



## Mid-infrared spectroscopy of Pr-doped materials

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### ABSTRACT

Solid state lanthanide doped lasers primarily operate in the ultraviolet, visible, near infrared and short-wavelength infrared out to around 2.1  $\mu\text{m}$ . At longer wavelengths, the transitions in conventional oxide crystal and glass materials become susceptible to multiphonon quenching due to their relatively large phonon energy. The use of low phonon materials can minimize the nonradiative quenching, opening up possibilities for solid state lanthanide lasers operating in the mid-infrared (MIR). This provides motivation to study the spectroscopy of lanthanide ions in bromide, chloride and fluoride materials, which have relatively low phonon energies. In this article, the MIR spectroscopy of praseodymium ions in five different host materials is studied, specifically  $\text{KPb}_2\text{Br}_5$  (KPB),  $\text{LaF}_3$ ,  $\text{KYF}_4$  (KYF),  $\text{BaY}_2\text{F}_8$  (BYF) and  $\text{YLiF}_4$  (YLF) host crystals. The MIR emission cross sections have been measured from 3 to 6  $\mu\text{m}$  and reciprocity of absorption and emission is utilized to validate the results. The lifetime dynamics in the MIR are covered for various pump and emission wavelengths. Results are also presented on MIR emission from 6.5 to 8.5  $\mu\text{m}$  in a Pr: KPB crystal, which, to the best of the authors knowledge, is the first such measurement of luminescence in this wavelength range that has been published. © 2018 Elsevier Science. All rights reserved

### 1. Introduction

Most lanthanide doped solid-state materials can produce laser wavelengths in the near-infrared (NIR) from 0.75 to 1.4  $\mu\text{m}$ , or short wavelength infrared (SWIR) from 1.4 to 3  $\mu\text{m}$ . However, it becomes increasingly difficult to generate wavelengths in the mid-wavelength infrared (MWIR) from 3 to 8  $\mu\text{m}$  and beyond. We use the term mid-infrared (MIR) to specifically refer to the MWIR wavelength range [1]. The great challenge in solid-state lasers for MIR operation is finding materials that offer low phonon energies. Solid-state lasers that have wavelengths longer than about 3  $\mu\text{m}$  are usually quenched by non-radiative processes, resulting from the generation of phonons, which are the quanta of the crystal lattice vibrations. When the energy gap between two adjacent manifolds is less than about 5 times the maximum phonon energy, the nonradiative transitions results in luminescence quenching of the upper manifold. Hence, developing efficient MIR lasers with wavelengths longer than about 3  $\mu\text{m}$  requires host materials with relatively low phonon energy. These typically include halide crystals (bromide, chloride and fluoride), sulfides (thiogallates) and glass materials like chalcogenides that can also be used.

Towards developing viable lasers in the MIR, we have investigated

the spectroscopy of Praseodymium ( $\text{Pr}^{3+}$ ) ions in five host materials from 3 to 6  $\mu\text{m}$ . The host materials investigated are  $\text{KPb}_2\text{Br}_5$  (KPB),  $\text{LaF}_3$ ,  $\text{KYF}_4$  (KYF),  $\text{BaY}_2\text{F}_8$  (BYF) and  $\text{YLiF}_4$  (YLF), which have maximum phonon energies of 138, 392, 350, 415 and 490  $\text{cm}^{-1}$ , respectively [2–6]. The Pr emission from 3 to 6  $\mu\text{m}$  is complicated by the fact that several different possible channels for the emission exists, including the  $^3\text{F}_4 \rightarrow ^3\text{F}_2$ ,  $^3\text{F}_3 \rightarrow ^3\text{H}_6$ ,  $^3\text{H}_6 \rightarrow ^3\text{H}_5$  and  $^3\text{H}_5 \rightarrow ^3\text{H}_4$ . To narrow the contributing channels, pump sources at 1.55  $\mu\text{m}$  and 1.9  $\mu\text{m}$  were used to excite the samples, but there was virtually no difference in the observed spectra. The 3–6  $\mu\text{m}$  Pr emission, therefore, is likely due to just the  $^3\text{H}_6 \rightarrow ^3\text{H}_5$  and the  $^3\text{H}_5 \rightarrow ^3\text{H}_4$  transitions. The measurements conducted include emission cross sections and lifetime dynamics. Reciprocity of absorption and emission is also used to validate the emission measurements with good agreement being found for all materials investigated.

