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Infrared spectroscopic properties of low-phonon lanthanide-doped KLuS₂ crystals

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Abstract
KLuS₂ single crystal samples undoped and doped with a low (5%) or high (38%) concentration of trivalent thulium or ytterbium ions were synthesized in the form of thin hexagonal plates. The low phonon energy (∼ 220 cm⁻¹) was confirmed using Raman spectroscopy. Samples were studied also by using optical absorption and emission as well as electron paramagnetic resonance spectroscopy and the observed spectral features are discussed. In particular, the 5% Yb doped samples demonstrate homogeneous dopant distribution inside the material over the lutetium sites. No other signals either from potassium site or the exchange coupled ions were detected. For infrared transitions the luminescence kinetic was determined. Significantly broad infrared emission bands (at 1.4, 1.8 and 2.3 μm for Tm³⁺, 1 μm for Yb³⁺) and long decay times (e.g. 0.4 ms from ³H₄ and 19 ms from ⁴F₄ levels of Tm³⁺, 1.4 ms from ⁵F₅/₂ level of Yb³⁺) make those materials perspective for future laser development.

Keywords:
Ternary sulfides, low-phonon laser materials, rare-earth doping, infrared lasers, golden ratio doping

1. Introduction

Rare-earth (RE) doped low-phonon matrices are important materials for construction of direct mid-infrared laser sources. [1, 2] The phonon energy influences the overall infrared transparency range, which is important for laser operation, the rate of multiphonon relaxation of laser transitions, and also the phonon-assisted energy transfer processes, which can depopulate (or populate) laser levels. [3, 4, 5, 6, 7]

The lowest phonon energies (Eph ∼ 140 – 200 cm⁻¹) in crystalline laser matrices have been reported for alkali-lead halides MPb₂X₄ (M = Rb, K; X = Cl, Br). [8, 9, 10, 11] Laser emission was successfully demonstrated with KPB₅Cl₅ doped by Pr⁴⁺, Nd³⁺, Dy³⁺, or Er³⁺ ions. [12, 13, 14, 15, 16] Important and well-developed low-phonon laser host materials are also chalcogenide crystals (Eph ∼ 200 – 350 cm⁻¹), like Cr²⁺ and Fe²⁺ doped II-VI semiconductor compounds, [17, 18, 19, 20, 21, 22, 23] or thiogallates CaGa₂S₄ or PbGa₂S₄, for which the laser action was obtained under Dy³⁺ doping. [12, 24, 25, 26] Great advantage of all these materials is low or zero hygroscopicity, but they usually suffer from low RE-dopant acceptance, which limits the doping concentration to several percent or less. [10]

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The family of ternary alkali RE sulfides with general formula \(\text{ALnS}_2\) (\(A = K, Rb, Ln = \text{RE elements, usually La, Gd, Lu, or Y}\)) belongs among the new promising low-phonon chalcogenide materials.\(^{[27, 28, 29]}\) The trivalent lanthanide cation site in \(\text{ALnS}_2\) structure has a suitable size to accommodate \(\text{RE}^{3+}\) ions, which allows a very high homogenous RE-doping without segregation or charge compensation problems.\(^{[29]}\) About 40 % larger distance between trivalent Ln-Ln cations in comparison with Ga-Ga distance in thiogallates also allows higher \(\text{RE}^{3+}\) doping levels before concentration quenching occurs.\(^{[27, 30]}\) This new family of RE-doped ternary sulfides shows prospective applications for X-ray and white LED phosphors and their spectroscopy in UV and VIS spectral range was studied in detail.\(^{[27, 28, 29, 31, 32, 33]}\) It was also confirmed that KLu\(_2\)S\(_2\) is a moisture-resistant, long-term and high-temperature stable material.

