

Comparative Fourier Spectroscopy of Ho^{3+} and Yb^{3+} in KYF_4 , BaY_2F_8 , and YLiF_4

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Abstract

Fourier spectroscopy gives accurate energy levels in (Ho,Yb) doped KYF_4 , BaY_2F_8 and LiYF_4 for upconversion energy transfer comparisons. The 1.7 K spectra reveal the presence of at least four sites in KYF_4 .

Yb, Ho upconversion energy transfer in different fluoride crystals has recently been compared[1] to demonstrate the promise of KYF_4 (KYF) as a host for green upconversion lasing as compared with BaY_2F_8 (BYF) and YLiF_4 (YLF). Here we compare the relevant energy levels and upconversion parameters determined from high resolution, low temperature absorption and photoluminescence spectra for the same three crystals.

Figure 1 presents a schematic of the upconversion process and defines parameters. Yb^{3+} ions are diode pumped (absorption A). Energy B is transferred to Ho^{3+} ions from excited Yb^{3+} ions in two steps, C and D, followed by emission in the green. Energy B-C should be small so that only a small number of phonons need be emitted in the first energy transfer. The energy δ should be large to prevent thermally activated back transfer. For all three crystals studied energy D is slightly larger than B, giving many pathways for an efficient second transfer. Energy A-D is a measure of the thermal energy needed for back transfer at the second stage; A-D should be large. The total Ho^{3+} ground term Stark splitting Δ_{Ho} should be large to minimize population of the terminal laser level.

Polarized transmission spectra from 500 to 22,000 cm^{-1} at a maximum resolution of 0.5 cm^{-1} were measured with a Bomem DA8 Fourier spectrometer. Photoluminescence, excited by a multiline Ar laser, was also measured by the Fourier spectrometer, which is

ideal for characterization of upconversion laser materials because of high frequency accuracy, being 0.004 cm^{-1} at 2000 cm^{-1} for the Bomem. Temperatures down to 1.7 K were achieved using a Janis Supravertemp, optical-access, liquid-helium cryostat with quartz or ZnSe windows.

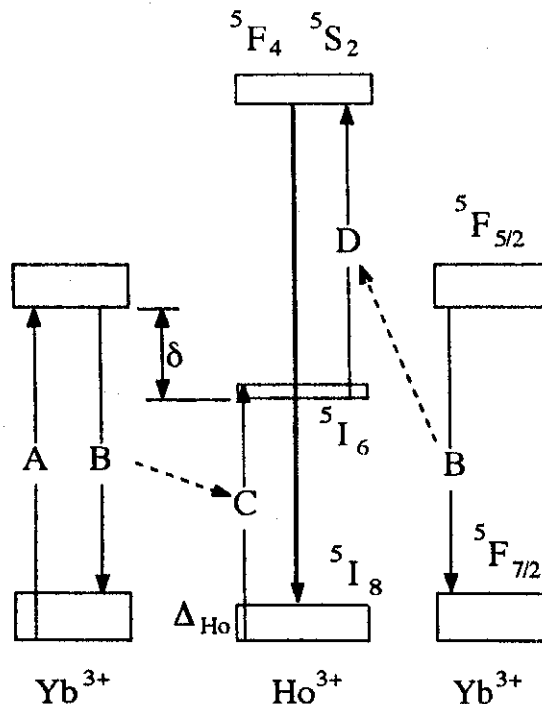


Figure 1. Schematic of upconversion process.

Figure 2 presents unpolarized $2F_{7/2} \rightarrow 2F_{5/2}$ transitions for Yb^{3+} in each of the three crystals at 1.7 K. These are the infrared transitions which are diode pumped to initiate upconversion. In each crystal, many

more lines appear than the three expected at this temperature. The frequency spread suggests that these are one-phonon side bands. With such heavy doping, pair lines are also likely. Multiple sites probably contribute[2] for KYF, for which recent X-ray analysis reveals six possible low-symmetry sites[3]. In contrast to YLF and BYF, no additional transitions (thermal replicas) appear at 80 K in the KYF spectrum from thermally populated ground-term Stark components. This, combined with the larger frequency spread of 1.7 K absorption features, indicates a larger crystal field splitting in KYF.

