

# Differences Between Czochralski and Hydrothermal Nd:KLiYF<sub>5</sub>

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## **Abstract**

Spectroscopy, x-ray crystallography, and lifetime data reveal different structures and number of sites for hydrothermal- and Czochralski-grown Nd<sup>3+</sup>:KLiYF<sub>5</sub>, a low threshold laser crystal. Temperature-dependent effects for intersite energy transfer are discussed.

## **Introduction**

The new crystal Nd:KLiYF<sub>5</sub> (Nd:KLYF) has been shown to be a low threshold laser crystal by groups in Russia[1] and CREOL[2]. Subsequent papers on this material have focussed on a controversy over the number of sites available for Nd doping. The Russian crystals, grown by the hydrothermal method [1], have been shown convincingly by photoluminescence spectroscopy[1] and x-ray crystallography[3] to have only a single site. On the other hand, high resolution Fourier transform photoluminescence and absorption spectroscopy[4], crystal-field analysis [5], and energy transfer studies [6,7] have shown equally convincingly that Nd<sup>3+</sup> ions occupy 2 sites with equal probability at all concentrations in the Czochralski (CZ) material grown at UCF. In this paper, we discuss the results of experiments which reveal in detail the minor structural differences which exist between the two types of material and which account for the discrepancies published previously. A comparison is made for the two materials of their photoluminescence, luminescence lifetimes, powder x-ray scattering, and the results of x-ray crystallography.

## **Experiment**

Hydrothermal KLYF<sub>5</sub> (HT-KLYF) samples were grown in Russia and consist of small pieces with mm

dimensions. The CZ KLYF samples were grown at the CREOL crystal growth lab and are large single crystals with cm dimensions. Details of their growth have been published previously[1,8].

All spectroscopy discussed in this paper was performed at the University of Central Florida using a high resolution Fourier spectrometer. For UV absorption measurements, the spectrometer resources included a D<sub>2</sub> lamp, a Al-coated quartz beam splitter, interference band-pass filters, and a Si photodiode detector. Photoluminescence was excited by an multiline Ar laser and collected by the spectrometer using a quartz beamsplitter and the Si detector. Samples are cooled using either a liquid-nitrogen cold finger cryostat, or a liquid-helium optical-access cryostat.

For luminescence-decay measurements, Nd<sup>3+</sup> ions were excited to their <sup>4</sup>F<sub>5/2</sub> + <sup>2</sup>H<sub>9/2</sub> levels using 0.5 second pulses of a ~10 mW 796 nm laser diode. The signal was collected by the Si detector, which was shielded from the laser light by a 950 nm long-pass interference filter, and 100 decays were averaged. Emission from the <sup>4</sup>F<sub>3/2</sub> level was the only contribution to the measured signal.

Rutherford back scattering experiments were performed[9] at Friedrich-Schiller-Universität in Jena on the CZ KLYF samples to determine their Nd concentrations. These measurements also confirm the chemical formula KLiYF<sub>5</sub> for CZ KLYF within experimental error. Other methods of determining the chemical formula, including wet chemistry and time-of-flight mass spectroscopy with excimer laser ablation, failed for a variety of reasons.

Preliminary powder x-ray scattering measurements were performed at CREOL. A complete crystallographic analysis, performed by A. Clearfield [10] on CZ KLYF, has provided the most reliable

determination of the chemical formula, space group, and the small structural differences which distinguish CZ and HT KLYF. The pictures of the local crystal structure surrounding  $Y^{3+}$  ions were prepared at UCF on a Sun microcomputer using Mathematica from Wolfram Research.

### Results and Discussion

First, we present new, previously unpublished evidence that the two-site nature of CZ KLYF is inherent to the crystal structure and has nothing to do with possible  $Nd^{3+}$  doping effects. Fig. 1 presents a UV absorption spectrum of the KLYF isomorph  $KLiGdF_5$  [3,4]. The  $Gd^{3+} \ ^6P_{3/2}$  transitions are evident. Only two transitions are expected, but four are observed, showing that  $Gd^{3+}$  occupies two sites which are inequivalent with respect to their crystal fields. The  $Gd^{3+} \ ^6P_{5/2}$  and  $^6P_{7/2}$  spectra also reveal this doubling in the number of expected lines.

