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Spectroscopy of Nd^{3+} in $KLiYF_5$ and $KLiGdF_5$

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High-resolution Fourier-transform absorption and photoluminescence spectroscopy with site-selective excitation reveal two sites for Nd^{3+} ions in each of the two new crystals $KLiYF_5$ and $KLiGdF_5$. Energy levels for the ^4I multiplets and the $^4F_{3/2}$ multiplet have been determined separately for each site in each crystal. Comparison of spectra and levels indicates that the crystal fields in each of the two materials are nearly identical. This suggests that $KLiGdF_5$ is isostructural to $KLiYF_5$.

I. INTRODUCTION

A new low-threshold laser-crystal Nd^{3+}:$KLiYF_5$, reported recently by Kaminskii and Khaidukov,[1] was found to have properties favorable for compact cavity configurations with diode-laser pumping. Spectroscopy[1] and x-ray crystallography[2] have suggested that $KLiYF_5$ (KLYF) is a single-site crystal with Nd^{3+} ions presumably substituting at the Y^{3+} site. The growth of large low-loss boules of KLYF by a modified Czochralski technique has recently been developed by Nicholls *et al.* and the laser performance of these crystals has been reported.[3] In addition the new crystal $KLiGdF_5$ has been developed[3] with the motivation that Gd^{3+} is closer in size to Nd^{3+} than is Y^{3+}, permitting the higher dopant concentrations desired for compact lasers.

We have applied high-resolution Fourier-transform spectroscopy to Nd:KLYF and Nd:KLGF in order to study differences in the two crystals. We find that the number, relative strengths, polarizations, and positions of the lines in the KLGF spectra are very similar to those for KLYF. This indicates that Nd^{3+} ions occupy sites of the same symmetry and almost identical crystal-field strengths in the two crystals, which strongly suggests that the two are isostructural. In contrast to the earlier spectroscopic and crystallographic studies, two sites are found in each crystal.[4,5] The two sites are nearly equally occupied by the dopant ions at all concentrations and are quite similar energetically. Accurate Stark levels for each site in each crystal were determined from absorption and photoluminescence data with the help of site selective excitation.

This paper is organized as follows. The experimental details are given in Sec. II. A detailed comparison of the spectra of Nd:KLYF and Nd:KLGF is presented in Sec. III. Section IV presents the discussion and summary.

II. EXPERIMENT

Single-crystal boules of KLYF and KLGF were grown by the top-seeded solution grown method (modified Czochralski technique).[6] The nominal Nd^{3+} concentrations in the samples studied here are 0.2%, 2.0%, and 5.0% in KLYF and 1.0%, 2.0%, and 5.0% in KLGF. KLYF has a monoclinic Bravais lattice,[2] and the samples were oriented with the *b* axes determined as the normal to internal cleavage planes.

A Bomem DA8 Fourier-transform spectrometer, with inherently-high frequency accuracy (0.004 cm^{-1} at 2000 cm^{-1}), collected polarized absorption and photoluminescence data at a resolution of 1 cm^{-1}. The beamsplitter was either quartz or Ge-coated KBr. The detector was either HgCdTe or InSb operating at 77 K or a room-temperature Si photodiode. The entire light path is evacuated, hence the positions of absorption and luminescence peaks are in vacuum wavenumbers. All the spectra presented here were collected at 80 K sample temperatures using a home-built liquid-nitrogen cold-finger cryostat. Peak positions were determined with an uncertainty of less than 0.5 cm^{-1} in most cases.

Site-selective excitation was accomplished using a jet-dye laser (DCM dye) pumped by a multiline argon-ion laser. The excitation frequency was selected with a birefringent plate calibrated to ± 3 cm^{-1} by directly measuring the laser output with the Fourier spectrometer. The full width at half maximum (FWHM) of the laser output was $\leqslant 2$ cm^{-1}. Nonselective excitation was achieved with the Ar laser alone.