Figure 3 presents polarized $\text{Ho}^{3+} 5I_8 \rightarrow 5I_6$ transitions for the three fluoride crystals at 1.7 K. Energy from excited Yb^{3+} ions transfers to the $5I_6$ levels in the first stage of the upconversion process. The number of lines in the YLF and BYF spectra agree with the predictions of group theory for a single site of S_4 or C_2 symmetry, respectively. At least 40 lines are observed in the KYF spectrum, indicating that Ho^{3+} occupies at least four sites with differing crystal field strengths. The larger frequency spread of KYF lines suggest a crystal field splitting 2-3 times larger than in YLF or BYF.

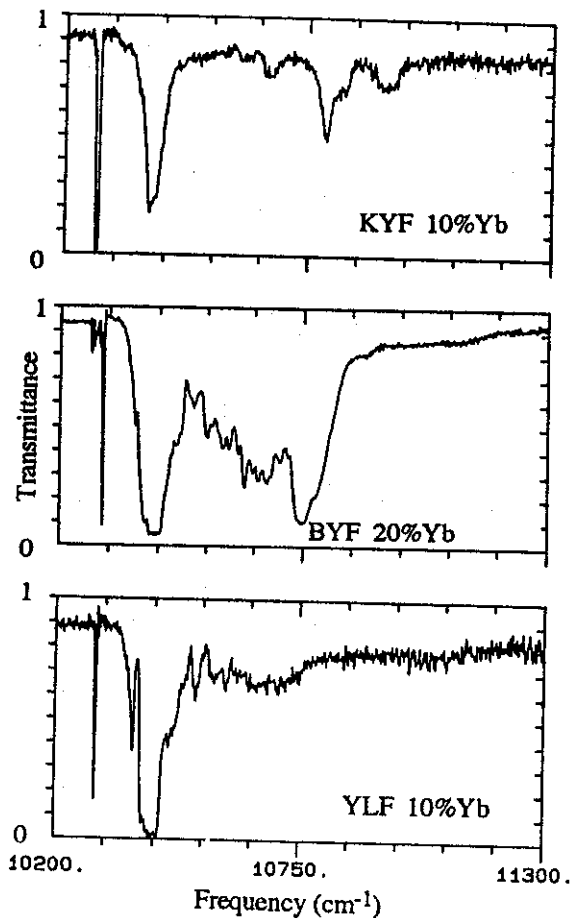


Figure 2. Unpolarized Yb^{3+} transmission spectra at 1.7 K. Sample thicknesses for YLF, BYF, and KYF are 1.5, 2.9, and 1.5 mm, respectively.

