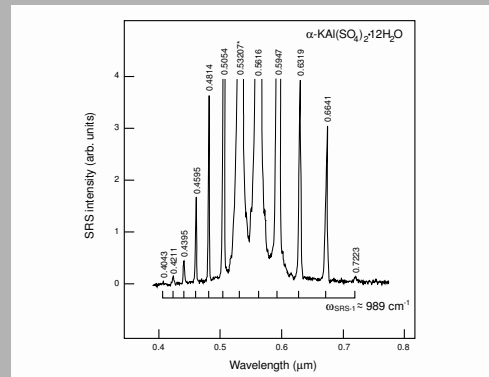


Abstract: Efficient high-order stimulated Raman scattering was excited under picosecond pumping in the visible and near-IR in four crystals of the α -alum family - novel isotropic $\chi^{(3)}$ -active crystalline materials. All observed Stokes and anti-Stokes lasing components were identified and attributed to the promoting $\approx 1000\text{ cm}^{-1}$ vibration modes of these crystals. Their one-micron steady-state first Stokes Raman gain coefficients were estimated as well.

Room-temperature steady-state SRS and RFWM spectra of $\alpha - \text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ recorded in excitation geometry as given in Table 3 under pumping in near-IR at $\lambda_{f2} = 0.53207\ \mu\text{m}$ wavelength.



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α -Alums: K,Rb,Tl and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ – a new family of $\chi^{(3)}$ -active crystalline materials for Raman laser converters with large frequency shifts

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1. Introduction

Cubic α -alums are one of the largest families of isostructural double salts, with a general formula $\alpha\text{-M}^+\text{X}^{3+}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$ (here M^+ is a monovalent cation like Na, K, Rb, Cs, Tl, NH_4 , NH_3CH_3 etc., and X^{3+} denotes a trivalent metal cation like Al, Ti, V, Cr, Fe, Ga etc, and R is S or Se) which can be grown in the form of big-size single crystals with perfect optical qual-

ity [1]. Their history is very long, they were classical subjects of many crystal studies since the beginning of the last century (see, e.g. [2, 3]). The recent discovery of an efficient stimulated Raman scattering (SRS) with a large frequency shift ($\approx 1000\text{ cm}^{-1}$) in inorganic crystals containing SO_4^{2-} -ionic units [4, 5] awakened our interest to α -alums. The preliminary SRS test conducted with $\alpha - \text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [6] showed that this class of materials could be attractive as $\chi^{(3)}$ -active crystals for Raman

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Crystal	Space group	Nonlinear property	Lasing Raman frequency shift (cm^{-1})	References
$\text{LiHCOO} \cdot \text{H}_2\text{O}$	$C_{2v}^9 - Pna2_1$	$\chi^{(3)}$	≈ 1372	[7]
C (diamond)	$O_h^7 - Fd3m$	$\chi^{(3)}$	≈ 1332	[8]
$\alpha\text{-NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	≈ 992	present work
NaN_3	$D_{3d}^6 - R\bar{3}2/c$	$\chi^{(3)}$	1068	[9]
$\text{Na}_2\text{SO}_4(\text{I})$	$D_{6h}^4 - P6_3/mmc$	$\chi^{(3)}$	≈ 987	[4, 5]
$\text{Na}_2\text{SO}_4(\text{V})$	$D_{2h}^{24} - Fddd$	$\chi^{(3)}$	≈ 992	[4, 5]
$\alpha\text{-KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	≈ 990	present work
CaCO_3	$D_{3d}^6 - R\bar{3}c$	$\chi^{(3)}$	≈ 1085	[10]
$\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	≈ 991	present work
$\text{Sr}(\text{NO}_3)_2$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	1057	[10]
$\text{Sr}_5(\text{PO}_4)_3\text{F}$	$C_{6h}^2 - P6_3/m$	$\chi^{(3)}$	950	[11]
$\text{Ba}(\text{NO}_3)_2$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	1049	[9]
$\beta' - \text{Gd}_2(\text{MoO}_4)_3$	$C_{2v}^8 - Pba2$	$\chi^{(2)} + \chi^{(3)}$	960	[12]
$\alpha\text{-TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	≈ 991	present work
$\text{Pb}(\text{NO}_3)_2$	$T_h^6 - Pa\bar{3}$	$\chi^{(3)}$	≈ 1045	[9]

Table 1 Selected inorganic nonlinear-laser crystals with SRS frequency shift more than 950 cm^{-1} .

