



Laser performance and spectroscopic properties of Nd³⁺-doped LiKYF₅ and LiKGdF₅ crystals

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Abstract

Spectroscopic and laser-pumped laser studies of Nd³⁺-doped LiKYF₅ and LiKGdF₅ are reported. The optical absorption and photoluminescence spectra are strongly polarised, the sense of polarisation of the ⁴I_{9/2} → ²F_{5/2}, ²H_{9/2} absorption near 800 nm being opposite to that of the ⁴F_{3/2} → ⁴I_{11/2} laser emission near 1.05 μm. At ambient temperature (~ 300 K) the luminescence decay times of excited Nd³⁺ ions are in both hosts of order 480–490 μs, and strongly concentration dependent above 2 at.% Nd³⁺. Efficient laser action (~ 25%) is observed under excitation with a long pulse Cr³⁺: LiSAF laser tuned to 797 nm, with low threshold energies of ca. 125 μJ.

There is much current interest in Nd³⁺-doped crystals as gain media in diode-pumped solid state lasers with emphasis on low threshold energies and high slope efficiencies in the laser active components of the ⁴F_{3/2} → ⁴F_J crystal field fluorescence channels of the Nd³⁺-doped ion. Laser action of Nd³⁺-doped calcium fluoroapatite (FAP) has received much attention in view of the ⁴F_{3/2} → ⁴I_{11/2} luminescence which predominantly feeds into a single crystal field transition [1]. This contrasts most other Nd³⁺-doped crystals for which a rich spectrum of crystal field transitions is observed. Several members of the NaREGeO₄ family of compounds, where RE = Y, Gd or Lu, also display crystal field selective spectral characteristics [2]. Lacking appropriate crystal field calculations it is not possible to predict which hosts will exhibit such polarisation sensitive, crystal field selective, luminescence spectra, although it is notable that in FAP and NaREGeO₄ the Nd³⁺ ion substitutes at very low symmetry sites. Low symmetry sites for the RE³⁺ ions are of primary importance for low threshold, high efficiency laser action.

Anisotropic fluoride crystals are also favourable hosts for rare earth ions and their associated optical properties include polarised optical spectra, transparency over large ranges of wavelength and low optical nonlinearities. Nevertheless, until recently, single inter-Stark luminescence transitions have not been observed in fluoride host crystals except in BaY₂F₈ [3], where the Y³⁺ site also has C₁ symmetry. Recently, Kaminskii et al. [4] reported the hydrothermal growth of unoriented single crystals of Nd³⁺:LiKYF₅ with dimensions of ca. 30 mm³. Also reported was flash-lamp and diode-pumped laser action at 1.05 μm [5,6], and comprehensive studies of the spectroscopic properties of the Nd³⁺-doped hosts [7]. The present paper reports the top seeded solution growth (TSSG) of large single crystals of Nd³⁺-doped LiKYF₅ and LiKGdF₅, and further aspects of the polarised absorption and luminescence spectra and low-threshold laser action.

LiKYF₅ is monoclinic with space group P2₁/c. The Y³⁺ site is eight-fold coordinated to F⁻ ions and has C₁ symmetry. The unit cell parameters of LiKYF₅ are *a* = 0.62925 nm, *b* = 1.1747 nm and *c* = 0.64669 nm. In common with other monoclinic crystals, LiKYF₅ cleaves readily in the (010)-plane. The isomorph LiKGdF₅ is expected to be isostructural with LiKYF₅. Both isomorphs

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melt incongruently and cannot be pulled from the melt by the Czochralski technique. Nevertheless, large single crystals of both compounds have been grown by TSSG, in which two spectroscopically distinct, and yet very similar Y^{3+} sites, have been reported for the Nd^{3+} substituent [8]. Only a single site is reported in hydrothermally grown crystals. The differences between the structures of crystals grown by TSSG and hydrothermally are discussed by Weidner et al. [9].

The distribution coefficient for Nd^{3+} in $LiKYF_5$ is estimated to be ca. 0.7; a slightly larger value (0.8) is expected in $LiKGdF_5$ in view of the better size match between Nd^{3+} and Gd^{3+} ions [10]. In such crystals as YLF and YAG, the Nd^{3+} concentration is limited by crystalline quality to ca. 2 at.%; much larger Nd^{3+} concentrations (up to ca. 5 at.%) may be substituted in $LiKYF_5$ and $LiKGdF_5$ without compromising crystal quality. For the present study $Nd^{3+}:LiKYF_5$ crystals were grown from melts containing 0.2, 3.3 and 5.0 at.% and $Nd^{3+}:LiKGdF_5$ crystals from melts containing 1, 2 and 5 at.% Nd^{3+} .