All ternary sulfides \(\text{ALnS}_2\) with \(A = K\) or Rb adopt the \(\alpha\)-NaFe\(_2\)O\(_4\)-type rhombohedral structure (space group \(R\overline{3}m\)) with alternating layers composed of edge-sharing \(\text{AS}_6\) and \(\text{LnS}_6\) octahedra. Generally, the structure is described in hexagonal setting as \(A^+\) ions occupying the \(3a\) Wyckoff sites (0 0 0), the \(\text{Ln}^{3+}\) ions residing at the \(3b\) sites (0 0 \(\frac{1}{2}\)), while sulfur anions can be found at the \(6c\) (0 0 \(z\)) sites.\(^{[30, 34]}\) The sulfur coordinate \(z\) determines the trigonal distortion of the \(\text{AS}_6\) and \(\text{LnS}_6\) octahedra, which are slightly elongated or shortened along the \(c\) axis, respectively, to better accommodate the larger alkali metals (K, Rb) and the smaller rare-earth elements. Thus, the ideal \(O_h\) symmetry reduces to a \(D_{6d}\) local symmetry in both types of octahedra. Recently, new structural determinations of \(\text{ALnS}_2\) \(^{[30, 34, 35]}\) were published that indicate a systematic error in former structure determinations. The fractional \(z(S^{2-})\) coordinate in alkali RE sulfides is a good parameter for simple monitoring of structural trends (see Fig. 6 in \([30, \text{Fig. 2 in } [35]](\text{Fig. 9 in } [34]))\). However, the lattice parameters are also extremely important structural parameters, with \(a\) being closely associated mainly with the size of rare-earth ions \((a \sim 3.8 - 4.3 \text{ Å})\) and \(c\) corresponding to the size of \(A^+\) \((c \sim 21.7 - 21.9 \text{ Å for K}, 22.7 - 22.9 \text{ Å for Rb})\).\(^{[30]}\) For Pr-doped RbGaS\(_2\) a linear increase in lattice parameter \(a\) was observed\(^{[36]}\) in accordance with the Vegard’s rule, indicating the presence of true solid solution and suitability of the host for incorporation of large amounts of lanthanide dopants.

In this paper, we focused on the study of Yb and Tm-doped KLu\(_2\)S\(_2\) ternary sulfides from the future infrared laser development point of view.

2. Material and methods

2.1. Sample preparation

The pure KLu\(_2\)S\(_2\) or doped KLu\(_{0.95}\)Tm\(_{0.05}\)S\(_2\), KLu\(_{0.62}\)Tm\(_{0.38}\)S\(_2\), KLu\(_{0.995}\)Yb\(_{0.005}\)S\(_2\), KLu\(_{0.95}\)Yb\(_{0.05}\)S\(_2\), KLu\(_{0.62}\)Yb\(_{0.38}\)S\(_2\) crystalline samples were synthesized according to the scheme given by \([27]\). The starting materials were 4N K\(_2\)CO\(_3\), 5N Lu\(_2\)O\(_3\), 3N Tm\(_2\)O\(_3\) (for KLu\(_{0.95}\)Tm\(_{0.05}\)S\(_2\)), 4N Tm\(_2\)O\(_3\) (for KLu\(_{0.62}\)Tm\(_{0.38}\)S\(_2\)) and 4N Yb\(_2\)O\(_3\) for KLu\(_{0.995}\)Yb\(_{0.005}\)S\(_2\), KLu\(_{0.95}\)Yb\(_{0.05}\)S\(_2\) and KLu\(_{0.62}\)Yb\(_{0.38}\)S\(_2\). The gases used during the synthesis were 5N Ar and 2N5 H\(_2\)S. The chemical reactions were carried out in a corundum boat (2N7 Al\(_2\)O\(_3\)). The tube was placed in an electric resistance furnace equipped with heating/cooling-rate regulation. Either Ar or H\(_2\)S gas was allowed to flow into the reaction tube. The gases were taken directly from pressurized cylinders using a three-way stopcock to switch between them. A mixture of the K\(_2\)CO\(_3\) with Tm\(_2\)O\(_3\) or Yb\(_2\)O\(_3\)-doped Lu\(_2\)O\(_3\) in the molar ratio 80 : 1 was used as the starting material. Tm or Yb doping was carried out by the simple mixing and grinding of Lu\(_2\)O\(_3\) and Tm\(_2\)O\(_3\) or Yb\(_2\)O\(_3\). For example, for the preparation of KLu\(_{0.62}\)Tm\(_{0.38}\)S\(_2\) 0.080 mol \((11.0564 \text{ g})\) K\(_2\)CO\(_3\), 0.000618 mol \((0.2459 \text{ g})\) Lu\(_2\)O\(_3\) and 0.000382 mol \((0.1474 \text{ g})\) Tm\(_2\)O\(_3\) was used. The molar quantities of Lu\(_2\)O\(_3\) and Tm\(_2\)O\(_3\) (or Yb\(_2\)O\(_3\)) were in the golden ratio in KLu\(_{0.62}\)Tm\(_{0.38}\)S\(_2\) or KLu\(_{0.62}\)Yb\(_{0.38}\)S\(_2\).

