and should be manifested in spontaneous Raman scattering. Analysis of the spontaneous Raman spectra of LiCaAlF₆ and the data [9] suggest that the $\chi^{(3)}$ -active mode with $\omega_{\text{SRS}} \approx 560 \text{ cm}^{-1}$ observed in our experiments corresponds to the totally symmetric A_{1g} vibrational mode of octahedral AlF_6^{3-} groups of this fluoride.

We estimated the Raman gain g_{SS} of steady-state SRS in a LiCaAlF₆ crystal at the wavelength $\lambda_{\text{st1}} = 0.5484 \mu\text{m}$ of its first Stokes component by comparing it with the gain observed in the known $\chi^{(3)}$ -active crystals KY(WO₄)₂ and PbWO₄. Our experimental conditions well provided this lasing regime because $\tau_p \gg T_2 = 1/\pi\Delta\nu_R = 1.5 \text{ ps}$ (where τ_p and $\Delta\nu_R \approx 7 \text{ cm}^{-1}$ are the phonon relaxation time and the linewidth of spontaneous Raman scattering, respectively). Using the approximate expression for the amplification increment $g_{\text{SS}}P_{\text{th}}l_R \approx 30$ [10] (where P_{th} is the power above which the generation was reliably observed at the first Stokes component at $\lambda_{\text{st1}} = 0.5484 \mu\text{m}$, and l_R is the active length of the crystal), we measured the required gain to be $0.22 \pm 0.07 \text{ cm GW}^{-1}$. We also estimated the efficiency of the $\chi^{(3)}$ process in LiCaAlF₆. Thus, the total conversion efficiency (into all the SRS components) in our LiCaAlF₆ crystals, which exhibited weak scattering by defects (losses no more than 0.2%), was about 5% at a pump power density of $\sim 2 \text{ GW cm}^{-2}$. The parameters of this unique optical material at 300 K, which were measured in this paper or are known from the literature, are presented below.

Thus, in this paper we excited and studied for the first

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| Space group (No. 163) | $D_{3d}^2 - P\bar{3}1c$ |
| Parameters of the unit cell /Å | $a = 5.007, c = 9.642, Z = 2$ |
| Local symmetry of cations and their fluoride coordination | $C_3(6)$ – for Ca^{2+} , $D_2(6)$ – for Li^+ и Al^{3+} |
| Density /g cm ⁻³ | ~ 2.99 |
| Melting temperature /°C | ~ 810 |
| The UV transparency boundary for a layer of thickness 1 mm/μm | ~ 0.12 |
| Energy of the SRS-active vibrational mode /cm ⁻¹ | ~ 560 |
| Extension of the phonon spectrum measured from SRS /cm ⁻¹ | ~ 585 |
| Refractive indices at 0.6328 μm (see also dispersion dependences in [11]) | $n_o = 1.3826$ $n_e = 1.3828$ |
| Linear dispersion $dn/dT / 10^{-6} \text{ K}^{-1}$ | -4.6 (c-axis) -4.2 (⊥ c-axis) |
| Heat conduction /W K ⁻¹ cm ⁻¹ | 0.051 (c-axis) 0.046 (⊥ c-axis) |
| Thermal expansion /10 ⁻⁶ K ⁻¹ | 3.6 (c-axis) 22 (⊥ c-axis) |
| Elastic constants /GPa | $c_{11} = 118, c_{33} = 107$ $c_{44} = 50, c_{66} = 38$ $c_{14} = \pm 19, c_{13} \approx 54$ |
| Active ions | Cr^{3+} и Ce^{3+} |

time steady-state SRS in a laser fluoride. We think that non-linear $\chi^{(3)}$ processes that we observed in a LiCaAlF₆ crystal should be taken into account (in particular, as possible spurious effects) in the development of high-power ultrashort-pulse lasers based on this crystal. Therefore, it is important to study SRS in other crystals of the fluoride family. The necessity of such studies is also stimulated by the observation of the red shift of the femtosecond lasing band of Cr^{3+} ions in LiSrAlF₆ and LiSrGaF₆ reported earlier in papers [12, 13].

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