Fig. 2 compares the  $^4F_{3/2} \rightarrow \ ^4I_{11/2}$  photoluminescence spectra at 80 K and  $1 \text{ cm}^{-1}$  resolution. The spectra are clearly different. The HT KLYF spectrum is essentially identical to that published in [1] and has fewer lines than the CZ KLYF spectrum. Previous analysis of such spectra [1,4,5] has shown convincingly that these are 1- and 2-site crystals, respectively, but this is the first time spectra for both materials have been measured by the same group using the same instrumentation.

Fig. 3 compares the 80 and 300 K  $^4F_{3/2}$  photoluminescence lifetimes as a function of Nd

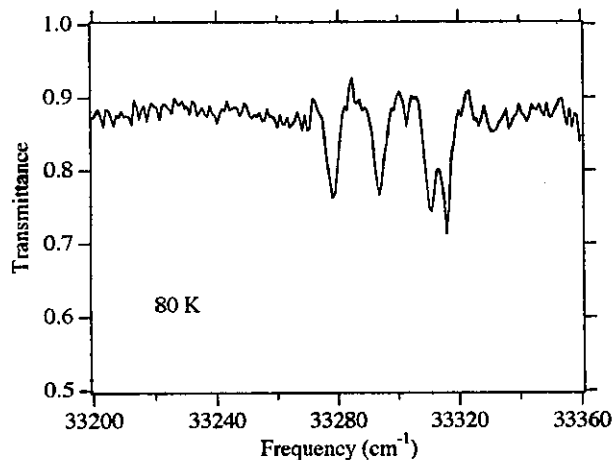


Figure 1.  $Gd^{3+} \ ^6P_{3/2}$  absorption lines in the CZ KLYF isomorph  $KLiGdF_5$  at 80 K.

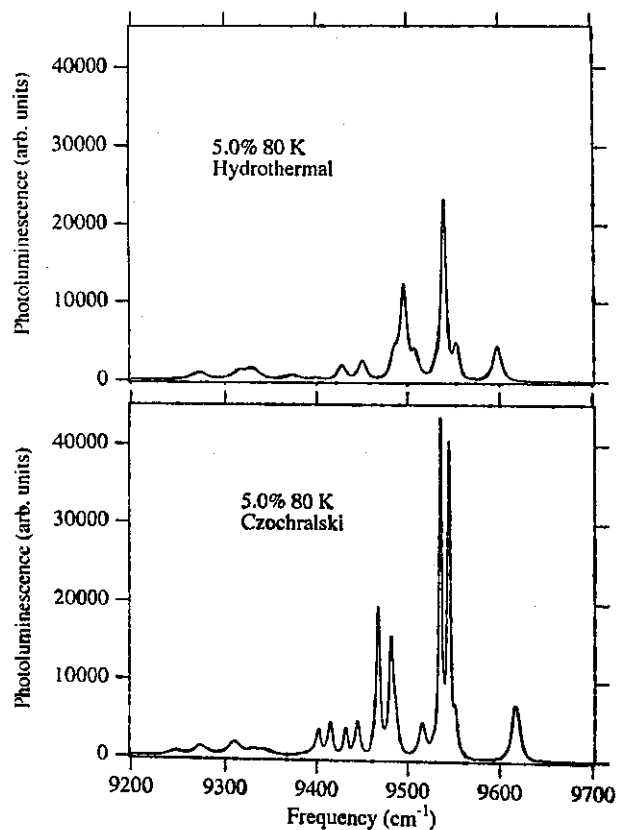


Figure 2. Comparison of the 80 K  $^4F_{3/2} \rightarrow \ ^4I_{11/2}$  emission of  $Nd^{3+}$  in HT and CZ KLYF.

concentration. The dependence is similar for the two materials, though the lifetime in HT KLYF is somewhat lower. At lowest concentration the lifetime drops with increasing temperature. This is well explained by local processes such as multiphonon relaxation. However, at moderately high concentrations, we find an increase in lifetime from 80 K to 300 K for both materials. We will discuss this phenomenon in the "Energy Transfer" section below.

Powder X-ray scattering spectra are compared for HT and CZ KLYF in Fig. 4. With the exception of a few lines, the X-ray spectra of the two materials differ significantly, showing convincingly that their structures differ. The complete crystallographic analysis [10] reveals that CZ KLYF is composed of two crystallographically inequivalent formula units. Its chemical formula can therefore be written as  $(KLiYF_5)_2$ . Compared with the four identical Y sites per unit cell in HT KLYF, CZ KLYF has a total of 8 Y sites divided equally into two inequivalent groups. The space group is identical for the two crystals. Both materials are monoclinic with very similar values for a, c, and  $\beta$ . However, the unit cell for CZ KLYF is about twice as long in the b direction. Details are summarized in Table 1.