III. RESULTS

Figures 1–5 compare transmission spectra for Nd:KLYF and Nd:KLGF. Dopant concentrations, polarization, and sample thicknesses are given in the figures. The transitions plotted in Figs. 1–5 are $^4I_{9/2} \rightarrow {}^4I_{11/2}$, $^4I_{13/2}$, $^4I_{15/2}$, $^4F_{3/2}$, and $^4F_{5/2} + {}^2H_{9/2}$, respectively. The close similarity in the spectra of the two materials with respect to the number, relative strength, and frequency positions of individual lines is apparent. Spectra for the two crystals also have nearly identical polarization dependences. Figure 5 presents the pumping band for diode-laser excitation of 1 μm lasing.

Figures 6–9 present the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ photoluminescence spectra, respectively. The excitation was nonselective. These spectra are uncorrected for detector and spectrometer response. Again, the spectra for

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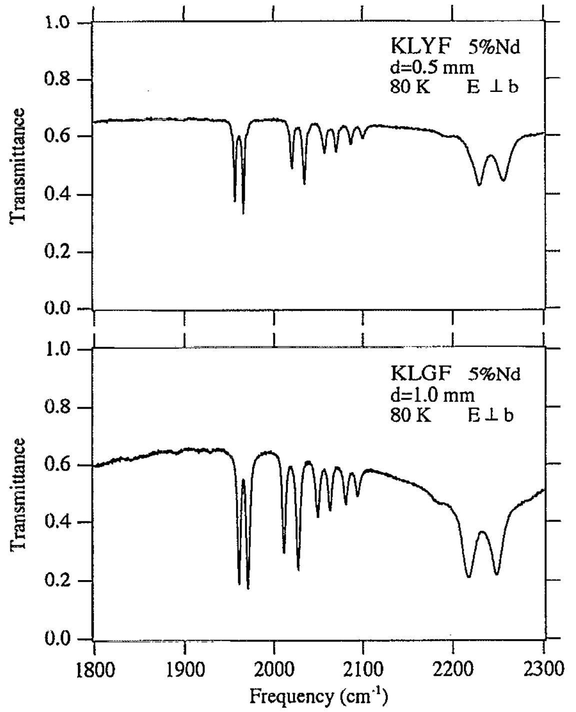

FIG. 1. Transmittance spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transitions.

the two materials appear nearly identical. The $^4F_{3/2} \rightarrow {}^4I_{15/2}$ emission is extremely weak. The quality of this spectrum for KLYF was very poor so Fig. 9 presents only the KLGF data, which appears still quite noisy.

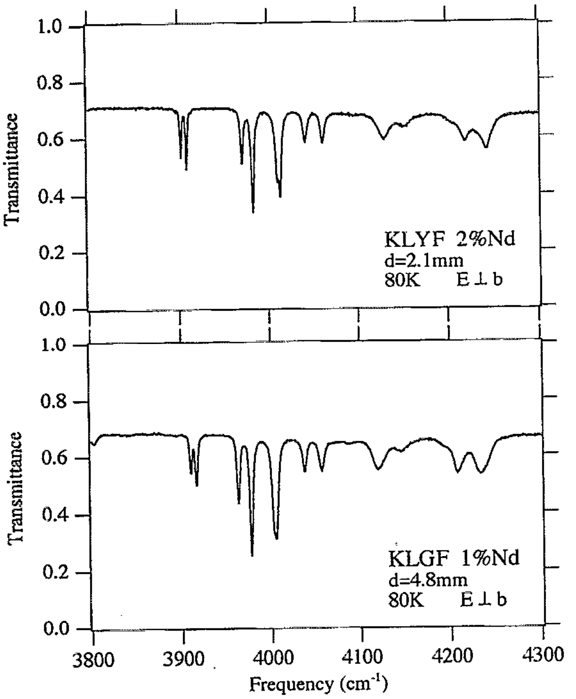

FIG. 2. Transmittance spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4I_{9/2} \rightarrow {}^4I_{13/2}$ transitions.