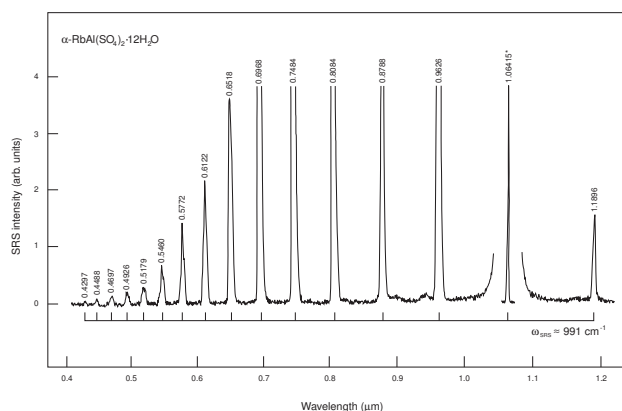


Figure 1 Room-temperature steady-state SRS and RFWM spectra of $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ recorded in excitation geometry as given in Table 3 under pumping in near-IR at $\lambda_{f1} = 1.06415 \mu\text{m}$ wavelength (pump line is asterisked). Wavelengths of all lines are given in μm and their intensity are shown without correction of spectral sensitivity of used analyzing CSMA system, Stokes and anti-Stokes lines related to SRS-active vibration mode of $\omega_{\text{SRS}} \approx 991 \text{ cm}^{-1}$ are indicated by the horizontal scale line.

laser converters. It is interesting that in this test a “potash- α -alum” crystal, bought in a Cairo bazaar shop of hygienic materials, was used. Over many years this wide-used crystalline materials were known also as a mordant in the dyeing industry. In present SRS investigations we studied four α -alums (K, Rb, Tl, and NH_4). All these single crystals manifested large Raman laser frequency shifts (see Table 1) and an efficient high-order Stokes and anti-Stokes generation. For comparison we placed in this table other

inorganic crystals known to us with SRS-active vibration modes (ω_{SRS}) more than 950 cm^{-1} .

2. Crystals preparation and some SRS experimental details

Relatively large K, Rb, Tl and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ α -alum single crystals ($\approx 5 \times \approx 5 \times \approx 5 \text{ cm}^3$) of sufficient good optical quality have been grown from aqueous solutions (controlled lowering of temperature between 320 and 300 K at a growth velocity of about 1 mm/day). The crystals are stable up to about 320 K in humid air (relative humidity larger than 40%). With the exceptions of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, which both are commercially available, we prepared the raw material by reacting an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$ and the corresponding M_2SO_4 in a stoichiometric proportion and subsequent evaporation at room temperature. For our stimulated and spontaneous scattering experiments oriented samples in the form of bars with active length 25–48 mm and 1-mm thick plates were fabricated. Their optical faces were polished plane-parallel but not anti-reflected coated. The crystallographic data and some known physical properties of these α -alums are listed in Table 2.

To study the single-pass SRS generation in our α -alum single crystals we used a home-made mode-locked $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ picosecond laser which can emit at two fundamental wavelengths $\lambda_{f1} = 1.06415 \mu\text{m}$ (with pulse duration $\tau_p \approx 110 \text{ ps}$) and $\lambda_{f2} = 0.53201 \mu\text{m}$ (SHG, $\tau_p \approx 80 \text{ ps}$). The spectral composition of the multiple SRS and Raman induced four-wave mixing (RFWM) generation components was measured with a spectrometric CSMA complex based on a grating monochromator and

