Sub-THz emission by IR-active shear phonons in $KRe(MoO_4)_2$

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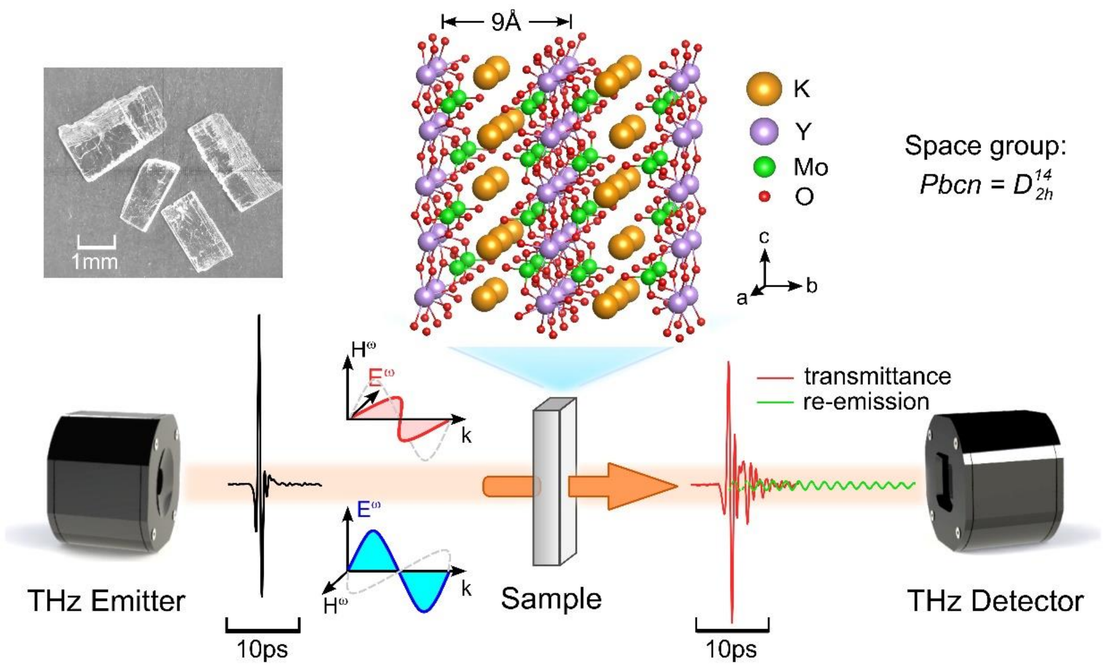
Introduction.

Double molybdates $MRe(MoO_4)_2$ (where M^+ is an alkali metal ion and Re^{3+} is a rare-earth or Y^{3+} ion) are optically transparent dielectric compounds with layered orthorhombic structure *Pbcn* (D^{14}_{2h}) formed by $[M]^+$ and $[Re(MoO_4)_2]^-$ layers. Layered structure of $MRe(MoO_4)_2$ leads to infrared-active shear lattice vibrations with energies below 3.7 meV, which corresponds to the frequencies below 900 GHz [1] where solid state monochromatic radiation sources are rare.
Terahertz time-domain spectroscopy (THz-TDS) is a widely used method to study optical properties of materials based on electromagnetic transients optoelectronically generated by ultrashort, usually femtosecond, laser pulses. Using THz-TDS setup the re-emission of the sub-THz monochromatic radiation by optical phonons in $MRe(MoO_4)_2$ single-crystals (where Re – Y, Dy, Er, Tm, Lu) pumped by a broadband THz excitation pulse has been studied.
In this report we demonstrate the experimental observation of such re-emission in $KRe(MoO_4)_2$ on the example of $KY(MoO_4)_2$.

Sample and experimental technique.



