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Slow Nonradiative Decay for Rare Earths in KPb_2Br_5 and $RbPb_2Br_5$

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Abstract: We report on spectroscopic investigations of Nd^{3+}- and Tb^{3+}- doped low phonon energy, moisture-resistant host crystals, KPb_2Br_5 and $RbPb_2Br_5$, and their potential to serve as new solid state laser materials at new wavelengths, especially in the long wavelength infrared region. This includes emission spectra, emission lifetime measurements, Raman scattering spectra as well as calculations of the multiphonon decay rate, radiative lifetimes and quantum efficiencies for relevant (laser) transitions in these crystals.
OCIS codes: (160.5690) Rare earth doped materials; (140.3380) Laser materials

1. Introduction

Potassium lead chloride (KPb_2Cl_5 or KPC) has been identified as a moisture resistant, low phonon energy host for mid-IR-applications [1,2]. KPC has been lased with the rare earth ions Nd^{3+} (1.06 μm), Dy^{3+} (2.43 μm), and Er^{3+} (1.7 μm, 4.5 μm) [3-5]. The longest achieved wavelength in a solid state laser material is 7.2 μm, using a lanthanum chloride ($LaCl_3$) host doped with Pr^{3+} [6], which has the disadvantage of being highly hygroscopic. The host crystals, potassium lead bromide (KPb_2Br_5 or KPB) and rubidium lead bromide ($RbPb_2Br_5$ or RPB) reported in this paper evidence similar properties to KPC but with the added advantage of even lower phonon energy. This will minimize the nonradiative decay due to multiphonon interactions, in principle permitting lasing in the long wavelength region. Here, we report on the spectroscopic investigation of Nd^{3+} doped KPB and RPB as well as Tb^{3+} doped KPB with respect to their potential to serve as new solid state laser materials.

Single crystals (up to 50 mm long) of KPB and RPB doped with Nd^{3+} were mainly grown at the Design and Technological Institute for Monocrystals by the Bridgman technique from a stoichiometric mixture. The Tb^{3+} doped KPB crystals (up to 60 mm long) were mainly grown at Fisk University and EIC Laboratories. The KPB crystal is biaxial and has a monoclinic crystal structure. RPB is negative uniaxial and has a tetragonal crystal structure [7].

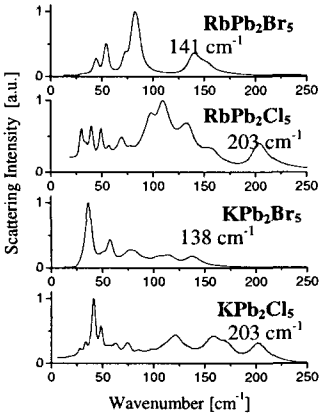

Fig. 1. Raman scattering spectra: the maximum phonon energy (highest energy peak value) in the MPb_2Br_5 crystals (M= K, Rb) is with 138 cm^{-1} or rather 141 cm^{-1} even lower than in the MPb_2Cl_5 crystals (203 cm^{-1}).

2. Spectroscopic results of RE^{3+} doped KPb_2Br_5 and $RbPb_2Br_5$

The Raman spectra of MPB (M=K, Rb) and MPC are shown in Fig. 1. The maximum phonon energy of KPB and RPB (Institute of Physics, Academy of Sciences of the Czech Republic) is 138 cm^{-1} and 141 cm^{-1} respectively. The phonon energy for $RbPb_2Cl_5$ (203 cm^{-1}) was measured from a single RPC crystal to be the same as the phonon energy of KPC [8]. The bromide phonon frequencies are reduced by a factor of 1.5 compared to the chlorides, which is close to the change predicted on the basis of the masses of the bromide and chloride ions.