Regarding applications, laser demonstrations in the MIR remain in their infancy, with very few examples to date. Efforts to develop MIR lanthanide based solid state lasers can be of substantial benefit in producing sources for the spectral ranges 3–8  $\mu\text{m}$ , a region that is rich in many atmospheric molecular gasses [1]. The impact is clear, and in the MIR region, broad spectral coverage buys access to chemical

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**Table 1**  
Atomic and crystallographic parameters.

Crystal Formula	Crystal Name	Crystal System	Space Group	Dopant Site	$N_c$	$N_f$	Lattice Parameters (Å)			Angular Parameters			$N_S$ ( $\times 10^{22}$ cm $^{-3}$ )
							a	b	c	$\alpha$	$\beta$	$\gamma$	
KPb <sub>2</sub> Br <sub>5</sub>	KPB	Monoclinic	14	Pb <sup>2+</sup>	2	4	9.256	8.365	13.025	90	~ 90	90	0.793
LaF <sub>3</sub>	LaF3	Trigonal	165	La <sup>3+</sup>	1	6	7.185	–	7.351	90	90	120	1.826
KYF <sub>4</sub>	KYF	Trigonal	144	Y <sup>3+</sup>	1	18	14.060	–	10.103	90	90	120	1.041
BaY <sub>2</sub> F <sub>8</sub>	BYF	Monoclinic	12	Y <sup>3+</sup>	2	2	6.983	10.519	4.264	90	99.7	90	1.304
YLiF <sub>4</sub>	YLF	Tetragonal	88	Y <sup>3+</sup>	1	4	5.166	–	10.733	90	90	90	1.396

"fingerprints," where molecules can be detected and distinguished with great sensitivity. In fact, the region of the MIR from 3 to 5  $\mu\text{m}$  is one of the "fingerprint regions" of interest for remote sensing.

## 2. Low phonon materials

The Pr-doped crystalline materials studied in this article were chosen for their relatively low phonon energies [2–6]. They consist of 1 bromide (KPB) and 4 fluorides (LaF<sub>3</sub>, KYF, BYF and YLF). In the case of the fluoride crystals, the Pr<sup>3+</sup> ions substitute for La<sup>3+</sup> in LaF<sub>3</sub>, and Y<sup>3+</sup> in KYF, BYF and YLF. For the bromide crystals (KPB), the Pr<sup>3+</sup> ions substitute for Pb<sup>2+</sup> with charge compensation. There are two nonequivalent octahedral sites for the Pb<sup>2+</sup> ions, but the predominant one is observed to be octahedral with a coordination number of CN = 6. The KPB and BYF crystals are biaxial, while the LaF<sub>3</sub>, KYF and YLF crystals are uniaxial. Table 1 gives the crystallographic and atomic parameters for KPB, LaF<sub>3</sub>, KYF, BYF and YLF [7–11]. In this table,  $N_c$  is the number of atoms in the atomic formula of the crystal for which the dopant ion replaces,  $N_f$  is the number of formula units per unit cell of the crystal. The lattice parameters of the unit cell are a, b, c, and the angular parameters of the unit cell are  $\alpha$ ,  $\beta$ ,  $\gamma$ . These parameters can be used to calculate the site density,  $N_S$ , of the available dopant sites as follows:

$$N_S = \frac{N_c N_f}{V_c} \quad (1)$$

where  $V_c$  is the volume of the unit cell. For monoclinic crystals,  $V_c = abc(\sin \beta)$ , for trigonal crystal symmetry with hexagonal axes,  $V_c = (3/4)^{1/2} a^2 c$ , and for tetragonal crystals,  $V_c = a^2 c$ . From these formulas for  $V_c$  and the values of  $N_c$  and  $N_f$ , the site densities,  $N_S$ , are calculated in Table 1. The concentration density of the dopant ions,  $N_D$ , is then found by multiplying the fractional concentration,  $C_S$ , by the site density, that is,  $N_D = C_S N_S$ , in units of 1/cm<sup>3</sup>.