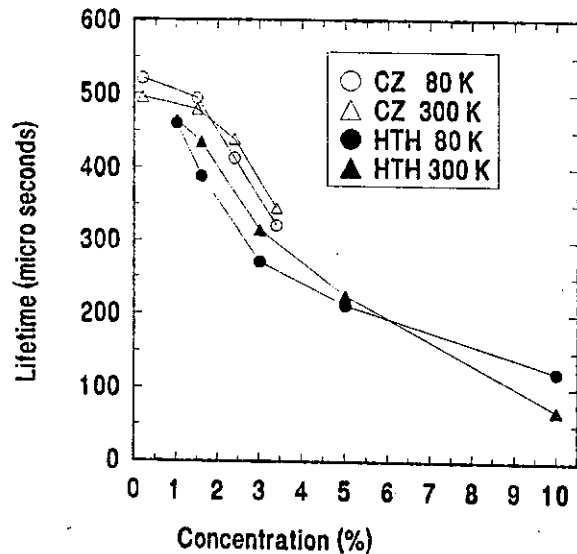


Figure 3. Photoluminescence lifetimes of  $\text{Nd}^{3+}$  in CZ and HT KLYF at 80 and 300 K.

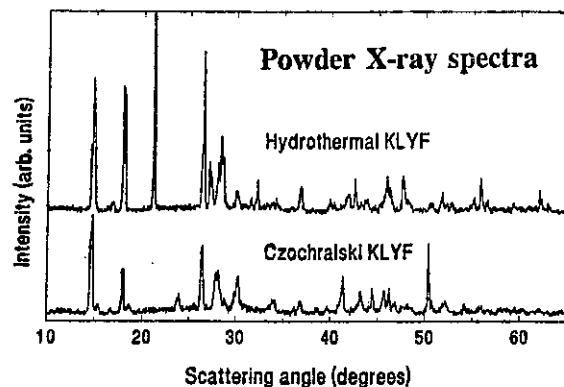


Figure 4. Comparison of powder X-ray spectra for CZ and HT KLYF.

Table 1. Structural information for Hydrothermal and Czochralski  $\text{KLiYF}_5$

	HT	CZ
Space group	$P2_1/c$	$P2_1/c$
a	6.2925 Å	6.39 Å
b	11.747 Å	23.69 Å
c	6.4669 Å	6.31 Å
$\beta$	113.715°	113.3°

With the help of the fractional positions of all ions, we may now explore the reasons for the differences in the  $\text{Nd}^{3+}$  spectra for the two materials. Since the crystal field responsible for the subtleties of rare-earth spectra are due primarily to the nearest neighbors, we start with the 8 surrounding fluorine ions. Figs. 5a-c show the  $\text{Y}^{3+}$  ion with its 8 F<sup>-</sup> neighbors for HT KLYF and CZ KLYF sites I and II, respectively. These pictures show very little difference in the angular distribution of the F<sup>-</sup> (medium size, medium rastering) around the  $\text{Y}^{3+}$  (larger size, tight rastering). The most apparent difference is the size of the gap between the two F<sup>-</sup> in the left front. This gap is very small for HT KLYF, is only slightly larger for site II in CZ KLYF, and is the largest for site I. Views from different eye points do not reveal more significant differences.

To reveal further differences, pictures including additional neighbors are constructed. Figs. 6a-c contain all ions whose centers fall within a 3.8 Å radius of the  $\text{Y}^{3+}$  ion for HT KLYF and sites I and II of CZ KLYF, respectively. The 3.8 Å radius was chosen because it dramatically reveals some differences by including or excluding a number of ions. For HT KLYF, a Li<sup>+</sup> (left front, small size, wide rastering) and a K<sup>+</sup> (lower right, largest size, wide rastering) appear. These ions are missing for CZ KLYF site I (Fig. 6b). Instead, a different Li<sup>+</sup> appears towards the right, and a  $\text{Y}^{3+}$  shows up in the lower left. The situation is again different for site II where the leftmost Li<sup>+</sup> reappears simultaneously with the extra  $\text{Y}^{3+}$  and the K<sup>+</sup>. The left Li<sup>+</sup> ion in Figs. 6a and 6c is especially interesting. Its closeness to the central  $\text{Y}^{3+}$  causes a stronger Coulomb attraction for the oppositely charged F<sup>-</sup> ions, pulling them closer together, as seen in Figs. 5a and 5c. Overall, the differences revealed in Figs. 5 and 6 are as small as the differences in the lattice parameters a, b, c, and  $\beta$  for the two materials (Table 1). However, these differences are sufficient to change transition frequencies by up to 10  $\text{cm}^{-1}$  and to cause transition-strength differences which are clearly observed (Fig. 2).