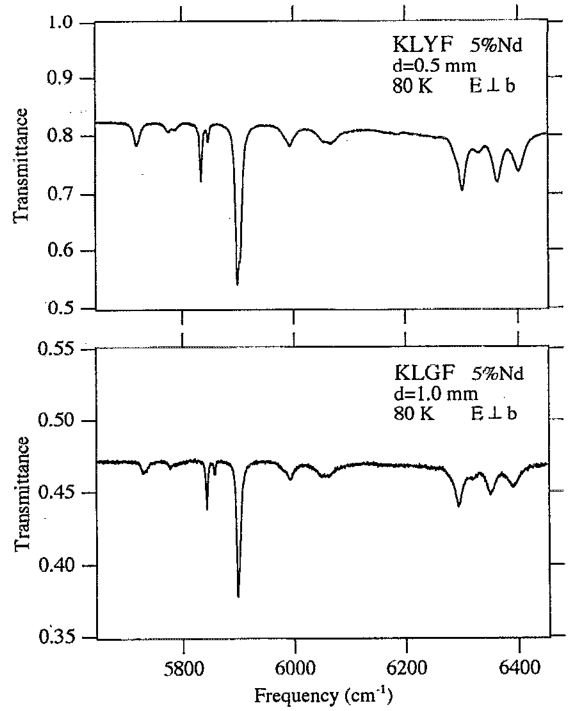

FIG. 3. Transmittance spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions.

For each spectrum there are generally twice the number of peaks expected from the known degeneracies of Nd^{3+} terms. This suggests that two sites exist in each crystal. Analysis of the observed transitions indicates two in-

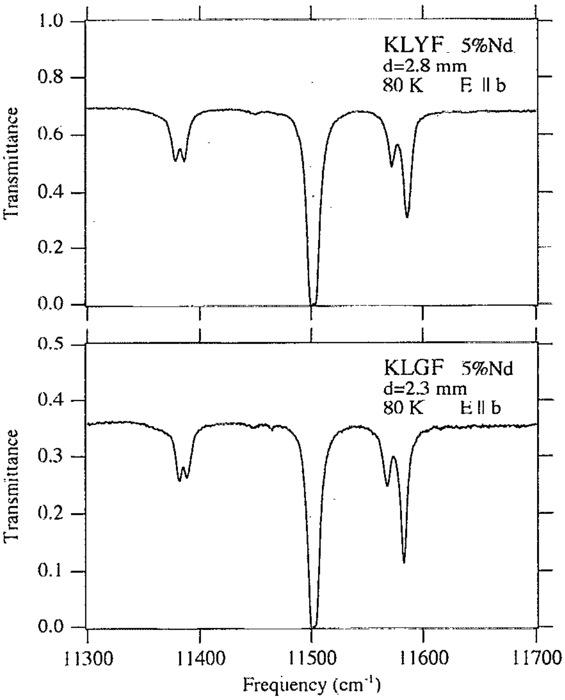

FIG. 4. Transmittance spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transitions.