Compound	Cell parameters, Å		m/M	E^{ω}IIa	E^{ω}IIc
				S_1 (THz)	S_2 (THz)
$KY(MoO_4)_2$	a=5.07, b=18.23, c=7.95	[2]	0.096	0.570	0.860
$KDy(MoO_4)_2$	a=5.0776, b=18.1214, c=7.9428	[3]	0.081	0.529	0.785
$KEr(MoO_4)_2$	a=5.0602, b=18.1965, c=7.8920	[3]	0.080	0.510	0.779
$KTm(MoO_4)_2$	a=5.047, b=18.28, c=7.892	[2]	0.080	0.505	0.775
$KLu(MoO_4)_2$	a=5.0292, b=18.2519, c=7.8174	[3]	0.079	0.495	0.764

Fig.2 Sketch of the THz-TDS experiment (in the left). Black trace shows THz waveform of incident pulse. Red and green curves show the components of the beam passed the sample. At the top of the figure shown the photo of the $KY(MoO_4)_2$ single-crystals and its crystallographic structure.
The table shows unit cell parameters of the $KRe(MoO_4)_2$ series, mass ratio of the $[K]^+$ and $[Re(MoO_4)_2]^-$ layers (m and M respectively) and phonon frequencies, obtained in this work using THz-TDS method, for two polarizations of incident light.

Experimental results.

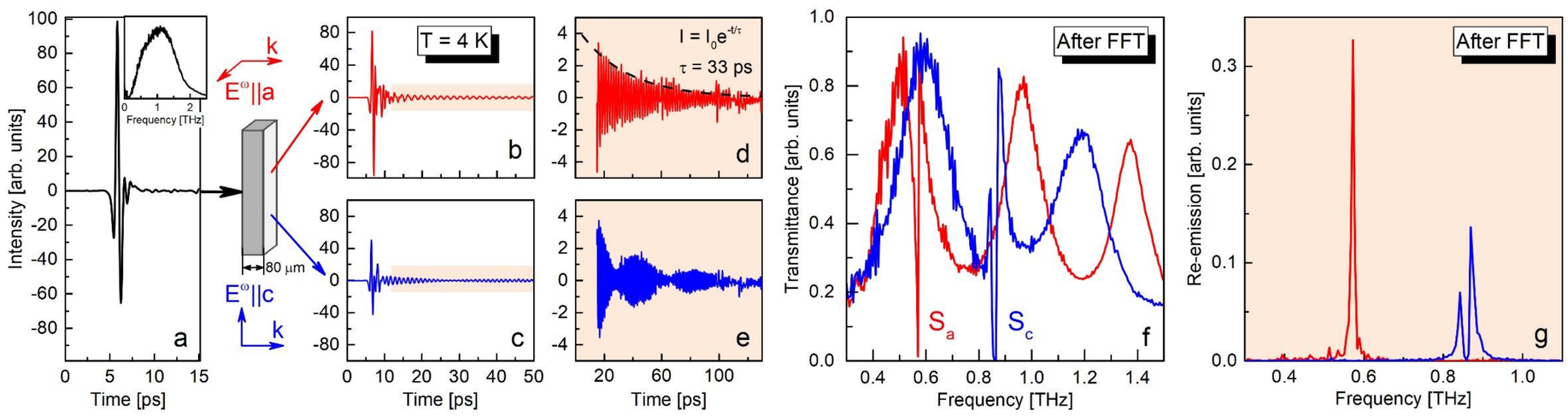


Fig.2. (a) The electric field waveform of the THz pulse before the sample. (b, c) Waveforms of the THz pulse passed the sample (for the case of 80 μm thick sample plate and T = 4 K). (d, e) Zoomed part of the waveforms in the time range 10 – 130 ps (re-emission tail). (f) The transmittance spectra (after FFT post-processing) for $KY(MoO_4)_2$. The periodic fringes in the spectra are caused by multiple reflections within the plane-parallel sample (Fabry-Perot type modulation). Sa and Sc – phonon modes with energies 568 and 860 GHz respectively. (g) The FFT of the waveforms shown in the Fig.1 (d, e). The spectra obtained at polarizations E^{ω}IIa and E^{ω}IIc denoted by red and blue colors respectively.