### Energy Transfer

The similarities in the immediate environment of the Y ions continue in the long range order. The Y sublattices in both materials are virtually identical (ignoring site I and II in CZ CLYF) and consist of almost flat planes perpendicular to the b axis. One such plane is shown in Fig. 7 for CZ KLYF. Each ion has three close neighbors of opposite site type separated by about half the distance between planes. This arrangement is favorable for strong intersite energy transfer and the similarities make it reasonable to

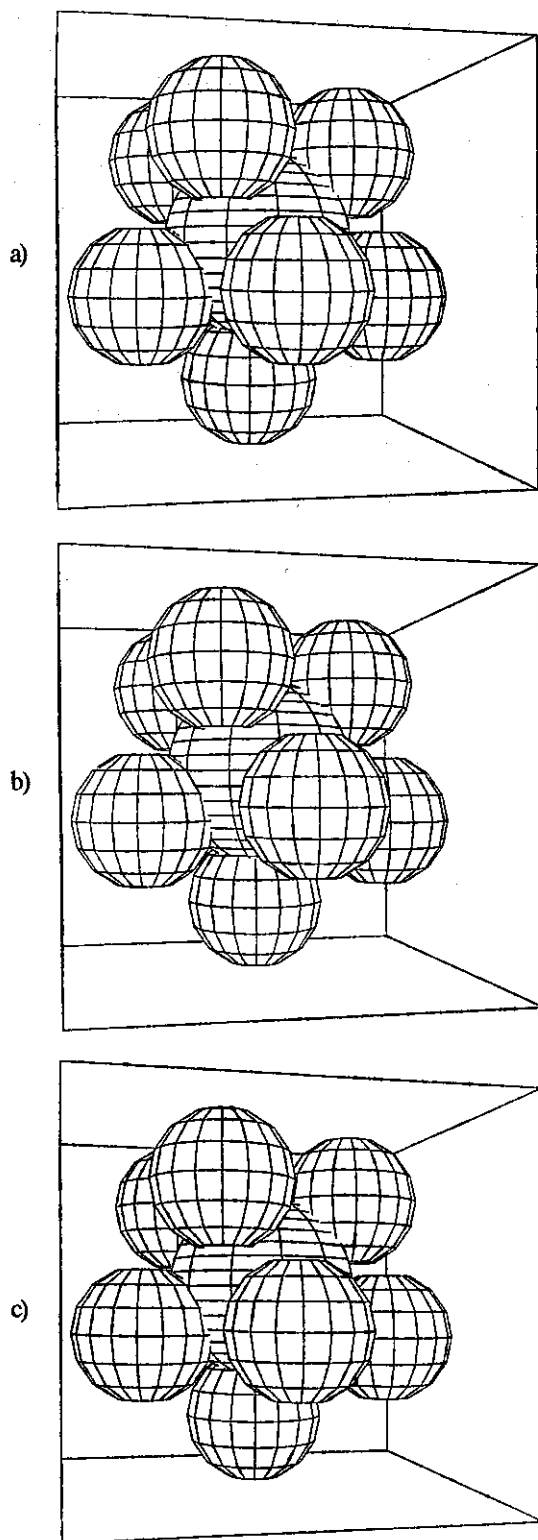


Figure 5.  $Y^{3+}$  ions (larger size, tight rastering) with 8 surrounding  $F^-$  ions (medium size, medium rastering) a) in HT KLYF; b) in site I and c) in site II of CZ KLYF.