Characteristics	M			
	K	Rb	Tl	NH ₄
Unit cell parameters (Å), a ₀	12.157	12.243	12.207	12.240
Formula units per cell	Z = 4			
Density (g·cm ⁻³), d _x	1.753	1.884	2.3215	1.6418
Site symmetry and coordination number (CN) of cations ²⁾	M ⁺ : S ₆ and CN = 6		Al ³⁺ : S ₆ and CN = 6 S ⁶⁺ : C ₃ and CN = 4	
Optical transmission (μm) ³⁾	≈0.19-1.43	≈0.19-1.43	≈0.22-1.43	≈1.9-1.43
Refractive index [13], n ⁴⁾	1.4562	1.4565	1.4973	1.4594
Piezo-optic constants (10 ⁻¹³ cm ² ·dyn ⁻¹) [13], q ₁₁	2.43	6.66	6.99	-0.55
q ₁₂	3.56	7.97	8.55	-1.22
q ₁₃	2.89	7.09	7.30	+0.58
q ₁₁ - q ₁₂	-4.23	-4.41 ⁵⁾	-4.20	-4.41
q ₁₁ - q ₁₃	-4.56	-4.99 ⁵⁾	-4.41	-5.94
q ₄₄	4.15	8.61 ⁵⁾	10.09	-1.09
Dielectric constants [14], ε ⁶⁾	6.364	6.051	7.512	6.391
Elastic stiffness (10 ¹⁰ Nm ⁻²) [1], c ₁₁	2.465	2.535	2.540	2.520
c ⁷⁾	2.610	2.628	2.648	2.615
c ₁₂	1.025	1.033	1.13	1.09
c ₄₄	0.865 ⁷⁾	0.844	0.814	0.811 ⁸⁾
Thermal expansion (10 ⁻⁶ ·K ⁻¹) [1], α	12.4	7.80	10.9	7.30
Thermoelastic constants (10 ⁻³ ·K ⁻¹) [1], T ₁₁	0.108	0.051	0.073	-0.23
T ⁷⁾	0.11	0.105	0.095	-0.206
T ₁₂	1.91	1.38	1.41	0.56
T ₄₄	-0.95	-0.60	-0.79	-0.69
Second order electroelastic components (10 ⁻¹⁰ NV ⁻²) [16]	9)	-	-	-
Quadratic electrostrictive coefficients (10 ⁻²⁰ m ² V ⁻²) [17], d ₁₁₁₁	0.63 (10)	-	-	-
d ₁₁₂₂	-0.15 ¹⁰⁾ (30)	-	-	-
d ₁₂₁₂	0.46 (1)	-	-	-
Frequency of SRS-active vibration modes (cm ⁻¹), ω _{SRS}	≈ 990	≈ 991	≈ 991	≈ 992
Linewidth of SRS-related peaks in spontaneous Raman scattering spectrum (cm ⁻¹), Δν _R	≈ 4.9 ¹¹⁾	≈ 4.1 ¹¹⁾	≈ 4.4	≈ 5.3
Phonon relaxation time (ps), T ₂	≈ 2.2	≈ 2.6	≈ 2.4	≈ 2
First Stokes steady-state Raman gain coefficient (cm·GW ⁻¹), g _{SSRS} ^{St1} ¹²⁾	≈ 2.7	≈ 2.7	≈ 2.6	≈ 2.5

¹⁾ Most data are given for ≈ 20 °C.

²⁾ All oxygen and hydrogen atoms occupy C₁-symmetry position.

³⁾ For ≈1-mm thickness plate.

⁴⁾ For the Na D-line.

λ(μm)	q ₁₁ - q ₁₂	q ₁₁ - q ₁₃	q ₄₄
0.481	-4.40	-5.05	-1.10
0.5461	-4.43	-5.12	-1.20
0.589	-4.41	-4.99	-1.22
0.686	-4.41	-5.08	-1.31

⁵⁾ Dispersion of piezooptic constants

⁶⁾ For f = 10 MHz.

⁷⁾ Along the direction [110].

⁸⁾ Pressure dependence of second-order elastic constants and inverse bulk compressibility, as well as temperature dependence of piezoelectric constants and inverse bulk compressibility for α-KAl(SO₄)₂·12H₂O and α-NH₄Al(SO₄)₂·12H₂O are given in [15].