Prior to the reaction itself, the reagents (K\(_2\)CO\(_3\) and Lu\(_2\)O\(_3\); Tm\(_2\)O\(_3\) or Lu\(_2\)O\(_3\); Yb\(_2\)O\(_3\)) were homogenized in an agate mortar. The mixture was placed in a corundum boat (2N7 Al\(_2\)O\(_3\)) and inserted into the corundum tube (inner volume about 1 dm\(^3\)). The mixture was then heated to 1323 K using the electric resistance furnace (heating rate 10 K/min) under a flow of Ar (30 dm\(^3\)/hour). After the desired temperature had been reached, the reaction mixture was annealed for 2 hours under a flow of H\(_2\)S (15 dm\(^3\)/hour). Following annealing, the system was cooled under a flow of Ar (0.5 K/min, 0.3 dm\(^3\)/hour). Upon reaching room temperature, the corundum boat was removed from the tube furnace and the reaction products were purified by suspension and decantation, three times with distilled water and once with acetone. K\(_2\)S was removed by water, while
pure or doped KLbS$_2$ samples were left behind. The resulting products consisted of $\sim 40\,\mu$m thick platelets with imperfect hexagonal morphology sized up to $3 \times 4$ mm. Photograph of the KLb$_{0.95}$Tm$_{0.05}$S$_2$ is presented in Fig. 1.

2.2. Methods of characterization

The structural characterization and phase purity assessment was performed by X-ray powder diffraction (XRD) using Rigaku MiniFlex 600 diffractometer equipped with Ni-filtered Cu X-ray tube and NaI:Tl scintillation detector. The diffraction patterns were recorded between 10$^\circ$ and 80$^\circ$ 2θ on pure or powdered samples, which were deposited onto glass holders. The diffraction patterns were then compared with the relevant ICDD PDF-2 database records and the lattice parameters were calculated from diffraction peak positions. EPR spectra were measured in the X-band (9.4 GHz) on a commercial Bruker X/Q-band E580 FT/CW ELEXSYS spectrometer at the 25 K in an Oxford Instruments ESR900 continuous flow cryostat. All simulations have been done in the Easyspin toolbox 5.1.12 program [37]. Raman spectra were measured by InVia Reflex micro-spectrometer from Renishaw with 442 nm He-Cd excitation laser and collected for 60 s by 50× objective. The laser mean power was 30 mW in order to eliminate sample heating. The absorption spectra of the samples were measured in the range from 200 to 2050 nm using a Shimadzu UV-3600 spectrophotometer (sampling interval 0.5 nm and resolution 5 nm). The fluorescence was excited by a pulsed laser diode emitting at $\lambda_{ex} = 793$ nm in the case of Tm-doped samples or 970 nm for Yb-doped samples (excitation pulse width 2 ms, repetition rate 10 Hz). The emission spectra of Tm-doped KLbS$_2$ in the vicinity of 800 nm were measured by fiber spectrometer StellarNet BlueWave NIR 50 (Si detector, sampling interval 0.5 nm). The same spectrometer in combination with fiber spectrometer Ocean Optics NIR 512 (InGaAs detector, sampling interval 1.75 nm) was used to record the emission of Yb-doped KLbS$_2$ samples in spectral region 900-1500 nm. Due to a strong decrease of Si-detector sensitivity, its response was calibrated in respect to the InGaAs detector using tungsten lamp and the data from both detectors were joined at 1025 nm. To separate the overlapping excitation and emission spectra, the BlueWave NIR 50 spectrometer acquisition was triggered 0.5 ms after the end of excitation pulse. The emission spectra of Tm-doped KLbS$_2$ in near infrared region from 1100 up to 2500 nm were measured by stepper-motor driven Oriel monochromator 77250 (grating no. 77301, sampling 2 nm, resolution 10 nm) with the PbS detector (PDA300G, Thorlabs). GaAs or Ge filters were used to suppress the rest of excitation radiation and to eliminate the higher diffraction orders. The fluorescence intensity decay measurement around the wavelength of 1 µm was performed using the Si-PIN photodiode (HP 5082-4220, Hewlett Packard) and long-pass filter (FEL1000, Thorlabs). The time development of fluorescence decay for radiation wavelength in the range from 1200 to 1600 nm was observed by an InGaAs photodiode (FGA10, Thorlabs). To separate the desired spectral range, the above mentioned monochromator was used in combination with appropriate long-pass or band-pass filter. The
fluorescence intensity decay measurement around wavelength 1.8 μm was performed using a GaInAsSb-PIN photoreceptor (model PD36-05-TEC, IBSG Co.) together with Ge and band-pass filter (FB1750-500, Thorlabs). The photodiode signal was recorded and digitalized via oscilloscope (TDS3052B, 500 MHz, 5 GS/s, Tektronix). For all measurements, the response time was better than 20 μs. All Raman, absorption and emission spectra together with fluorescence decay were measured at temperature $T = 300$ K.