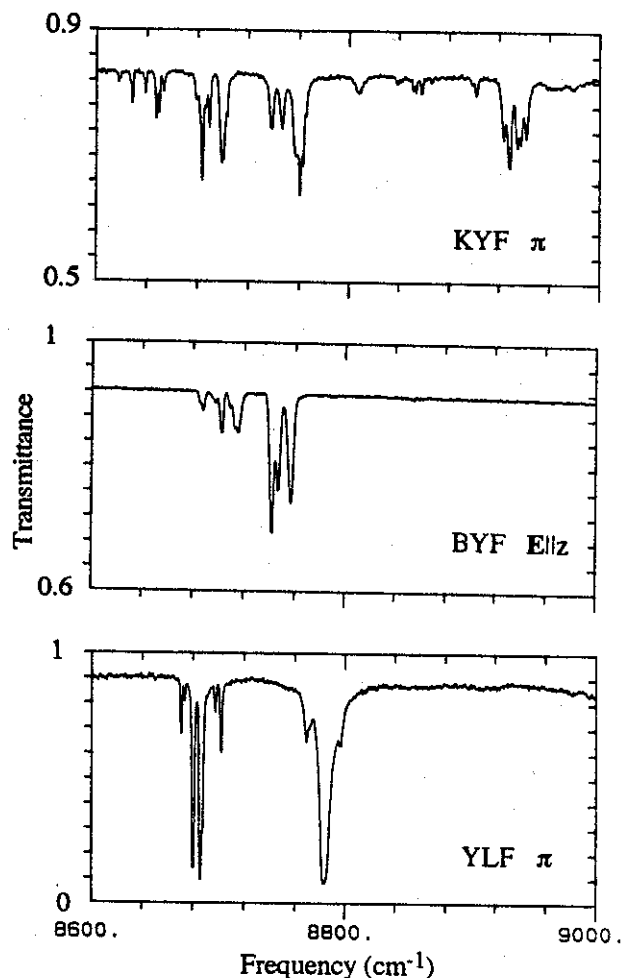


Figure 3. Polarized $\text{Ho}^{3+} 5I_8 \rightarrow 5I_6$ transmission spectra at 1.7 K. Concentrations and sample thicknesses for YLF, BYF, and KYF are 6, 0.1, 0.4 % and 4.7, 6.6, 6.4 mm, respectively.

Figure 4 presents transmission (4 to 8 K) and photoluminescence (80 K) in the green region for Ho^{3+} . The upper terms are $5F_4, 5S_2$. Polarizations are the same as in Fig. 3. For YLF and BYF the number of lines agrees with the predictions of group theory. (The weak absorption features on the high energy baseline of YLF are probably one-phonon side bands.) The large number of lines in the KYF spectrum and the relatively large frequency spread and small number of 80 K thermal replicas again suggest multiple sites and a larger crystal field splitting than for YLF or BYF. The energy difference between the lowest absorption line and the lowest photoluminescence line is the Ho^{3+} ground term splitting Δ_{Ho} .

Energy levels determined from these data are presented in Table 1.

Table 1. Ho³⁺ energy levels (cm⁻¹).

YLF	BYF	KYF		
5I_6				
8671.2	8685.9	8617.8	8699.4	8853.7
8673.7	8687.9	8619.2	8700.9	8858.4
8680.7	8695.4	8627.1	8703.6	8865.9
8686.3	8697.7	8628.8	8738.5	8899.0
8687.8	8702.8	8639.2	8746.8	8902.4
8697.8	8709.4	8646.7	8757.7	8923.9
8702.1	8713.0	8647.9	8760.9	8928.8
8769.1	8715.7	8650.0	8763.3	8935.1
8784.0	8728.5	8653.8	8766.0	8938.0
8796.8	8731.5	8679.8	8807.9	8942.3
	8742.4	8682.2	8838.6	8960.9
	8747.4	8684.2	8840.5	8978.6
	8757.4	8687	8842.3	
		8689.9	8851.5	
$^5S_2, ^5F_4$				
18490.7	18505.6	18440.5	18620.8	18776.4
18522.6	18519.1	18469.6	18629.0	18780.6
18533.6	18538.9	18474.2	18637.3	18788.2
18598.2	18550.0	18479.8	18653.6	18792.0
18605.9	18554.3	18492.9	18659.6	18797.3
18614.8	18589.0	18499.9	18673.6	18802.7
18678.5	18598.2	18515.1	18680.5	18827.8
18685.5	18649.6	18521.8	18690.9	18832.2
18700.9	18685.7	18534.7	18712.5	18834.1
18712.2	18696.6	18542.2	18716.9	18837.5
	18706.7	18582.1	18757.9	18874.8
	18718.0	18593.1	18769.3	18878.6
	18743.8	18604.0	18771.5	

Determination of Yb³⁺ levels from Fig. 2 is ambiguous; only the range of 1.7 K absorption can be stated. For YLF, BYF, and KYF, the range is 10289.5 to ~10910, 10270.2 to ~11120, and 10270.2 to 11060 cm⁻¹, respectively. The Yb³⁺ ground term Stark splitting is determined by comparing 1.7 K absorption to photoluminescence. This was done by us for KYF; for BYF and YLF we quote [4].