⁹⁾ For α-KAl(SO₄)₂·12H₂O crystal they are:

z ₁₁₁ = -18(1)	z ₁₁₂ = -18(1)	z ₁₁₃ = -18(1)
z ₁₂₁ = -11(18)	z ₁₂₂ = -8(9)	z ₁₂₃ = -6(2)
z ₄₄₁ = -5.7(11)	z ₄₄₂ = -7.6(13)	z ₄₄₃ = -7.3(12)
z ₄₅₆ = -4.9(6)	z ₁₄₄ = -3.8(17)	z ₁₅₅ = +8(6)
z ₁₆₆ = -11(6)		

¹⁰⁾ Arithmetic mean of d₁₁₂₂ and d₂₂₁₁.

¹¹⁾ See Fig. 4.

¹²⁾ For pumping at λ_{f1} = 1.06415 μm. The first Stokes lasing wavelength are given in Table 3.

Table 2 Some physical properties of χ⁽³⁾-active cubic (space group T_h⁶ - Pa $\bar{3}$, No.205) crystals of α-alums MAI(SO₄)₂·12H₂O (here M = K, Rb, Tl, and NH₄)¹⁾.

λ_f (μm)	Stokes and anti-Stokes generation				Line	Attribution ⁴⁾
	Wavelength (μm) ¹⁾					
	K ²⁾ ($l_R \approx 40$)	Rb ²⁾ ($l_R \approx 44$)	Tl ²⁾ ($l_R \approx 25$)	NH ₄ ³⁾ ($l_R \approx 48$)		
1.06415	0.4300	0.4297	-	-	AS _{t14}	$\omega_{f1} + 14\omega_{\text{SRS}}$
	0.4491	0.4488	-	0.4486	AS _{t13}	$\omega_{f1} + 13\omega_{\text{SRS}}$
	0.4700	0.4697	-	0.4695	AS _{t12}	$\omega_{f1} + 12\omega_{\text{SRS}}$
	0.4929	0.4926	-	0.4924	AS _{t11}	$\omega_{f1} + 11\omega_{\text{SRS}}$
	0.5182	0.5179	-	0.5177	AS _{t10}	$\omega_{f1} + 10\omega_{\text{SRS}}$
	0.5462	0.5460	0.5460	0.5457	AS _{t9}	$\omega_{f1} + 9\omega_{\text{SRS}}$
	0.5775	0.5772	0.5772	0.5769	AS _{t8}	$\omega_{f1} + 8\omega_{\text{SRS}}$
	0.6125	0.6122	0.6122	0.6120	AS _{t7}	$\omega_{f1} + 7\omega_{\text{SRS}}$
	0.6520	0.6518	0.6518	0.6515	AS _{t6}	$\omega_{f1} + 6\omega_{\text{SRS}}$
	0.6970	0.6968	0.6968	0.6965	AS _{t5}	$\omega_{f1} + 5\omega_{\text{SRS}}$
	0.7487	0.7484	0.7484	0.7482	AS _{t4}	$\omega_{f1} + 4\omega_{\text{SRS}}$
	0.8086	0.8084	0.8084	0.8082	AS _{t3}	$\omega_{f1} + 3\omega_{\text{SRS}}$
	0.8790	0.8788	0.8788	0.8786	AS _{t2}	$\omega_{f1} + 2\omega_{\text{SRS}}$
	0.9627	0.9626	0.9626	0.9625	AS _{t1}	$\omega_{f1} + \omega_{\text{SRS}}$
	1.1895	1.1896	1.1896	1.1898	St ₁	$\omega_{f1} - \omega_{\text{SRS}}$
0.53207	0.4043	-	-	-	AS _{t6}	$\omega_{f2} + 6\omega_{\text{SRS}}$
	0.4211	-	-	-	AS _{t5}	$\omega_{f2} + 5\omega_{\text{SRS}}$
	0.4395	0.4394	-	-	AS _{t4}	$\omega_{f2} + 4\omega_{\text{SRS}}$
	0.4595	0.4594	0.4594	0.4593	AS _{t3}	$\omega_{f2} + 3\omega_{\text{SRS}}$
	0.4814	0.4813	0.4813	0.4813	AS _{t2}	$\omega_{f2} + 2\omega_{\text{SRS}}$
	0.5054	0.5054	0.5054	0.5054	AS _{t1}	$\omega_{f2} + \omega_{\text{SRS}}$
	0.5616	0.5617	0.5617	0.5617	St ₁	$\omega_{f2} - \omega_{\text{SRS}}$
	0.5947	0.5948	0.5948	0.5949	St ₂	$\omega_{f2} - 2\omega_{\text{SRS}}$
	0.6319	0.6320	0.6320	0.6322	St ₃	$\omega_{f2} - 3\omega_{\text{SRS}}$
	0.6741	0.6743	-	0.6745	St ₄	$\omega_{f2} - 4\omega_{\text{SRS}}$
	0.7223	-	-	-	St ₅	$\omega_{f2} - 5\omega_{\text{SRS}}$

¹⁾ Measurement accuracy is $\pm 0.0003 \mu\text{m}$.