3. Results and Discussion

3.1. Composition of KLuS$_2$

The doped KLuS$_2$ samples were obtained in the form of transparent thin platelets with similar morphology as in pure KLuS$_2$ [31]; therefore, mainly the highly-doped samples (38% Yb or Tm) were analyzed by XRD to determine phase purity of the material. Diffraction patterns of pristine platelets, oriented parallel to the surface of the glass sample holder, presents only the (0 0 1) lines consistent with KLuS$_2$. No other diffraction lines of KLuS$_2$ were observed, indicating perfect orientation of the crystals in the platelets, their normal vector coinciding with the c axis. After powdering of the samples in a ceramic mortar, strong preferred orientation in ⟨001⟩ direction remained, but weak diffraction lines corresponding to other directions of rhombohedral KLuS$_2$ appeared as well. No other diffraction lines or peak splitting were detected, confirming that the crystals were a single pure phase. Based on the diffraction lines positions, lattice parameters $a = 3.953(4)$ Å, $c = 21.862(3)$ Å and $a = 3.965(6)$ Å, $c = 21.865(6)$ Å were determined for KLu$_{0.62}$Yb$_{0.38}$S$_2$ and KLu$_{0.62}$Tm$_{0.38}$S$_2$, respectively. The lattice parameter $c$ is fully consistent with K-based AlS$_2$ ternary sulfides, whereas $a$ is somewhat increased compared to that of pure KLuS$_2$ ($a = 3.9490(4)$ Å, $c = 21.871(3)$ Å [36]) due to the incorporation of slightly larger Yb$^{3+}$ or Tm$^{3+}$ ions, respectively. Based on the reported lattice parameters of KYb$_2$ ($a = 3.9615(2)$ Å, $c = 21.810(3)$ Å [34]) and KTM$_2$ ($a = 3.9761(5)$ Å, $c = 21.841(3)$ Å [34]) and the assumption of Vegard’s rule, the values of $a$ for the KLu$_{0.62}$Yb$_{0.38}$S$_2$ and KLu$_{0.62}$Tm$_{0.38}$S$_2$ samples should be approximately 3.954 Å and 3.959 Å, respectively. The measured values are within statistical uncertainty (imposed by the weak intensity of non-c-oriented peaks), indicating that the lanthanide ions are present in the crystals as a solid solution. However, the statistical uncertainties are large compared to the rather small difference between terminal compounds of the solid solution. Longer or more thorough grinding may improve the statistics, but at the risk of structural changes or increased microstructural strain.

3.2. EPR spectroscopy of KLuS$_2$:Yb

To have an insight into the local structure, energy levels and paramagnetic properties of the Yb$^{3+}$ (4f$^{13}$ outer shell) inside the KLuS$_2$ host electron paramagnetic resonance measurements were carried out. The EPR spectrum measured at the B⊥c external magnetic field orientation is shown in Fig. 2(I).

![EPR spectrum](image)

Figure 2: I – EPR spectra, the experimental and the calculated one, with the hyperfine structures from the $^{171,173}$Yb indicated by grates. II – experimental angular dependence (dots) of the Yb$^{3+}$ resonances in the B⊥c → B∥c rotational plane fitted by the calculated one.
The spectrum has been fitted by the calculated one using the following spin-Hamiltonian:

\[
\hat{H} = g \beta_s \vec{S}_z B + A \begin{pmatrix} 171 \text{Yb} \end{pmatrix} \vec{S}_z \hat{I}_z + A \begin{pmatrix} 173 \text{Yb} \end{pmatrix} \vec{S}_z \hat{I}_s + A \begin{pmatrix} 173 \text{Yb} \end{pmatrix} \vec{S}_s \hat{I}_s
\]  

(1)

where \( g, \beta_s, B \) are the \( g \) factor, Bohr magneton, and magnetic field, respectively; \( A \begin{pmatrix} 171, 173 \text{Yb} \end{pmatrix} \) are the \( 171 \text{Yb} \) (nuclear spin \( I = 1/2 \), abundance \( \sim 14\% \)) and \( 173 \text{Yb} \) (nuclear spin \( I = 5/2 \), abundance \( \sim 16\% \)) hyperfine (HF) constants; \( \vec{S}_s, \hat{I}_s \) are the effective electron and nuclear \( z \)-component spin operators. The \( g = 3.2333 \) and \( A \begin{pmatrix} 171 \text{Yb} \end{pmatrix} = 2666.4 \text{MHz}, A \begin{pmatrix} 173 \text{Yb} \end{pmatrix} = 700 \text{MHz} \).  