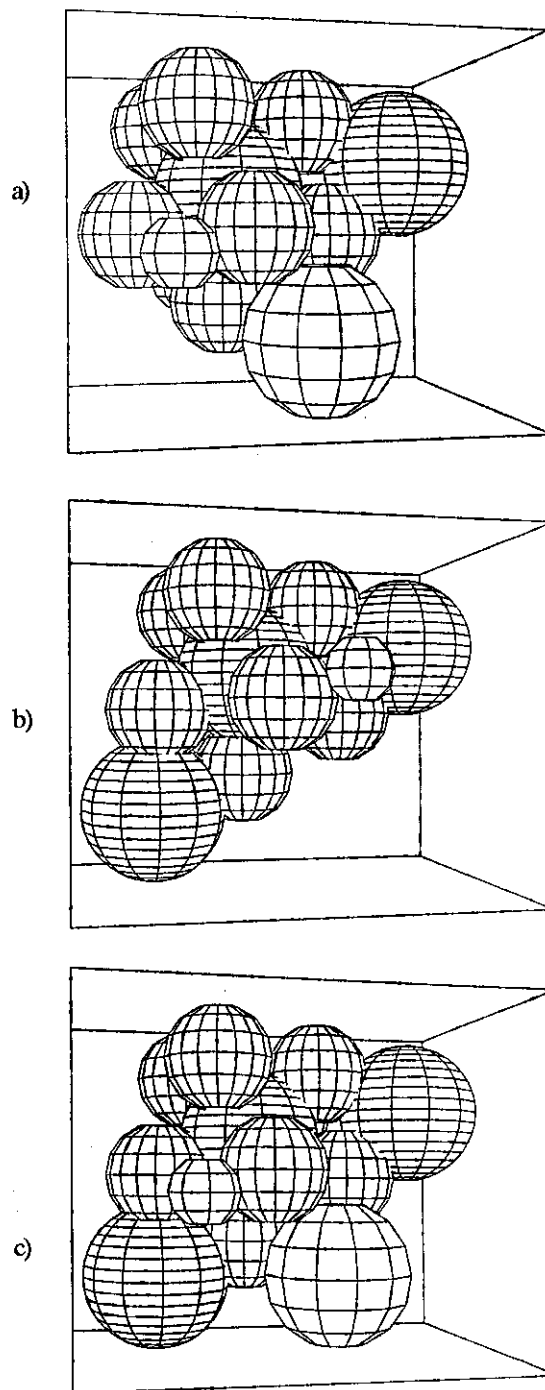


Figure 6.  $Y^{3+}$  (large size, tight rastering) with those ions whose centers lie within 3.8 Å for a) HT KLYF, b) site I, CZ KLYF, and c) site II CZ KLYF. ( $Li^+$  = small size, wide rastering;  $F^-$  = medium size, medium rastering;  $K^+$  = largest size, wide rastering)

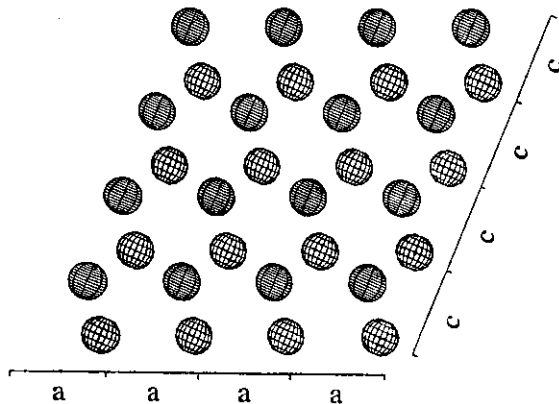


Figure 7. Plane of the Y<sup>3+</sup> sublattice in CZ KLYF (different sites = different rastering)

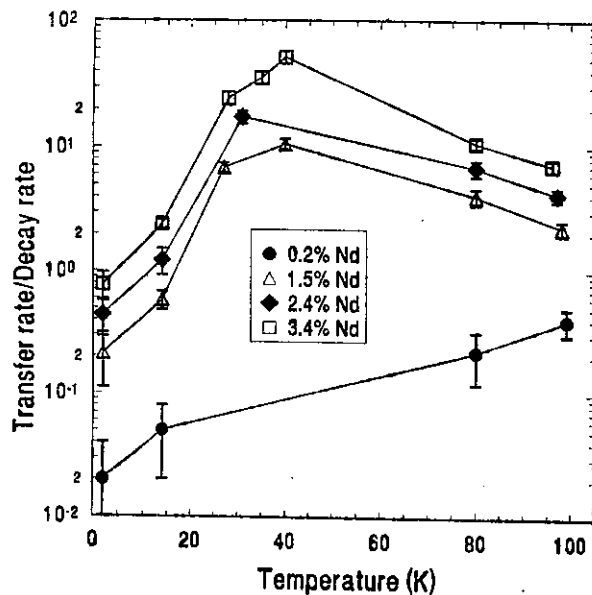


Figure 8. Rate of intersite energy transfer between Nd<sup>3+</sup> in CZ KLYF vs temperature.

assume that this is true also for HT KLYF with the exception that there is no difference between sites. Now we can approach our goal of a better understanding of the energy transfer dynamics that have been studied in CZ KLYF[6,7] and apply our new understanding also to HT KLYF.