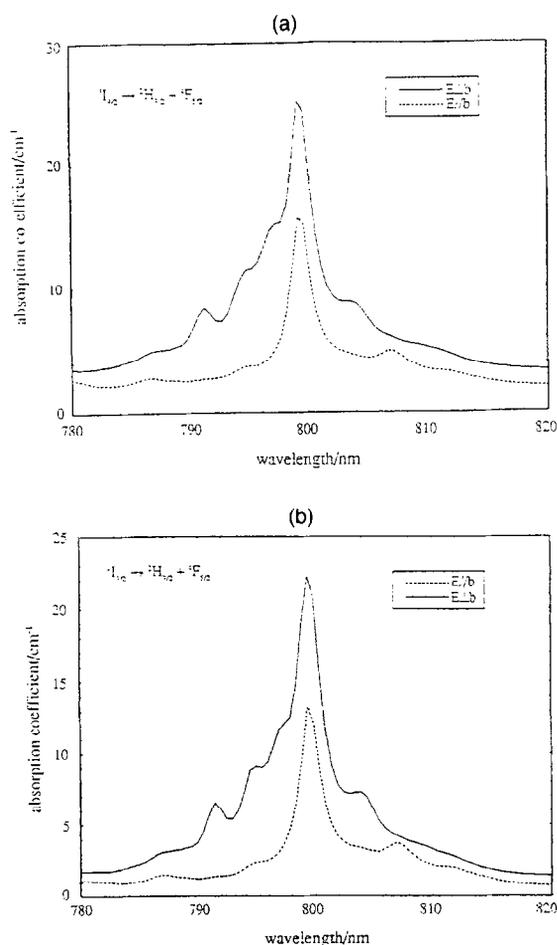


Fig. 1. Room temperature polarised absorption spectra of 5% Nd^{3+} -doped $LiKYF_5$ (a) and $LiKGdF_5$ (b).

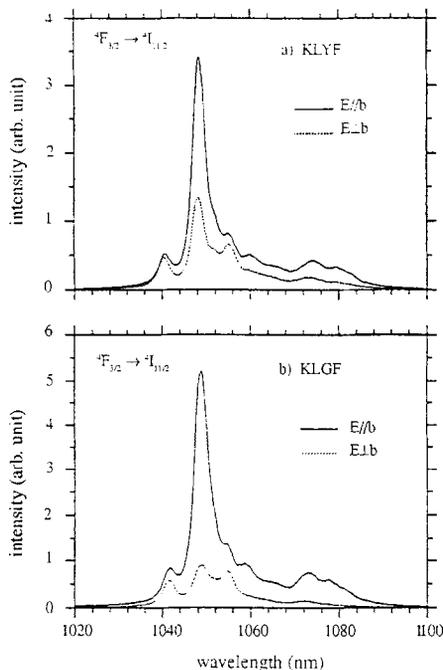


Fig. 2. Room temperature polarised emission spectra in the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ channel of 5% Nd^{3+} in $LiKYF_5$ (a) and $LiKGdF_5$ (b).

Optical absorption spectra were measured using a Perkin-Elmer 220 spectro-photometer. Photoluminescence was excited using a GaAs laser diode which operates at 810 nm and pumps into the ${}^4F_{5/2}$ and ${}^2H_{9/2}$ manifolds. The luminescence signal was detected by a Si multichannel detector, through a $\frac{1}{4}$ -metre monochromator with a resolution of 1 nm. A Q-switched Cr:LiSAF laser with pulse widths of 80 ns and tuned to 797 nm was used to measure luminescence decay patterns. The decaying luminescence signal was detected by a cooled S1 photomultiplier tube after passing through the $\frac{1}{4}$ -metre monochromator. The electrical signal from the phototube was recorded using a Tektronix 244–300 MHz digital oscilloscope.