²⁾ Pumping and registration along [110] direction and polarization both emissions perpendicular [110].

³⁾ Pumping and registration along $[1\bar{1}\bar{2}]$ direction and polarization both emissions perpendicular $[11\bar{2}]$.

⁴⁾ The ω_{SRS} values for the studied α -alum crystals are given in Table 2.

Table 3 Spectral composition of room-temperature Stokes and anti-Stokes Raman generation in cubic K-, Rb-, Tl-, and NH_4 - α -alum crystals under picosecond $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ -laser excitation at $\lambda_{f1} = 1.06415 \mu\text{m}$ and $\lambda_{f2} = 0.53207 \mu\text{m}$ (SHG) wavelengths. In brackets are given (in mm) length of crystals along which SRS was excited.

a Si-CCD sensor matrix with maximum sensitivity in the red spectral area. Due to similarity we present here only two Stokes and anti-Stokes lasing spectra (Figs. 1 and 2) together with the results of identification of all registered lines with SRS-active vibration modes of our α -alum crystals. Full lists of registered $\chi^{(3)}$ -lasing wavelengths are given in Table 3.

We also experimentally estimated the steady-state of our SRS regime (because, $\tau_p \gg T_2 = 1/(\pi\Delta\nu_R)^{-1}$, here T_2 and $\Delta\nu_R$ are the phonon relaxation time and the linewidth of the corresponding ‘‘SRS-active’’ lines in spontaneous Raman scattering spectra, respectively) and the Raman gain coefficient for the first Stokes generation ($g_{\text{SSR}}^{St_1}$) of the studied α -alums under one micron excitation. In this comparative experiment we measured the ‘‘threshold’’ pumping (I_{thr}) for the known $\chi^{(3)}$ -active monoclinic α -KY(WO₄)₂ tungstate as a reference crystal. From these data and the well-known approximate expression for the gain increment (see, e.g. [5]) $g_{\text{SSR}}^{St_1} I_{thr} l_R \approx 30$, we calculated the

$g_{\text{SSR}}^{St_1}$ coefficients. The results of these estimations are listed in Table 2.

3. Spontaneous Raman scattering and SRS-active vibration modes

Four 48-atomic $\text{MAI}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ molecules are present in the unit cell of the centrosymmetric $T_h^6 - Pa\bar{3}$ cubic structure of α -alums (see Fig. 3 and Table 2). The univalent and trivalent cations occupy sites of S_6 symmetry, while the SO_4^{2-} units occupy sites of C_3 symmetry. One of the interesting features of the crystal structure of the α -alums is the presence of disordered sulfate groups. The sulphur atoms of the tetrahedral SO_4^{2-} units are located on threefold symmetry axes. Two crystallographically different sites are found for the 12 water molecules, which are located in general sites. The Al^{3+} ion is coordinated by six H_2O molecules forming a quite regular octahedron