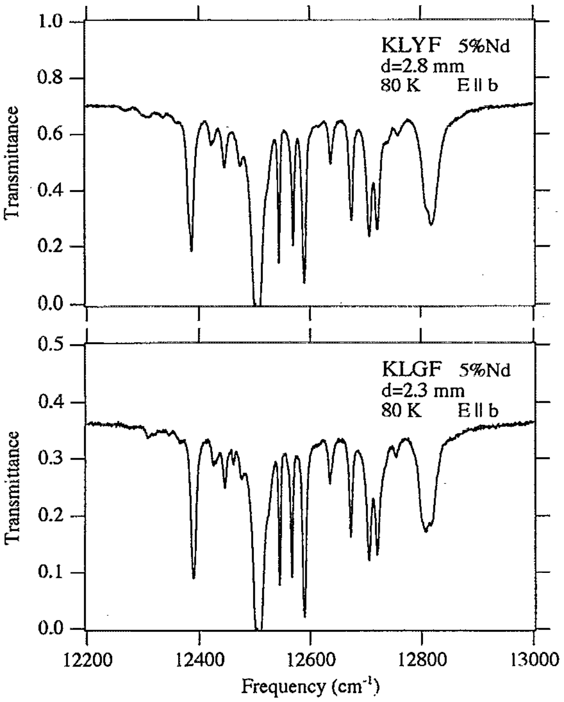

FIG. 5. Transmittance spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4I_{9/2}\rightarrow{}^4F_{5/2}+{}^2H_{9/2}$ transitions. These are the diode-pumped bands for compact laser applications.

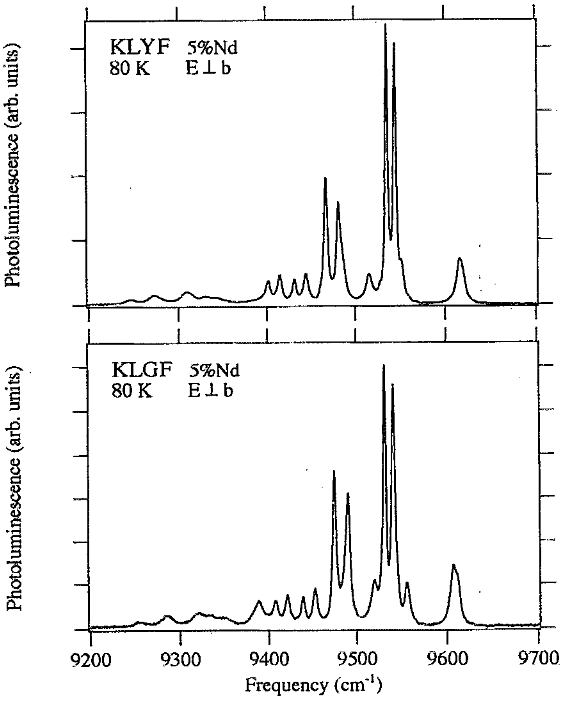

FIG. 7. Photoluminescence spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transitions. The excitation is nonselective.

dependent sets of energy levels. Note that lines of nearly equal strength and shape frequently appear grouped in pairs. Each site generally contributes one line to each such pair.

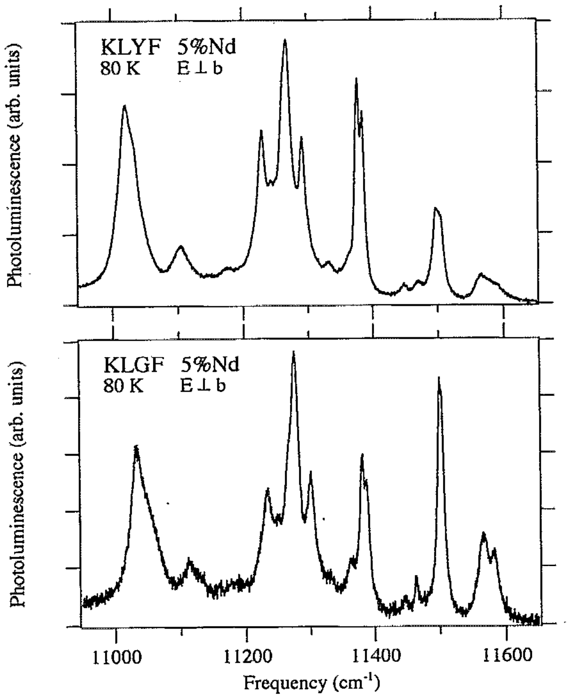

FIG. 6. Photoluminescence spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions. The excitation is nonselective.