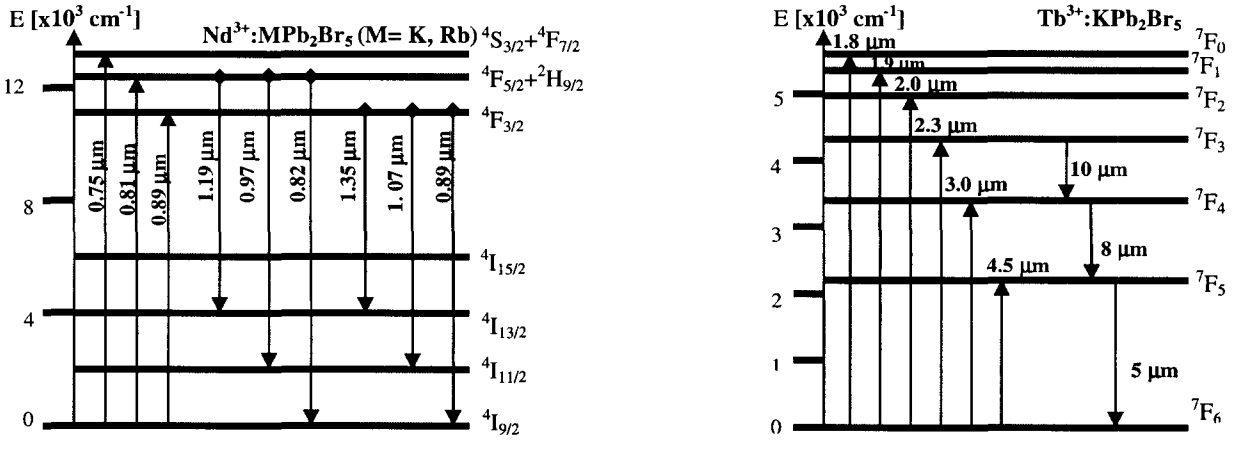

Fig. 2. The energy level diagram of Nd:MPB (M= K, Rb) displays the possibility of pumpable, new laser transitions from the ($^4F_{5/2}$+ $^2H_{9/2}$) level beside the transitions resulting from the $^4F_{3/2}$ level. The energy level diagram of Tb:KPB displays the possibility of direct pumping of long-wavelength transitions.

The energy level diagram of Nd:MPB (M= K, Rb) (Fig. 2) displays the possibility of pumpable, new laser transitions from the ($^4F_{5/2}$+ $^2H_{9/2}$) level beside the transitions resulting from the $^4F_{3/2}$ level. The emission spectra of a Nd:KPB crystal and a Nd:RPB crystal (Fig. 3) were obtained by excitation of the

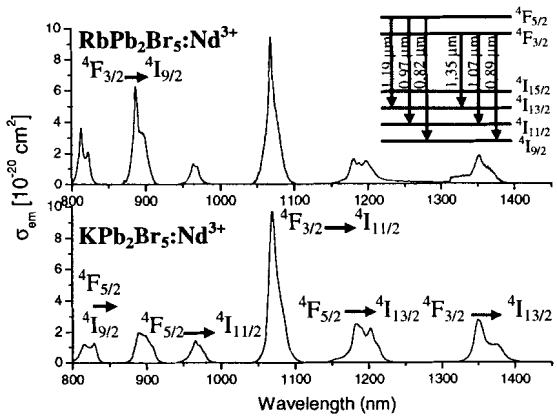

Fig. 3. Corrected room temperature emission spectra obtained by excitation of the $^4F_{7/2}$ level of Nd^{3+} doped MPb_2Br_5 (M=Rb, K) crystals.

$^4F_{7/2}$ level at 0.75 µm (Fig. 2). The emission cross section was determined with the Fuechtbauer-Ladenburg equation by using branching ratios determined from the emission spectrum and radiative lifetimes (Tab. 1) obtained through a Judd-Ofelt calculation [8, 9]. The comparatively high emission originating on the ($^4F_{5/2}$+ $^2H_{9/2}$) level, compared to the Nd:KPC crystal [8], demonstrates the reduced multiphonon decay due to lower phonon energy, which is encouraging for proving laser activity at these new wavelengths (e.g. at 1.19 µm). From these emission spectra we determined the quantum efficiency of the ($^4F_{5/2}$+ $^2H_{9/2}$) level to be 0.44 for Nd:KPB and 0.71 for Nd:RPB. This is considerably higher than the value of 0.013 reported for Nd:KPC [8]. The decays from the combined ($^4F_{5/2}$+ $^2H_{9/2}$) level and the $^4F_{3/2}$ level of Nd^{3+} doped MPB (M=Rb, K) were deduced with an exponential fit (Tab. 1). These are longer than the 2 µs (Table 1) or 3.4 µs [8] lifetime of the analogous transition resulting from the ($^4F_{5/2}$+ $^2H_{9/2}$) level in Nd:KPC since multiphonon decay competes less effectively with the radiative rate.

Table 1. Measured decay times τ^{meas} and radiative lifetimes τ^{rad} of the ($^4F_{5/2}$+$^2H_{9/2}$) level and the $^4F_{3/2}$ level of MPb_2X_5:Nd^{3+} (left). Measured decay times τ^{meas}, calculated radiative lifetimes τ^{rad} and radiative quantum efficiencies η_{eff} for different KPb_2Br_5:Tb^{3+} crystal samples (right).

Energy level	τ^{meas} (µs), (τ^{rad} (µs))		
	Nd:KPb$_2$Br$_5$	**Nd:RbPb$_2$Br$_5$**	**Nd:KPb$_2$Cl$_5$**
$^4F_{3/2}$	145 (126)	119 (115)	255
$^4F_{5/2}$+$^2H_{9/2}$	124 (208)	126 (214)	2

Energy level	τ^{meas} (ms)	τ^{rad} (ms)	η_{eff}
	Tb:KPb$_2$Br$_5$		
$^7F_4$	0.19- 0.42	13	0.02-0.03
$^7F_5$	3-22	36	0.08-0.60