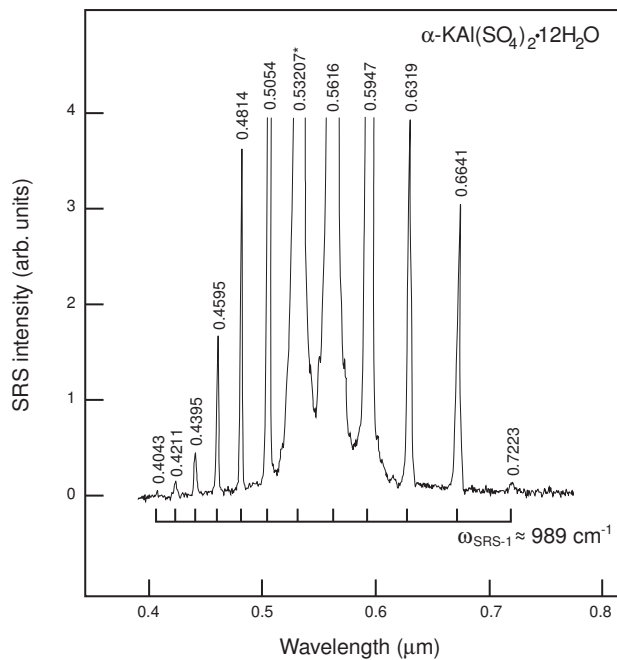


Figure 2 Room-temperature steady-state SRS and RFWM spectra of α -KAl(SO₄)₂·12H₂O recorded in excitation geometry as given in Table 3 under pumping in near-IR at $\lambda_{f2} = 0.53207 \mu\text{m}$ wavelength. Notations as in Fig. 1.

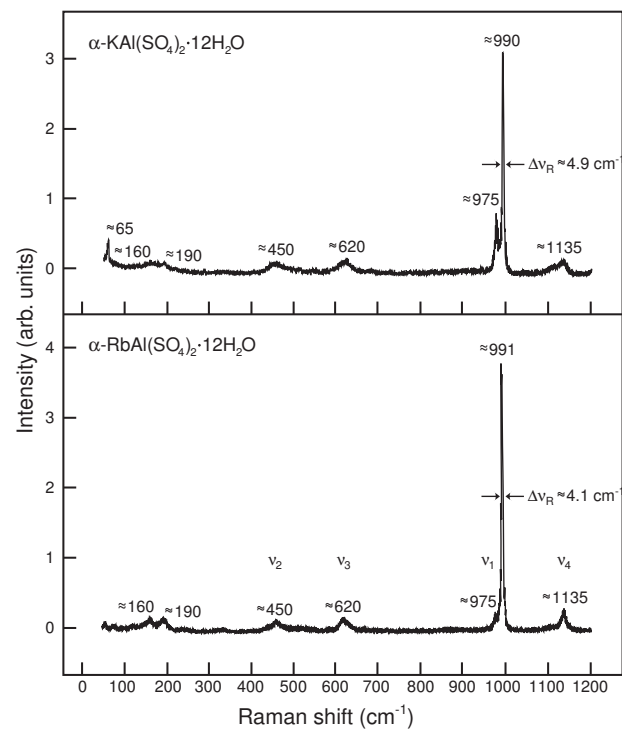


Figure 4 Room-temperature polarized spontaneous Raman scattering spectra of α -RbAl(SO₄)₂·12H₂O and α -KAl(SO₄)₂·12H₂O single crystals registered in excitation geometry as given in Table 3. Raman shifted intensive lines are given in cm⁻¹. The arrows at zero correspond to pumping 0.488 μm wavelength of Ar-ion laser.

T_h -mode species	Vibration modes ¹⁾					Activity	
	U	T	T'	R	i	Raman	IR
A _g	26	0	7	7	12	$x^2 + y^2 + z^2$	-
E _g	26	0	7	7	12	$z^2, x^2 - y^2$	-
F _g	66	0	21	21	24	xy, xz, yz	-
A _u	28	0	9	7	12	-	-
E _u	28	0	9	7	12	-	-
F _u	72	1	26	21	24	-	x, y, z

¹⁾ U, T, T', R, and i denote unit-cell modes, number of acoustic, translatory and rotatory lattice, and internal modes, respectively.

Table 4 Factor group analysis of the cubic α -RbAl(SO₄)₂·12H₂O crystal ($T_h^6 - Pa\bar{3}$).

(see Fig. 3). The other six water molecules around the M⁺ cations are arranged in a trigonal antiprism. As may be inferred from our spectroscopic Raman measurements with K, Rb, Tl, and NH₄ α -alums, their vibration properties are very similar. Therefore, we briefly consider some results of the analysis only for α -RbAl(SO₄)₂·12H₂O. The group theoretical analysis (see, e.g. [18]) predicts overall degrees of freedom for its vibrations $3NZ = 576$, which with symmetry degeneracy are reduced to 277 modes (Table 4).