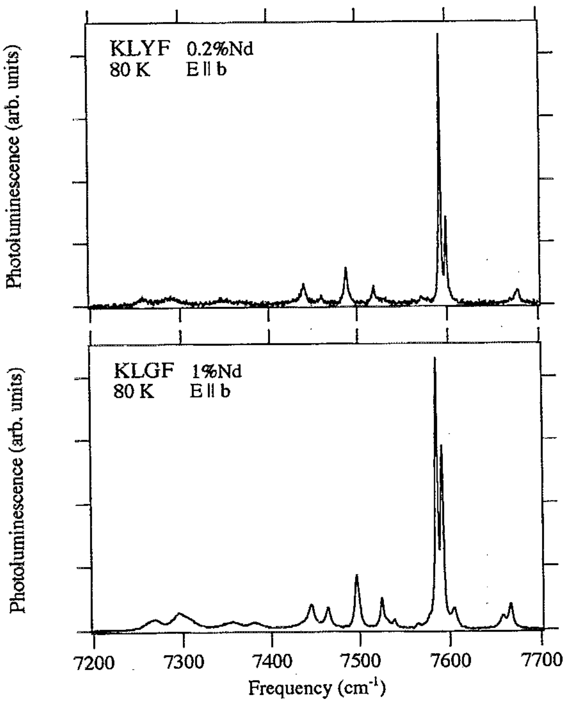

FIG. 8. Photoluminescence spectra for Nd-doped $KLiYF_5$ and $KLiGdF_5$ showing the $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions. The excitation is nonselective.

Analysis of spectra such as Figs. 1–9 is insufficient to unambiguously assign all transitions to individual sites. Photoluminescence excited site selectively, on the other hand, clearly distinguishes the contributions from each

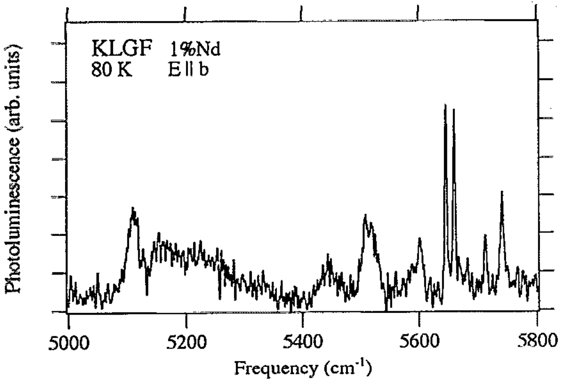

FIG. 9. Photoluminescence spectra for Nd-doped KLiGdF$_5$ showing the $^4F_{3/2}\rightarrow{}^4I_{15/2}$ transitions. The excitation is nonselective.

site, at least for the three strongest emission bands. In Fig. 10 we present typical results for KLYF. The inset shows a portion of the $^4I_{9/2}\rightarrow{}^4F_{9/2}$ absorption band. The central pair of absorption lines labeled A and B are pumped to excite the luminescence bands shown. Tuning the laser resonant with absorption line A produces the upper emission spectrum, while pumping line B results in the lower spectrum. Comparison of the two spectra reveals that there are two groups of lines which change strength independently. These two groups are indicated by the two sets of connected vertical bars in the upper figure. The group of lines which become strong when absorption line A(B) is pumped are labeled A(B). Figure 10 confirms convincingly the existence of two sites, which we henceforth label A and B.