The corrected emission spectra (Fig. 4) of Tb:KPB were measured by pumping into the $^7F_2$ level (Fig. 2) at ~ 2 µm. The emission cross section was determined with the Fuechtbauer-Ladenburg equation by using branching ratios and radiative lifetimes (Table 1) obtained by Judd-Ofelt calculation. Especially the broadband 8 µm emission spectrum is encouraging for the goal of a tunable LWIR-laser for remote sensing in the vibrational fingerprint region. The emission lifetimes for the $^7F_4$- and $^7F_5$- level (Table 1) were taken for six Tb^{3+} doped KPB samples of different concentrations (0.35-2.2 $\cdot 10^{20}$ cm^{-3}) and grown under different growth conditions by pumping into the $^7F_2$ level. The variation of the lifetimes and quantum efficiencies (Table 1) for the studied samples is likely due to impurities in the crystals and/or concentration dependent effects. The emission lifetime of the $^7F_4$ level is shorter than the $^7F_5$ level because of the smaller energy gap. The 3 µm and 8 µm emissions both originating from the $^7F_4$ level

have the same lifetime. The long emission lifetime due to the low phonon energy for the $^7F_5$ level with several ms and the $^7F_4$ level lifetime in the μs range is encouraging for proving laser activity in these crystals in the LWIR region.

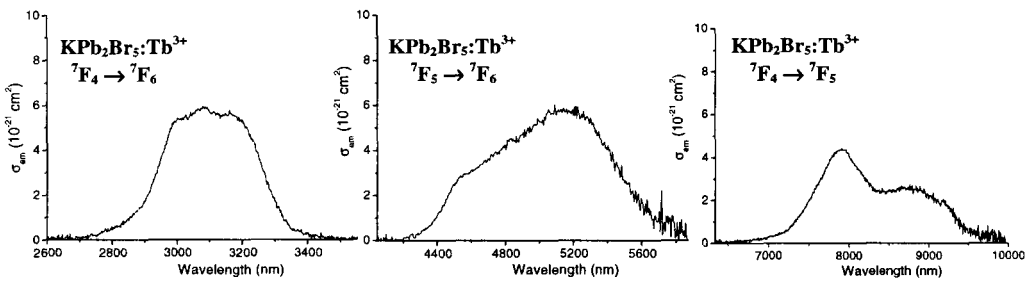

Fig. 4. Corrected room temperature emission spectra around 3 μm, 5 μm and 8 μm resulting from the $^7F_5$ and $^7F_4$ levels in Tb^{3+} doped KPb_2Br_5.

The multiphonon decay rate (estimated by the energy gap law [8]) versus the energy gap to the next lowest level is shown in Fig. 5 for KPb_2Br_5 in comparison to different bromide, chloride and fluoride host lattices [8,9]. The measured values of the nonradiative rate in rare earth doped KPB are indicated with triangles. They are calculated by substracting the radiative rate $1/\tau^{rad}$ from the measured rate $1/\tau^{meas}$ by neglecting the concentration dependent component of the decay. Here, the radiative lifetimes of 208 μs for Nd^{3+} and 12.5 ms for Tb^{3+}, and the measured lifetimes of 124 μs for Nd^{3+} and 360 μs for Tb^{3+}, were used. The smallest energy spacing of the $^4F_{5/2}+^2H_{9/2}$ - $^4F_{3/2}$ transition in Nd^{3+} doped KPB was assumed to be 974 cm^{-1} due to first low temperature Stark level measurements of these levels. The energy gap of the $^7F_4$- $^7F_5$ transition in Tb^{3+} doped KPB was determined to be 1070 cm^{-1} by taking the maximum emission wavelength of the 8 μm emission spectrum (Fig. 4).

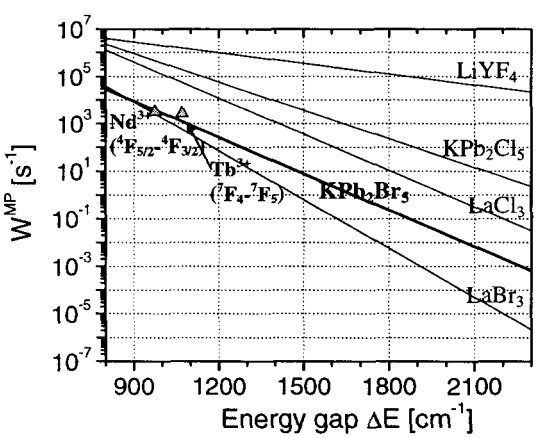

Fig. 5. Multiphonon decay rate versus energy gap between two levels for different host lattices determined by the energy gap law [8]. The measured value of the nonradiative rate in rare earth doped KPB is calculated by substracting the radiative rate $1/\tau^{rad}$ from the measured rate $1/\tau^{meas}$ The values are indicated with triangles.

3. Summary

We have identified, grown and studied two novel low phonon energy host crystals MPb_2Br_5 (M= Rb, K) doped with the rare earth ions Nd^{3+} and Tb^{3+}. Higher quantum efficiencies have been achieved in the

bromide host crystals compared to the KPC host crystal for transitions from the ($^4F_{5/2}$+$^2H_{9/2}$) level into the ^4I_J levels in Nd^{3+} doped bromide crystals as well as for the LWIR emission from the ^7F_J levels around 3 μm, 5 μm and 8 μm in Tb:KPB. The nonradiative decay competes less effectively compared to the radiative rate in these rare earth doped bromide host crystals. The moisture resistant property of these bromide crystals, the potential to incorporate rare earth ions, and their low phonon frequency render them potentially useful laser crystals.

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