The unit-cell optical modes for α -RbAl(SO₄)₂·12H₂O and other α -alum crystals are described by the irreducible representations (at $\mathbf{k} = 0$) as

$$\Gamma_{\text{optic}} = 26A_g + 26E_g + 66F_g + 28A_u + 28E_u + 71F_u.$$

They could be further subdivided into:

$$\Gamma_{\text{Rb+Al}} = 2A_u + 2E_u + 5F_u,$$

$$\Gamma_{\text{sulf}} = A_g + E_g + 3F_g + A_u + E_u + 3F_u,$$

and

$$\Gamma_{\text{aq}} = 6A_g + 6E_g + 18F_g + 6A_u + 18F_u$$

translatory lattice modes of the Rb⁺+Al³⁺ cations, SO₄²⁻ and H₂O units, respectively;

$$\Gamma_{\text{R(sulf)}} = A_g + E_g + 3F_g + A_u + E_u + 3F_u$$

and

$$\Gamma_{\text{R(aq)}} = 6A_g + 6E_g + 18F_g + 6A_u + 6E_u + 18F_u$$

rotatory lattice modes of the SO₄²⁻ and H₂O units, respectively; and

$$\Gamma_{\text{i(sulf)}} = 6A_g + 6E_g + 6F_g + 6A_u + 6E_u + 6F_u$$

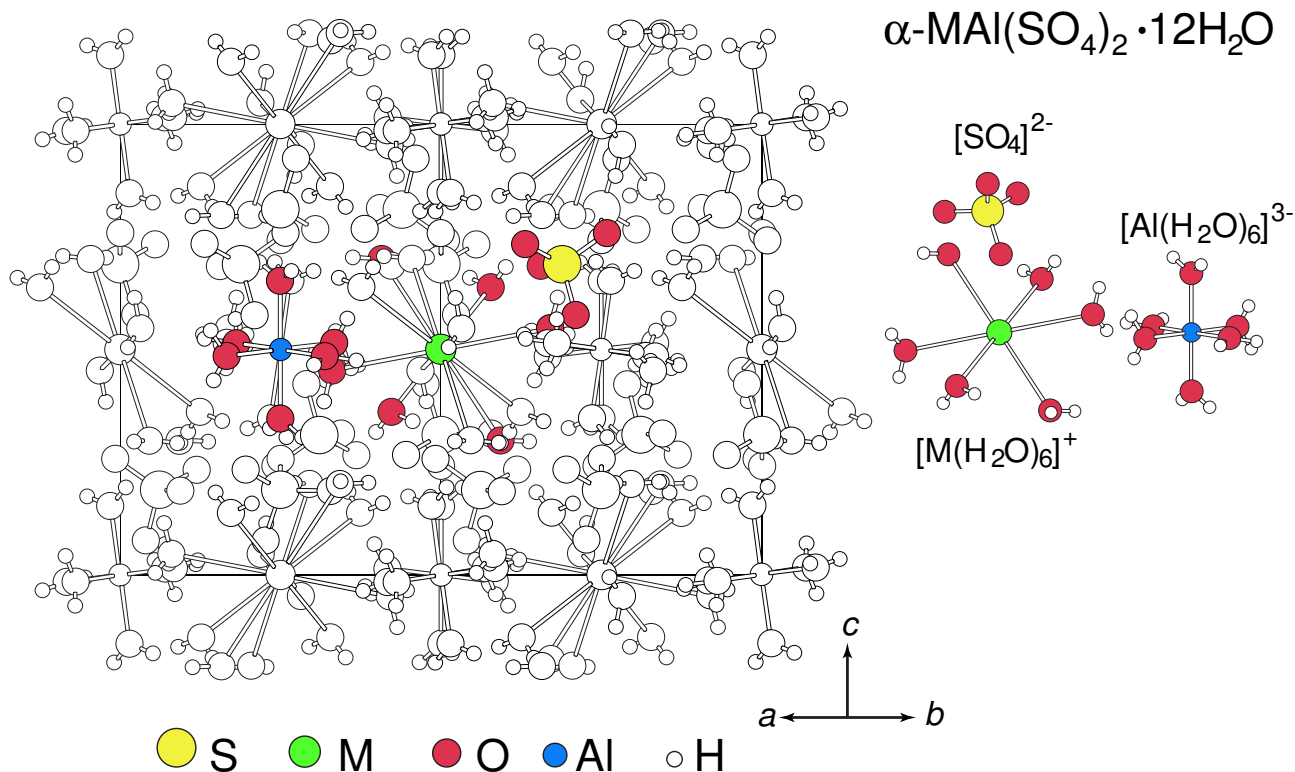


Figure 3 (online color at www.interscience.wiley.com) Projection of the unit cell of $\alpha\text{-MAI}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystals (here M = K, Rb, Tl and NH_4) along [110] with indication (by color) one formula unit and three fragments of its structure.

and

$$\Gamma_{i(\text{aq})} = 6A_g + 6E_g + 18F_g + 6A_u + 6E_u + 18F_u$$

internal modes of the SO_4^{2-} and H_2O units, correspondingly. The vibrations of the SO_4^{2-} tetrahedra are characterized by four normal modes: stretching ν_1 and ν_3 and bending ν_2 and ν_4 . Since there are eight SO_4^{2-} anions in the unit cell the number of respective bands in the Raman and IR spectra are as follows:

$$\nu_1 - 4A_g + 4A_u, \quad \nu_2 - 4E_g + 4E_u,$$

$$\nu_3 - A_g + E_g + 3F_g + A_u + E_u + 3F_u,$$

and

$$\nu_4 - A_g + E_g + 3F_g + A_u + E_u + 3F_u.$$

The vibration bands corresponding to these modes are observed in the Raman and IR spectra at the following frequencies (see Fig. 4 and corresponding spectra in [19]): at $990\text{-}1035\text{ cm}^{-1}$ for ν_1 , at $450\text{-}480\text{ cm}^{-1}$ for ν_2 , at $1100\text{-}1135\text{ cm}^{-1}$ for ν_3 , and at $615\text{-}655\text{ cm}^{-1}$ for ν_4 . The unit cell of α -alums studied comprises 48 water molecules. Each H_2O molecule has three vibration degrees of freedom characterized by two stretching modes ν_1 and ν_3 , as well as one bending mode ν_2 . Respective Raman and IR