Experimental angular dependence of the spectrum center of gravity resonance magnetic field was plotted in Fig.2(II) in the B|c \rightarrow B|c rotational plane along with the calculated fitting curve. For the fitting the first term in spin-Hamiltonian in Eq.1 was used. The \( g \) tensor main values as well as the principal axes frame orientation were determined by Euler angles were determined: \( g_\parallel = 3.2333 \pm 0.0003 \) and \( g_\perp = 0.27 \pm 0.05 \), \( \alpha = \beta = 0^\circ, \beta = -6^\circ \). The \(-6^\circ \) deviation from \(0^\circ \) in the \( \beta \) angle is most probably due to very small sample dimensions and inhomogeneous sample thickness (flake shape). This has caused slight \( c \) axis deviation from the external magnetic field direction due to the creation of stable tensions inside the sample bulk. Along with this the large error in the \( g \) value determination is due to very steep angular dependence when approaching the \( c \) axis during the sample rotation. In the \( [0001] \) rotational plane the spectrum exhibits almost isotropic feature and thus it has not been taken into consideration.

Since only one EPR spectrum was measured (Fig. 2(I)) and \( \text{Yb}^{3+} \) and \( \text{Lu}^{3+} \) crystal radii are very similar, 1.008 Å and 1.001 Å [38], respectively, the \( \text{Yb}^{3+} \) ions were supposed to occupy only lutetium sites in the \( \text{KLuS}_2 \) host. No signs of the doublets of resonance lines which might originate from the \( \text{Yb}^{3+} - \text{Yb}^{3+} \) exchange coupling (dimers) were observed in the EPR spectra unless these coupled ions are too far from one another so the interaction between them is of the order of the resonance linewidth (\( \sim 20 \) G, Fig. 2(I)). The 20 G linewidth is, most probably, the result of dipolar broadening [39, 40]. This corroborates homogeneous distribution of the ytterbium ions inside the material without clustering.

The lowest \( \text{Yb}^{3+} \) energy level due to spin orbit coupling is \( ^2F_{7/2} \) [39, 40]. The local crystal field of trigonal symmetry, for example, in [41] it was supposed to be \( D_{3d} \) for the \( \text{Eu}^{3+} \), will split it into four Kramers doublets \( |J, M_J\rangle: [7/2, \pm 7/2], [7/2, \pm 5/2], [7/2, \pm 3/2] \) and \( [7/2, \pm 1/2] \). Calculations done similarly to that reported for \( \text{Ce}^{3+} \) [39, 40] show that the doublet results in \( g_\parallel = 4.57 \) and \( g_\perp = 1.14 \). Other doublets are responsible for much higher \( g \) factors. Therefore, one may conclude comparing these values with the ones obtained experimentally that the first order of the crystal field theory or even in the second could not be reached. This leads to conclusion that the symmetry is lower allowing mixing of the states which differ in \( M_J \) by \( 3 \) [39]. The symmetry should allow high order terms to a Hamiltonian. It can be \( C_{3v} \), a subgroup of the \( D_{3d} \). By trying simple calculations in the first order with the lowest doublet composed under this requirement: \( \cos \theta |7/2, \pm 1/2\rangle \pm \sin \theta |7/2, \mp 5/2\rangle \) [39] it was impossible to find \( \theta \) satisfying experimental \( g \) factor values, however, if the \( g_\perp = 3.2333 \) held on, the lowest \( g_\perp = 0.27 \) could be reached with \( \theta \sim 14^\circ \), which is still almost three times larger than the \( g_\perp = 0.27 \) experimental value. Therefore, in the second order, the mixing of the triply split excited \( ^2F_{7/2} \) state to the ground \( \cos \theta |7/2, \pm 1/2\rangle \pm \sin \theta |7/2, \mp 5/2\rangle \) is expected. This is well described for the \( \text{Ce}^{3+} \) in double lanthanide nitrates [43]. Our experimental data do not allow to carry out quantitative analysis of this problem.