Table 2. Upconversion energy parameters (cm⁻¹)

parameter	YLF	BYF	KYF
B-C	1013	1055	711
δ	1619	1584	1652
A-D	470	450	447
Δ_{Ho}	341	413	383
Q	158	176	241

We now have enough information to determine the upconversion parameters discussed above. These are presented in Table 2. Energy B-C is significantly smaller for KYF than for BYF and YLF, so the A→B transfer is energetically more favorable in KYF. The back transfer parameter δ is larger for KYF than for BYF and YLF; for all three crystals δ is large compared with kT (200 cm⁻¹ at 300 K). The A-D backtransfer energy parameter is similar for all three

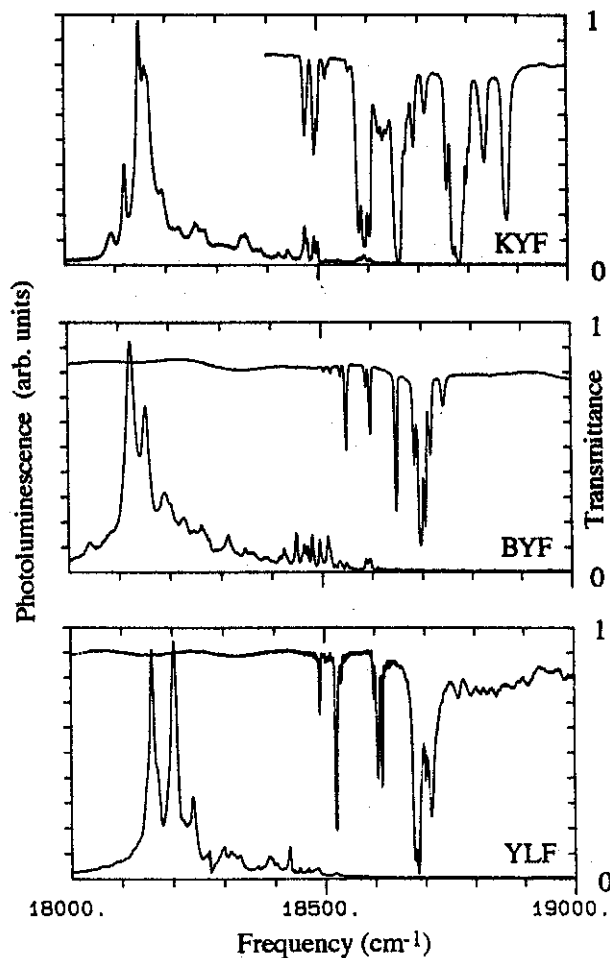


Figure 4. Transmission (5 - 8 K) and photoluminescence (80 K) in the green. The concentration in KYF is 0.8 %.

crystals, though slightly smaller for KYF. The Ho^{3+} ground term Stark splitting Δ_{Ho} for KYF is intermediate between YLF and BYF. We may define an upconversion quality factor $Q = \Delta_{\text{Ho}}(A-D)/(B-C)$, neglecting δ which is sufficiently large in all cases. Values for Q are presented in Table 2.

Combined with the work presented in [1], these Q values indicate that KYF is a better host for potential $\text{Yb} \rightarrow \text{Ho}$ room-temperature upconversion lasing than either BYF or YLF. We caution though that if the center of gravity for Stark splitting differs greatly for different KYF sites, the values presented in Table 2 may be misleading. We plan to study this problem in detail by site-selective photoluminescence Fourier spectroscopy. In addition, the parameter A-D insufficiently characterizes the back transfer problem, so we plan to study the overlap between normalized Yb^{3+} absorption and $\text{Ho}^{3+} 5F_4, 5S_2 \rightarrow 5I_6$ emission as a function of temperature.

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