The polarised optical absorption spectra of $LiKYF_5$ and $LiKGdF_5$ samples containing 5 at.% Nd^{3+} in the melt are shown in Fig. 1, corresponding to the ${}^4I_{9/2} \rightarrow {}^4F_{9/2}$, ${}^2H_{9/2}$ spectra appropriate for pumping with 810 nm laser diodes. The absorption spectrum is clearly strongest when the electric vector, E , of the radiation is perpendicular to the b -axis of the crystal. The position, relative intensities and polarisations of the inter-Stark absorption components of the two samples are very similar. Higher resolution optical absorption studies at lower temperatures have shown that in crystals grown by TSSG there are two, almost identical, sites for Nd^{3+} in both $LiKYF_5$ and $LiKGdF_5$ [9,10]. The two sites are not distinguishable in optical absorption and luminescence measurements at 300 K as a consequence of phonon-induced homogeneous broadening

processes. Homogeneous broadening leading to overlap of the different crystal field components of ${}^4I_{9/2} \rightarrow {}^2H_{9/2}$, ${}^4F_{5/2}$ transitions is useful in tests of diode pumped laser action since the excitation beam may then be more conveniently matched to pump transitions.

The polarised ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ photoluminescence spectra of the 5 at.% Nd^{3+} doped crystals of $LiKYF_5$ and $LiKGdF_5$ crystals measured at room temperature are illustrated in Fig. 2 with the E vector of the radiation parallel (a) and perpendicular (b) to the b -axis of the crystal. For both samples the luminescence is strongly polarised parallel to the b -axis, this sense of polarisation being orthogonal to the absorption spectra shown in Fig. 1. The predominant inter-Stark transition in Fig. 2 occurs at $1.048 \mu m$ and with E -vector of the radiation parallel to b -axis, the luminescence is channelled into this single intense crystal field transition. In other, higher symmetry crystals (e.g. YAG and YLF), the luminescence transition tends to be more evenly distributed in all crystal field transitions. The photoluminescence spectra for E perpendicular to the b -axis is much weaker, with no single crystal field transition dominant.

The structure of the crystal field spectra of $Nd^{3+}:LiKYF_5$ and $KGdLiF_5$ revealed by the absorption and luminescence spectra shown in Figs. 1 and 2 are almost identical, indicating the extreme similarity of crystal structures of $LiKYF_5$ and $LiKGdF_5$, despite the differences in ionic radii of Y^{3+} (0.09 nm) and Gd^{3+} (0.103 nm) ions. Table 1 shows the decay times for Nd^{3+} photoluminescence measured at 300 K for the two isomorphs as a function of dopant concentration. At low concentrations the decay times are almost identical ($\tau_R \approx 490 \pm 10 \mu s$) for both crystals, as is the case also for $Nd^{3+}:YLF$ and $Nd^{3+}:GLF$ [8,10].

The samples used for pulsed lasing experiments contained 5 at.% Nd^{3+} and were those used in optical absorption measurements. The sample lengths of 2.65 mm for $LiKYF_5$ and 2.85 mm for $LiKGdF_5$ corresponded to transmissions of 7% and 10% respectively, at the pump wavelength of 797 nm. The cut samples were polished by hand so that the end faces, which contained the b -axis, were roughly parallel. For optimum absorption efficiency the pump polarisation at 797 nm was perpendicular to the b -axis of the crystal, whereas the $1.048 \mu m$ emission

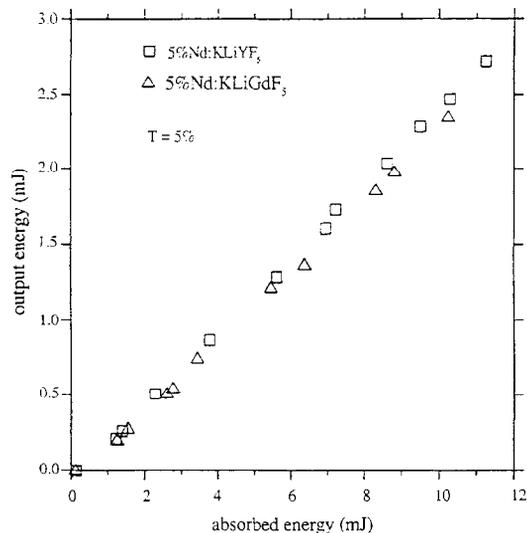


Fig. 3. Pulsed laser performance of 5% Nd^{3+} -doped $LiKYF_5$ and $LiKGdF_5$ at room temperature.

polarisation was polarised parallel to the b -axis. The laser cavity was formed by a concave reflector with 100 mm radius of curvature and 100% reflectivity and a flat output mirror with 95% reflectivity at the laser wavelength ($1.05 \mu m$). Laser oscillations were excited at room temperature by a long pulse $Cr^{3+}:LiSAF$ laser tuned to 797 nm. As Fig. 3 shows the behaviour of $Nd^{3+}:LiKYF_5$ and $LiKGdF_5$ are almost identical with the threshold for amplified stimulated emission being very low, typically $120 \mu s$. As expected for 4-level operation on the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, the output power scales linearly with the input power giving a slope efficiency of ca. 25%, despite the poor surface finish and imperfectly parallel end faces. Such performance is expected to improve significantly after appropriate sample optimisation.