3.3. Raman spectroscopy of \( \text{KLuS}_2 \)

Pure \( \text{KLuS}_2 \) and \( \text{KLu}_{0.62} \text{Tm}_{0.38} \text{S}_2 \) samples were characterized by Raman spectroscopy; resulting spectra are depicted in Fig. 3 in the energy range of 95 – 550 cm\(^{-1} \). From the results it follows that the substitution of a significant part of lutetium ions by thulium ions with similar mass had no significant influence on Raman spectrum and both samples give similar spectral features: a strong band at 221 cm\(^{-1} \) and weak bands peaking around 145 and 287 cm\(^{-1} \). The vibrational origin of the measured bands has been discussed in literature [44]. The most prominent band at 221 cm\(^{-1} \) (10 cm\(^{-1} \) FWHM) and the second one peaking at 287 cm\(^{-1} \) could be assigned to the Raman active modes \( E_g \) and \( A_{1g} \) of point group \( D_{3d} \), respectively.
As it was shown by Rademaker [9], the highest observed energy peak position can be a first approximation for effective phonon energy $E_{ph}$ of host crystalline matrices. For KLmS$_2$ it was estimated to be $E_{ph} \sim 220\,\text{cm}^{-1}$, which is comparable to other low-phonon materials like ZnSe ($E_{ph} \sim 250\,\text{cm}^{-1}$) or KB$_2$Cl$_5$ ($E_{ph} \sim 200\,\text{cm}^{-1}$). This reduces the multiphonon interactions and should minimize the non-radiative decay, which could permit efficient radiative transitions at new wavelengths - both in mid-infrared and visible region.

![Graph showing Raman spectra of pure KLmS$_2$ and KLm$_{0.62}$Tm$_{0.38}$S$_2$ samples.](image)

Figure 3: The Raman spectra of pure KLmS$_2$ and KLm$_{0.62}$Tm$_{0.38}$S$_2$ samples.

![Graph showing absorption spectra of KLm$_{0.62}$Tm$_{0.38}$S$_2$ sample.](image)

Figure 4: The absorption spectra of KLm$_{0.62}$Tm$_{0.38}$S$_2$ sample.

### 3.4. Absorption spectra of Tm- and Yb-doped KLmS$_2$ samples

The measured absorption spectra of KLm$_{0.62}$Tm$_{0.38}$S$_2$ and KLm$_{0.62}$Yb$_{0.38}$S$_2$ samples are plotted in Fig. 4 and in Fig. 5, respectively. The form of investigated samples, especially the small thickness ($\sim 40\,\mu\text{m}$), caused that the absorption modulation was low and measured spectra were noisy even for highly doped samples. At the same time, for both Tm$^{3+}$ and Yb$^{3+}$ ions, the low strength of forbidden 4f-4f transition makes the measurements even more complicated. In spite of that, the presence of Tm$^{3+}$ and Yb$^{3+}$ ions in
both samples is well manifested by their characteristic absorption lines. The non-zero background in visible part of absorption spectra could be explained by an uncorrected Fresnel losses or scattering on the samples. The strong and sharp absorption of Tm$^{3+}$ at 1220 nm in KLus$_2$ is remarkable, which is probably caused by the Tm$^{3+}$ ion $^3\!H_6 \rightarrow ^3\!H_4$ magnetic dipole transitions forced by the crystal field. This line is about one magnitude stronger than other lines, which could be interesting for applications in which interaction with the magnetic component of light takes place [45]. On the contrary, the mid-infrared absorption line corresponding to the $^3\!H_6 \rightarrow ^3\!F_4$ transition of the Tm$^{3+}$ ion was not observed in the absorption spectrum probably due to its low intensity. Because the corresponding emission was detected well, as will be discussed later, this transition is probably very broad and absorption modulation was lost in the noise. The absorption corresponding to the $^2\!F_{7/2} \rightarrow ^2\!F_{5/2}$ transition of Yb$^{3+}$ ion ranging from 900 up to 1040 nm is also exceptionally broad (see Fig. 5).
3.5. Fluorescence spectra of Tm- and Yb-doped KLuS$_2$ samples

The fluorescence spectra of tested Tm- and Yb-doped KLuS$_2$ samples with low and high doping were recorded at the broadest available range; the results are shown in Figures 6, 7, and 8.