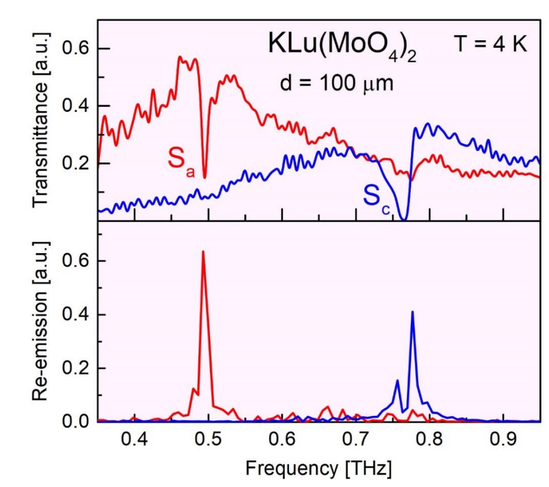


Fig.3. The transmittance and re-emission spectra (after FFT post-processing) for $KLu(MoO_4)_2$.
The same results obtained for all other compounds of this series.

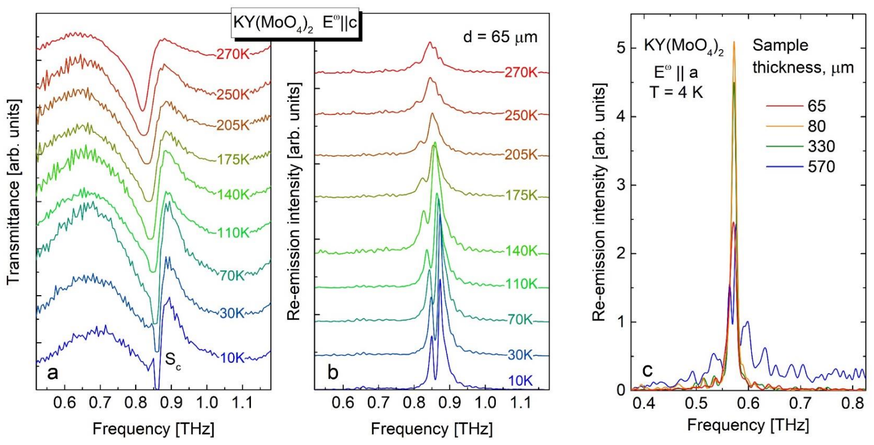


Fig.4. Temperature evolution of the transmittance (a) and re-emission (b) spectra obtained with 65 μm thick sample for E^{ω}IIc. The re-emission spectra were obtained in the same manner as in Fig. 2e. (c) The re-emission spectra for E^{ω}IIa vs. sample thickness.

[1] S. Poperezhai et al., *J. Phys.: Condens. Matter*, 29, 2017, 095402
[2] S. Chong et al., *Acta Cryst.* E76, 1871-1875 (2020).
[3] Spitsin V. I. and Trunov V. K. Dokl. Akad. Nauk SSSR 185, (1969) 854.

Conclusions.

- Experimentally observed the re-emission of monochromatic sub-THz electromagnetic radiation by IR-active optical phonons in dielectric material $KY(MoO_4)_2$ at frequencies 568 and 860 GHz for polarizations E^{ω}IIa and E^{ω}IIc consequently.
  - The revealed re-emission has large decay time (> 30ps), which is exceptionally long for the oscillators with frequencies below 1 THz.
  - The splitting of the re-emission peak for polarization E^{ω}IIc caused by strong intensity of S_c phonon and prohibits the propagation of resonance frequency in material, while the lattice vibrations on frequency near by the resonance efficiently re-emit the electromagnetic radiation. Such effect confirmed by temperature evolution of the spectra when increasing the temperature leads to the disappearing of the phonon saturation (Fig.4a,b).
  - The sample thickness 80 μm (for E^{ω}IIa) provided the maximal magnitude of the re-emission (Fig.4c).
- The re-emission by low-frequency IR-active phonons has been found for all compounds of studied series of double molybdates. Significantly large decay time, high intensity of re-emitted radiation and chemical stability of these materials make these compounds attractive for a variety of electrooptical applications.