The present experiments have shown that host crystals $LiKYF_5$ and $LiKGdF_5$ will sustain high Nd^{3+} concentrations without deleterious consequences for laser action. High Nd^{3+} levels coupled with the strong crystal field distortions at the RE^{3+} site lead to strongly enhanced absorption transition rates near 800 nm. In consequence, $Nd^{3+}:LiKYF_5$ and $Nd^{3+}:LiKGdF_5$ are potential host crystals for miniature, diode-pumped solid state lasers. The orthogonal polarisations of the pump (${}^4I_{9/2} \rightarrow {}^4F_{5/2}$, ${}^2H_{9/2}$) and laser (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) channels, and the concentration of stimulated emission into a single, intense crystal field transition at $1.048 \mu m$ are additional beneficial features for efficient laser operation.

The Y^{3+} (Gd^{3+}) sites in these isomorphous crystals are of low symmetry (C_1): in consequence, all transitions between the different levels of the crystal field split manifolds are allowed by the selection rules [11]. The 4f–4f transitions of Nd^{3+} ions are split by the even-parity distortions at the RE^{3+} sites. However, the transition rates of

Table 1
Fluorescence lifetime measurements of the ${}^4F_{3/2}$ state of Nd^{3+} in $LiKYF_5$ and $LiKGdF_5$ measured at 300 K

Nd:LiKYF ₅		Nd:LiKGdF ₅	
Concentration (at.%)	Decay time (μs)	Concentration (at.%)	Decay time (μs)
0.1	486	1.0	491
3.3	422	3.0	445
5.0	321	5.0	300

the individual lines, and their polarisation characteristics are determined by the symmetry and strengths of the odd-parity crystal field terms which allow weak electric dipole transitions between the crystal field levels. In view of the luminescence data it is probable that in LiKYF₅ and LiKGdF₅ the odd-parity distortion parallel to the *b*-axis removes the centre of inversion at the rare earth ion site. Since the splittings of the ⁴F_{3/2} and ⁴I_{11/2} multiplets in these hosts are comparable with other Nd³⁺ hosts such as YLF [12], it is apparently the odd-symmetry distortions that distinguish the optical properties of these laser gain media.

These studies demonstrate the importance of the polarisation state of the optical transitions in these fluoride crystals. For monoclinic crystals, such as LiKYF₅ and its isomorphs, there are three independent polarisation directions, labelled α , β and γ . Only β -polarisation corresponds to a principal axis of the crystal, i.e. the *b*-axis. The other directions of polarisation are in the plane perpendicular to *b*-axis. The monoclinic isomorphs LiKYF₅ and LiKGdF₅ are novel in the respect that the laser transition is β -polarised. In the monoclinic hosts BaY₂F₈ [3], La₂BeO₅ [13], and Y₂SiO₅ [14] the Nd³⁺ laser performance is limited by the electric field of the laser radiation being in the *a*-*c* plane, but the α - and γ -polarisations are not coincident with the *a*- and *c*-axes. The polarisation direction of the laser may, in consequence, shift as the temperature changes [15]. Such temperature-induced laser depolarisation, which may result in loss of output power, is not a characteristic of Nd³⁺:LiKYF₅ and Nd³⁺:LiKGdF₅ lasers. The measured slope efficiency of 25% is well below the theoretical limit, largely as a consequence of the poor sample quality and the un-optimised laser cavity. The present research programme seeks to improve the quality of crystals through refinements in the growth process. CW lasing experiments are also ongoing.

In summary, this paper reports a survey of the spectroscopic and laser properties of monoclinic Nd:LiKYF₅ and Nd:LiKGdF₅. Efficient room temperature lasing at 1.048 μ m has been demonstrated in both crystals with orthogonal pump and laser polarisations. The almost identical spectral properties of both gain media testify that LiKYF₅ and LiKGdF₅ have congruous structures. In both hosts the ⁴F_{3/2} \rightarrow ⁴I_{11/2} laser channel pumped near 800 nm is strongly polarised in the *b*-axis direction, this polarised emission corresponding primarily to one single inter-Stark transition. Such behaviour is assigned to the unique rare earth site environment in these hosts. Concentration

quenching of the ⁴F_{3/2} state's fluorescence lifetime is moderate and high Nd³⁺ doping levels are attainable without sacrificing the high optical quality needed for good laser performance.

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