![Figure 7: The fluorescence spectra of Tm-doped KLuS$_2$ samples. The inset, containing the energy level diagram of Tm$^{3+}$, serve to denominate the observed emission bands.](image)

![Figure 8: The fluorescence spectra of Yb-doped KLuS$_2$ samples.](image)

In the case of Tm-doped KLuS$_2$, the $^3$H$_4$ manifold was excited and five emission lines having a maxima around 0.81, 1.22, 1.45, 1.82, and 2.32 μm were recorded and identified (see Fig. 6 and Fig. 7). The spectra for $^3$H$_4 \rightarrow ^3$H$_5$ transition corresponding to ~800 nm emission are shown for both Tm-doping concentrations in Fig. 6. In both cases the spectrum is ~40 nm wide (FWHM) with four well resolved peaks. The small depletion of 795 nm peak in case of highly doped KLuS$_2$:Tm could be caused by fluorescence reabsorption, thus more precisely specifying the corresponding absorption peak position (see Fig. 4). Spectra for the other four fluorescence lines are shown in Fig. 7. There is also no significant difference between both samples varying in the Tm-doping. The first fluorescence line with maximum at 1220 nm corresponds to the $^3$H$_5 \rightarrow ^3$H$_6$ transition. This line is remarkably intense confirming the low phonon energy of KLuS$_2$ – for materials with higher phonon energy the population of the $^3$H$_4$ level is depleted due to a non-radiative transition to
the $^3F_5$ level and 1.2 $\mu$m line in fluorescence spectrum is not present. The next emission band, peaking at 1435 nm, corresponds to the $^3H_4 \rightarrow ^3F_4$ transition. The line in the vicinity of 2.3 $\mu$m originates from the same level and corresponds to the $^3H_4 \rightarrow ^3H_6$ transition. Both these transitions, together with above mentioned $^3H_4 \rightarrow ^3H_2$ transition, are available for laser action and their presence in the emission spectrum proves that processes depopulating the $^3H_4$ level, like cross-relaxation, are limited in KLuS$_2$:Tm even for very high Tm-doping concentration. The probability of such processes could be reduced for two reasons: the low phonon energy in KLuS$_2$ may not be high enough to compensate for the energy difference between the $^3H_4 \rightarrow ^3F_4$ and $^3H_6 \rightarrow ^3F_4$ transitions; cross-relaxation is strongly sensitive to the donor-acceptor separation and the shortest possible distance between adjacent Tm-positions is relatively high.[27, 30] It should be noted that radiative transition from the $^3H_5$ to the $^3F_4$ level, which should correspond to emission around 3.7 $\mu$m, was not detected. The strongest line ($\sim 220$ nm FWHM), peaking at 1.82 $\mu$m, corresponds to the $^3F_4 \rightarrow ^3H_6$ transition, which is commonly used for Tm-laser emission at 2 $\mu$m spectral region. The smooth and slowly decreasing long-wavelength tail of this line is promising for broad-band tuning and short pulse laser generation.

Due to the simple structure of Yb$^{3+}$ ion levels, the fluorescence spectra of KLuS:Yb contain only one line corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition – see Fig. 8. This fluorescence band, having a maximum at 1013 nm, looks very compact and the observed differences between samples doped by 0.05, 5, and 38% Yb is probably caused mainly by fluorescence reabsorption. For samples containing 5 and 38% of Yb, this emission line has an exceptionally long and smooth tail lasting up to 1.2 $\mu$m; if the lasing will be reached, broad-band tuneability and short pulse generation could be expected.

3.6. Fluorescence decay of Tm- and Yb-doped KLuS$_2$ samples

The fluorescence decay curves related to the observed Tm$^{3+}$ and Yb$^{3+}$ ions transitions were recorded and are shown in Figures 9, 10, and 11 for Tm-doped KLuS$_2$, and in Fig. 12 for Yb-doped KLuS$_2$ samples, respectively. To estimate the corresponding fluorescence decay time(s) $\tau_1$ ($\tau_2$), double-exponential model ($I(t) = A\exp(-t/\tau_1) + (1-A)\exp(-t/\tau_2)$) was used to fit the recorded fluorescence decay curve $I(t)$. The obtained results are presented together with the specific decay curve.

![Figure 9: The fluorescence decay curve of Tm-doped KLuS$_2$ samples ($^3H_4$ level).](image)