bands of this unit appear at wavelengths [19]: $1600\text{-}1735\text{ cm}^{-1}$ for ν_2 and $2900\text{-}3420\text{ cm}^{-1}$ for ν_1 and ν_3 . The lattice modes of $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ crystal appear in the regions at $\approx 500\text{-cm}^{-1}$ (translatory H_2O modes), at ≈ 80 and $\approx 190\text{ cm}^{-1}$ (for the translatory and rotatory SO_4^{2-} modes, respectively).

The comparison of the energy spacing between observed Stokes and anti-Stokes generation components (see Figs 1 and 2 and Table 3) and Raman shifted strong narrowing peaks in spontaneous Raman scattering spectra (see Fig.4) indicated conclusively that $\approx 990\text{ cm}^{-1}$ vibrations are the promoting phonons in the SRS lasing of $\alpha\text{-RbAl}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and the other three studied α -alums. The above given analyses have also shown that these promoting $\omega_{\text{SRS}} \approx 990\text{ cm}^{-1}$ modes are totally symmetric optical vibrations $A_g(\nu_1)$ of the SO_4^{2-} tetrahedral units of the studied crystals.

4. Conclusion

Efficient $\chi^{(3)}$ -lasing in four T_h^6 -cubic α -alums ($\alpha\text{-MAI}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, here M=K, Rb, Tl, and NH_4), have been observed. The discovered nonlinear properties were effectively manifested by the generation of multiple high-order Stokes and anti-Stokes sidebands in the visible and

near-IR regions, which were also identified and attributed to the SRS-active fully symmetric vibration $A_g(\nu_1)$ -modes of tetrahedral SO_4^{2-} groups of the studied novel solid-state nonlinear-laser materials. The steady-state Raman gain coefficient for their first Stokes $\approx 1.2\text{-}\mu\text{m}$ generation was estimated as well. We classify the α -alum crystals as promising media for up- and down-Raman laser-frequency converters.

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