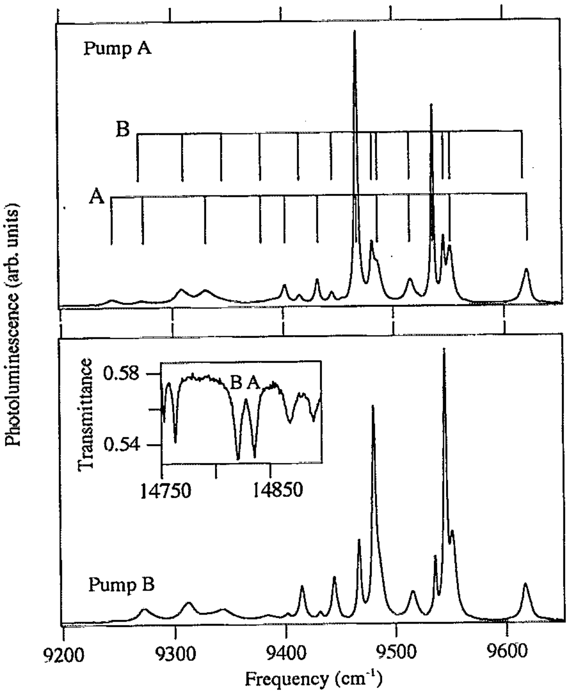

FIG. 10. Site selective $^4F_{3/2}\rightarrow{}^4I_{11/2}$ photoluminescence spectra for 0.2% Nd:KLiYF$_5$ at 80 K polarized with $E\perp b$. The inset presents part of the $^4I_{9/2}\rightarrow{}^4F_{9/2}$ absorption spectrum which identifies the transitions pumped to excite the luminescence.

TABLE I. Stark levels (cm^{-1}) of the ^4I and $^4F_{3/2}$ multiplets for Nd^{3+} in KLiYF$_5$.

Multiplet	Site B	Site A
$^4I_{9/2}$	0	0
	123.5	115.6
	209.5	231.8
	239.5	271.6
	487.0	482.1
$^4I_{11/2}$	1956.2	1965.9
	2020.6	2034.6
	2057.3	2070.3
	2086.7	2100.2
	2193.0	2215.9
	2232.2	2255.2
$^4I_{13/2}$	3903.7	3909.3
	3972.4	3983.2
	4010.8	4012.3
	4042.4	4064.1
	4130.0	4149.5
	4203.7	4240.8
	4217.5	
$^4I_{15/2}$	5847.1	5833.9
	5899.1	5903.8
	5993.0	5984.6
	6054.2	6067.8
	6210.4	6231.9
	6253.4	6293.1
	6301.2	6330.4
	6363.1	6401.6
$^4F_{3/2}$	11501.8	11501.8
	11572.8	11586.2

The separate energy levels for Nd^{3+} ions in sites A and B are determined by analysis of site-selective emission spectra, such as Fig. 10, together with the absorption spectra. Because no Stokes shifts between absorption and emission values were observed within the experimental uncertainty, emission and absorption values were averaged. The accuracy with which the experimental values are known is about ±0.5 cm^{-1} in most cases. The Stark levels for the ^4I J multiplets of Nd^{3+} in KLYF and KLGF at 80 K are presented in Tables I and II, respectively.

IV. DISCUSSION AND SUMMARY

Our identification of two sites in KLYF contradicts the earlier spectroscopic study[1] which showed evidence for just one site. X-ray crystallography[2] also indicates that there should be just one crystal-field environment for Nd^{3+} ions which substitute for Y^{3+} ions. On the other hand, the existence of a glide plane shows that the YF$_8$ polyhedra in KLYF are divided into two groups such that members of one are mirror images of the other. Perhaps slight differences between the two groups in bond lengths and angles exist but were unresolved in the x-ray analysis because of room temperature thermal motions. This is conceivable

TABLE II. Stark levels (cm^{-1}) of the ^4I and $^4F_{3/2}$ multiplets for Nd^{3+} in KLiGdF$_5$.

Multiplet	Site B	Site A
$^4I_{9/2}$	0	0
	120.8	113.6
	199.7	225.0
	267.1	251.6
	453.6	468.5
$^4I_{11/2}$	1960.6	1970.7
	2011.7	2027.3
	2049.0	2063.0
	2080.6	2094.1
	2182.0	2171.4
	2217.9	2248.5
$^4I_{13/2}$	3910.0	3916.2
	3963.0	3977.4
	4003.0	4005.3
	4038.0	4057.3
	4120.8	4145.9
	4196.2	4207.4
	4234.2	4242.0
$^4I_{15/2}$	5856.1	5841.8
	5898.0	5901.9
	5992.6	5980.8
	6047.9	6062.0
	6293.4	6317.2
	6348.8	6391.7
$^4F_{3/2}$	11502.0	11502.0
	11567.9	11582.6

since the difference in crystal field at the two sites is observed spectroscopically to be very small. One may even speculate that all YF$_8$ polyhedra are identical at room temperature, but that a phase transition occurs at low temperature which introduces small differences. It is impossible to verify this speculation spectroscopically because at room temperature the linewidths become larger than the separation between transition pairs.