In the case of KLuS$_2$:Tm(5%), the fluorescence decay was well modelled as a single-exponential with well-defined fluorescence decay time. The exceptionally long decay time for fluorescence starting from the $^3H_4$ level ($\sim 430$ $\mu$s) suggests that the effect of phonon-assisted cross-relaxation process ($^3H_4 \rightarrow ^3F_4$, $^3H_6 \rightarrow ^3F_4$) is negligible for this Tm-doping level.[6] This fact could be interesting for future 2.3 $\mu$m laser construction. The lifetime of the potential 2$\mu$m upper laser level ($^3F_4$) is also remarkably long, reaching 19 ms. The
relatively long decay time 1.6 ms of unquenched 1.22 µm emission originating from the $^3\text{H}_5$ level is also worth mentioning. Stronger influence of some kind of ion-ion interaction resulting in fluorescence quenching and double-exponential decay was observed for the highly Tm-doped KLuS$_2$ sample only. Here, the mentioned cross-relaxation process depopulating the $^3\text{H}_4$ level is probably much stronger and the measured decay time is close to 30 µs. The decay time for the $^3\text{F}_4$ level was strongly quenched as well, but the fast decay component was still reasonably long (2.7 ms). Because the slow component of the $^3\text{H}_5$ level decay has a similar value ($\sim 2.5$ ms), one can consider that there is some coupling between the $^3\text{H}_5$ and $^3\text{F}_4$ levels or that some new optical center was formed in the highly doped KLuS$_2$:Tm, but in fact the origin of double-exponential decay is not clear.

In the case of the KLuS$_2$:Yb, only the fluorescence from the very-low doped sample (0.05 % of Yb) had a single-exponential character with the decay time 1.72 ms. For both higher doped KLuS$_2$:Yb samples, the observed fluorescence decay curves had double-exponential character and concentration quenching is evident (see Fig. 12). In the case of low doping (5 % of Yb), the fast component ($\tau_1 = 0.29$ ms) represented $\sim 1/3$ of
the fluorescence signal and the stronger slow component has a reasonably long decay time ($\tau_2 = 1.44$ ms). In the case of highly Yb-doped KLuS$_2$ (38% of Yb), the concentration quenching had even stronger influence on the fluorescence decay and the decay times dropped significantly ($\tau_1 = 0.08$ ms, $\tau_2 = 0.40$ ms).

4. Conclusions

In this study, we present KLuS$_2$ single crystal as a new promising low-phonon, non-hygroscopic laser host for high-concentration lanthanide doping. In our case, Tm$^{3+}$- and Yb$^{3+}$-ion doped KLuS$_2$ samples were investigated. The transparent hexagonal-shaped platelets were shown to be pure rhombohedral phase consistent with KLuS$_2$ even in highly-doped samples, with small increase in lattice parameter $a$ due to a larger size of dopants compared to Lu$^{3+}$. Based on the EPR data one may infer that the Yb$^{3+}$ ions distribution inside the material (KLuS$_2$:5% Yb) is homogeneous since no signals which might come from coupled Yb$^{3+}$-Yb$^{3+}$ ions (dimers) were observed in EPR spectra unless they are masked by the single ion spectrum. The ions are not creating clusters. As long as only one sort of signal from the Yb$^{3+}$ was observed and comparing ionic radii of the Yb$^{3+}$ and Lu$^{3+}$ in the same octahedral coordination, the activator was assumed to occupy the Lu$^{3+}$ sites, exclusively. Using Raman spectroscopy we found that the KLuS$_2$ phonon energy $E_{ph} \sim 220$ cm$^{-1}$. We tested this material under low and high Tm- and Yb-doping. Even though the used preparation method allowed to synthesize the crystals only in the form of ~40 µm thick hexagonal plates with ~2 mm cross-section, the absorption was high enough to be measured using standard spectrophotometer, which allows us to identified positions of suitable excitation bands. Using laser diode, we were able to excite infrared emission. For particular transitions the corresponding emission spectra and luminescence decay time were measured. An exceptionally broad emission line of the KLuS$_2$:Yb was observed, spanning the wavelength range from 0.95 µm to 1.20 µm with the decay time ~ 1.4 ms for the reasonable level of doping (5% of Yb). In the case of the KLuS$_2$:Tm samples, five infrared emission lines with the maxima around 0.81, 1.22, 1.45, 1.82, and 2.32 µm were detected. The emission lines at 0.81, 1.43 and 2.4 µm originating from the $^3H_4$ level of the Tm$^{3+}$ ion, usually quenched in well-established Tm-doped materials, were remarkably strong. In the case of the KLuS$_2$:Tm (5%) a single-exponential decay curve with the time constant ~ 430 µs was recorded, which proves that Tm-Tm cross-relaxation process depopulating the $^3H_4$ level is significantly reduced in low-doped KLuS$_2$:Tm and transitions starting from this level could be available for lasing. We can conclude that if future crystal growth process allows to obtain larger and thicker crystals, KLuS$_2$:Tm and KLuS$_2$:Yb will be interesting materials for broad-band infrared laser construction.
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References