## 3. Experiment

Transmission spectra were recorded with a Perkin-Elmer Frontier Optica FT-IR spectrophotometer in the range 3–6  $\mu\text{m}$  at room temperature. A wire grid polarizer was used in the sample chamber to record polarized spectra. The transmission data was corrected for Fresnel losses at the sample faces and used to obtain the absorption cross section. For continuous luminescence measurements, a 1.5  $\mu\text{m}$  erbium doped fiber amplifier (EDFA) and a 1.9  $\mu\text{m}$  diode laser were used as pump sources. The collected luminescence was focused by a CaF<sub>2</sub> lens on the slit of a 0.5-meter SPEX monochromator after passage through a chopper providing the reference signal for a lock-in amplifier. The grating was 150 gr/mm blazed at 5.0  $\mu\text{m}$ . Detection of the signal was achieved with a liquid nitrogen cooled Judson J15D12 mercury cadmium telluride (MCT) detector. A Stanford Research Systems model SR530 DSP lock-in amplifier was used for signal amplification and digitization. The digitized signal was collected by scanning software on the computer for storage. Polarization selection of the luminescence signal was achieved by placing a wire grid polarizer between the focusing lens and the entrance slit of the spectrometer. Appropriate cut-off filters discriminated against wavelengths below ~3  $\mu\text{m}$ . A Mercury

(Hg) lamp was used to calibrate the wavelength and an Oriel blackbody source, model 67036, was used to correct for grating efficiency, detector response and other optical elements of the system. Lifetimes were measured using a VIBRANT (HE) 355 II OPO pulsed laser source, tunable from 0.4 to 2.4  $\mu\text{m}$ , and an MCT detector and amplifier combination signal was processed by a digital oscilloscope for storage. Narrow band filters were used to select the wavelength of the luminescence. Concentrations of the Pr doping is 1.0%, 1.5%, 1.25%, 1.0% and 1.0% in KPB, LaF<sub>3</sub>, KYF, BYF and YLF samples, respectively.

## 4. Results

The most general form for the emission cross section using the beta-tau method is the following [12],

$$\sigma_p(\lambda) = \frac{\lambda^5}{8\pi c n^2 (\tau_r/\beta)} \frac{I_p(\lambda)}{\int \frac{1}{3} [I_a(\lambda) + I_b(\lambda) + I_c(\lambda)] \lambda d\lambda} \quad (2)$$

where p is the polarization. n is the index of refraction,  $\tau_r$  is the radiative lifetime and  $\beta$  is the branching ratio. For isotropic crystals a = b = c, while for uniaxial crystals a = b, and for biaxial crystals a, b and c are unique. The crystals in this study are uniaxial and biaxial. For the case of uniaxial crystals there is  $\pi$  (E || c) and  $\sigma$  (E  $\perp$  c) polarization, denoting whether the electric field of the luminescence is parallel to or perpendicular to the c-axis, respectively. For biaxial crystals, there are E || a, E || b and E || c, denoting the polarizations for the electric field of the luminescence parallel to the respective axis.

The absorption cross sections for a given polarization is determined with knowledge of the dopant concentration and absorption path length according to [12],

$$\sigma_{abs}(\lambda) = -\frac{1}{C_S N_S l} \ln \left[ \left( \frac{n^2 + 1}{2n} \right) T(\lambda) \right] \quad (3)$$

where  $N_S$  is the site density available to the dopant ion,  $C_S$  is the fractional dopant concentration in percent/100, l is the absorption path length, n is the index of refraction, and T( $\lambda$ ) is the transmission of the sample as measured by the spectrophotometer. The factor  $(n^2 + 1)/2n$  accounts for the Fresnel reflections at the surfaces of the crystal. Refractive index values are found in the literature [2,12–14]. Values for KYF were not available, so refractive index values for YLF were used instead.

The emission and absorption cross sections are related through a reciprocity relation requiring some knowledge of the energy levels of the ground state manifold and an excited state manifold [12],

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_l}{Z_u} \exp \left( \frac{E_{ZL} - hc/\lambda}{kT} \right) \quad (4)$$

where  $Z_l$  and  $Z_u$  are the partition functions of the lower and upper manifolds, respectively.  $E_{ZL}$  is the zero-line energy, defined as the energy difference between the lowest Stark levels of the upper and lower manifolds. k is Boltzmann's constant and T is the temperature.

Polarized emission spectra were measured in the region from 3 to 6  $\mu\text{m}$ . The spectra were corrected for system response (grating efficiency, detector response and other elements of the collection system)

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