The existence of two sites in KLYF (and KLGF) is unlikely to have any effect on laser performance. Both sites are so similar spectroscopically, that there can be little difference in their radiative or nonradiative decay rates or in their emission cross sections. With such similar energies, energy transfer between sites is likely at the high concentrations desired for compact lasers, but neither site should act as a quenching center for the other because of the above mentioned similarities.

The effective ionic radii of Y^{3+}, Gd^{3+}, and Nd^{3+} in eightfold fluoride coordination are 1.16, 1.20, and 1.26 Å, respectively.[7] Because Gd^{3+} is closer in size to Nd^{3+} than is Y^{3+}, higher Nd concentrations are expected in KLGF than in KLYF. However, the spectra reveal little evidence for a difference in each material's ability to accept dopant ions. For example, in Figs. 4 and 5, where both materials have the same 5% nominal concentration and nearly the same thickness, the lines are approximately of the same strength, which indicates that actual concentrations are equal. In addition, fluorescence decay rates are nearly identical in KLYF and KLGF samples with the same nominal concentrations,[3] again indicating no difference in actual concentrations.

The nearly identical spectra and energy levels obtained in the two crystals explains why their lasing properties are nearly identical.[3] The spectral similarities imply that Nd^{3+} ions reside in sites of identical symmetry and nearly identical crystal-field strength in the two materials. In other words, the nearest and second nearest neighbors of the dopant ions are likely to have the same charge and position relative to the dopant in each crystal, which strongly suggests that the two crystals are completely isostructural. Nearly identical Raman spectra for KLYF and KLGF tends to confirm this.[8] We predict that x-ray crystallography will find that the new crystal KLGF is isostructural to KLYF but that it has slightly larger lattice constants since Gd^{3+} is larger than Y^{3+}.

In summary, we have demonstrated that two sites exist in KLiYF$_5$ and that these sites are occupied nearly equally by Nd^{3+} ions. We have presented spectroscopic evidence that suggests KLiGdF$_5$ is isostructural to KLiYF$_5$. We have determined the energy levels for each site in each crystal in the energy range of interest for 1 μm lasing.

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[1] A. A. Kaminskii and N. M. Khaidukov, Phys. Status Solidi A **129**, K65 (1992).

[2] A. V. Goryunov, A. I. Popov, and N. M. Khajdukov, Mater. Res. Bull. **27**, 213 (1992).

[3] J. F. H. Nicholls, X. X. Zhang, G. D. Loutts, B. Henderson, M. Bass, and B. H. T. Chai, in *Growth, Characterization, and Applications of Laser Host and Nonlinear Crystals II*, edited by B. H. T. Chai (SPIE, Washington, 1993), Vol. 1863, p. 13.

[4] R. E. Peale, H. Weidner, P. L. Summers, X. X. Zhang, and B. H. T. Chai, Technical Digest of the International Conference on Luminescence, Storrs, CT, August 1993, paper M4-40.

[5] F. G. Anderson, H. Weidner, P. L. Summers, R. E. Peale, X. X. Zhang, and B. H. T. Chai, J. Lumines. (in press).

[6] B. Chai, A. Pham, and G. Lutts, in *Growth, Characterization, and Applications of Laser Host and Non-linear Crystals II*, edited by B. H. T. Chai (SPIE, Washington, 1993), Vol. 1863, p. 19.

[7] A. A. Kaminskii, *Laser Crystals, Their Physics and Properties*, 2nd ed. (Springer, Berlin, 1990), Table 2.1 on p. 457.

[8] A. Schulte and X. X. Zhang, Department of Physics, University of Central Florida, Orlando, FL, 32816, 1993 (unpublished).