Some new information about CZ KLYF is that the energy transfer between Nd ions in the two sites has a strong and unusual temperature dependence, as shown in Fig. 8. Within the temperature range from 2 to 40 K, the observed energy transfer increases by almost two orders of magnitude. It then drops by a factor of about five when the temperature is further increased to 100 K. Above 100 K, the luminescence singles from the two sites cannot be separately resolved so that we lose direct information about energy transfer. We also have insufficient data at this point to include the 0.2% sample in the discussion at this time.

Only that part of ongoing transfer which is externally accessible via emitted photons is directly probed in our experiments. We believe that the observed drop in transfer rate is in large part due to excitation quenching by means of cross relaxation (for example). Since both transfer and cross relaxation are more rapid at small distances, those parts of the crystal volume with rapid transfer are also where excitation quenching is most likely. If cross relaxation is thermally activated above 40 K by increasing spectral overlap via line broadening and/or thermal population effects, it will kill excitations in volumes with rapid transfer and will increase the statistical weight of volumes with less rapid transfer. This effectively lowers the energy transfer rate determined from our experiments.

A second way in which increased temperature can lower the observed transfer rate is by populating the upper  $^4F_{3/2}$  Stark level, which has much less spectral overlap between the two sites[6,7]. However, such a population shift can remove at most half of the overlap, and therefore this mechanism alone is unable to explain all of the reduction in transfer rate observed above 40 K. However, by reducing migration, this mechanism keeps excitations from falling into the cross relaxation traps. By (partially) removing a decay path, the observed luminescence lifetime is reduced less, which appears in Fig. 3 as an apparent increase. In contrast, transfer and cross relaxation are less important for low concentration samples and therefore cannot change the overall trend of decreasing luminescence lifetime.

For the 10% HT KLYF, sample the picture is special. Here, the distances between Nd<sup>3+</sup> ions are so small that migration is strong even with the thermally induced reduction reduction in spectral overlap. Cross relaxation centers remain accessible, and the increase in cross relaxation probability with temperature now dominates the effects of reduced migration. Fast photoluminescence decay caused by this strong cross

relaxation is apparent in Fig. 9. Only a very small fraction of excitations are unable to migrate to a trap and these left overs are responsible for the late part of the decay curve, where a rate identical to the low concentration sample is observed.

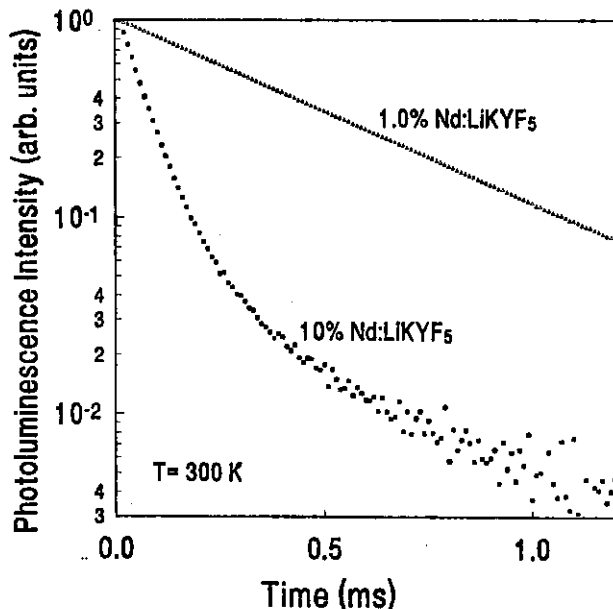


Figure 9. Room temperature photoluminescence decay for HT KLYF with 1% and 10% [Nd].

### Conclusions

X-ray crystallography settles the controversy about the number of sites available for Nd substitution in  $\text{KLiYF}_5$ . There are two similar but different crystalline phases with the chemical formula  $\text{KLiYF}_5$ : a hydrothermally grown phase with only one site and a second phase grown by Czochralski method with two slightly different sites. While the differences are sufficient to explain different optical and X-ray spectra, the similarities are numerous. Similar  $\text{Y}^{3+}$  sublattices for the two materials let us apply our information about energy transfer obtained from the two site CZ KLYF to HT KLYF. We are able to explain details in the common photoluminescence decay behavior at least qualitatively. Our studies[6,7] of the model two site system  $\text{Nd}^{3+}$  in CZ KLYF have thus found a first application.

### Acknowledgments

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