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Infrared Up-Conversion Emission Observed in Ho^{3+}-Doped Potassium Lead Chloride

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Abstract

In this work, we present the infrared emission properties of Ho^{3+} doped KPb_2Cl_5. Following optical excitation at 907nm, we observed several IR emission bands with center wavelengths at 1.064μm, 1.2μm, 1.33 μm, 1.67μm, 2.9μm and 3.9μm. While the 1.2μm, 1.67μm, 2.9μm and 3.9μm are from known energy transitions, the transitions leading to the 1.064μm and 1.33 μm emissions are not immediately obvious. Analysis of the transition mechanism suggests that these 'unknown transitions' are possible infrared up-conversion arising from excited state absorption.

Keywords: Lasers, fluorescence, up-conversion, excited state absorption, multi-phonon relaxation.

1. Introduction

Trivalent Holmium (Ho^{3+}) doped crystals and glasses continue to attract interest as suitable gain media for solid-state lasers with laser transitions ranging from the visible (0.55 μm) to the mid-infrared (3.9 μm) spectral region (Wang *et al.*, 2007). The favourable energy level structure of Ho^{3+} leads to several important infrared (IR) laser transitions in the NIR and MIR spectral regions (Kirkpatrick *et al.*, 1997). That such emissions could arise from the doped crystal emanates from the absorption peaks introduced by the dopant ions into the otherwise transparent KPb_2Cl_5 host (Henderson and Imbusch, 1989), making it possible for the crystal to be excited to energy levels from where spontaneous emissions can arise (Kirkpatrick *et al.*, 1997). The spectra of trivalent rare earth (RE) ions in crystals are interpreted using the systematic spectral measurements made of RE^{3+} ions in the Lanthanide Chloride ($LaCl_3$) host by Dieke and Crosswhite (1963) and presented in the so called Dieke energy level diagram

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shown in figure 1. From this, energy transitions corresponding to Ho^{3+} absorption peaks obtained from the transmission studies are shown in figure 2. Excitation to any of the energy levels above the ground state can result in spontaneous emission, depending on the phonon spectrum of the host matrix (Kenyon, 2002). Such emission sometimes arises in the form of up-conversion.

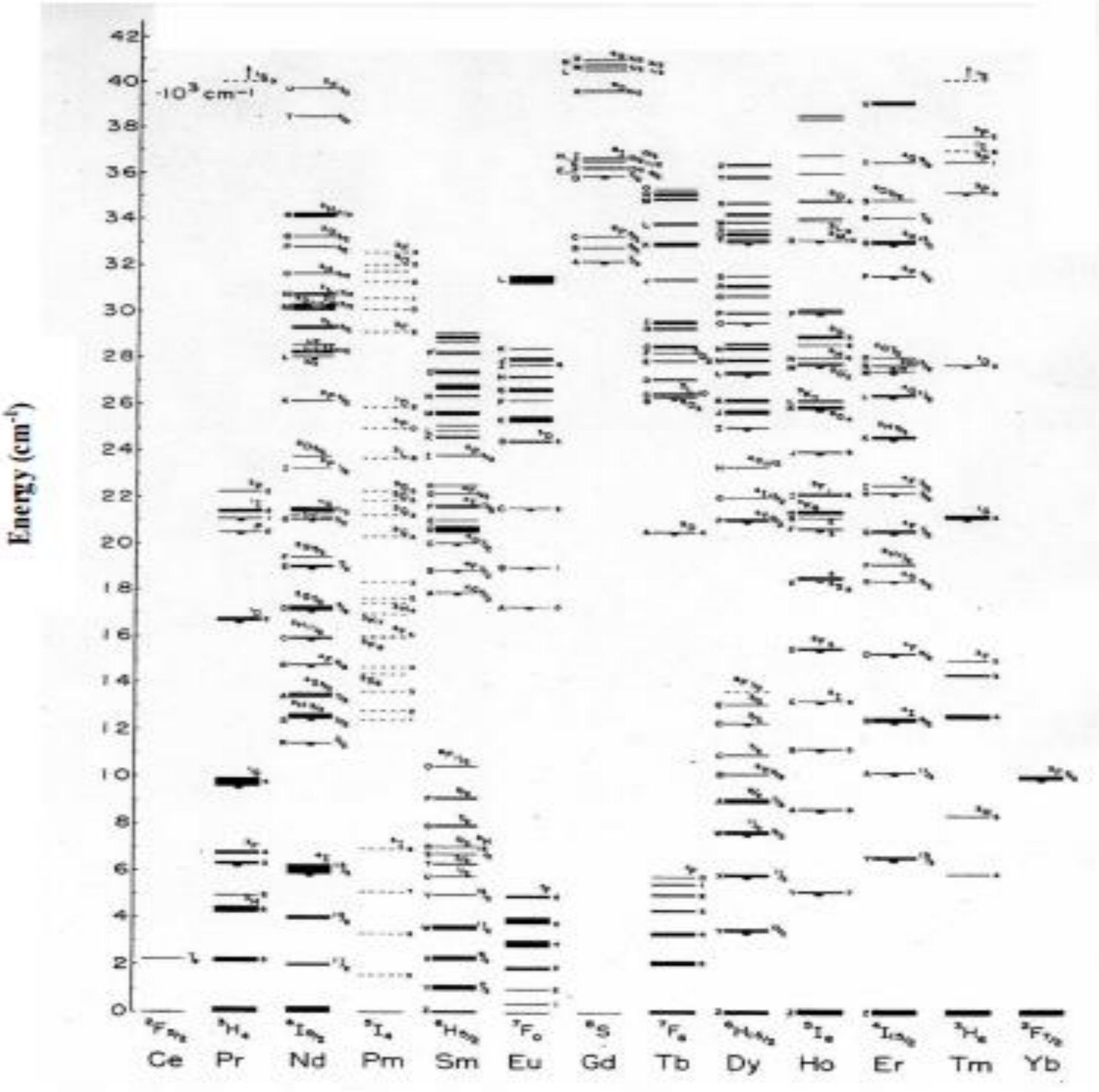

Figure 1: An energy level diagram of trivalent rare earth ions in $LaCl_3$ (Dieke and Crosswhite, 1963).

Up-conversion is the conversion of excitation light into emissions of shorter wavelengths in luminescent materials (Lisiecki *et al.*, 2004). Frequency up-conversion of infrared to visible radiation in rare-earth doped materials has been a subject of extensive research interest and has been widely reported in literature (Balda *et al.*, 2002). The interest in up-conversion research is mainly due to the need for visible laser sources pumped by NIR sources for a variety of applications, including high capacity data storage optical devices, bar-code reading, submarine communications, laser printing, and biotechnology (Som and Karmakar, 2009).

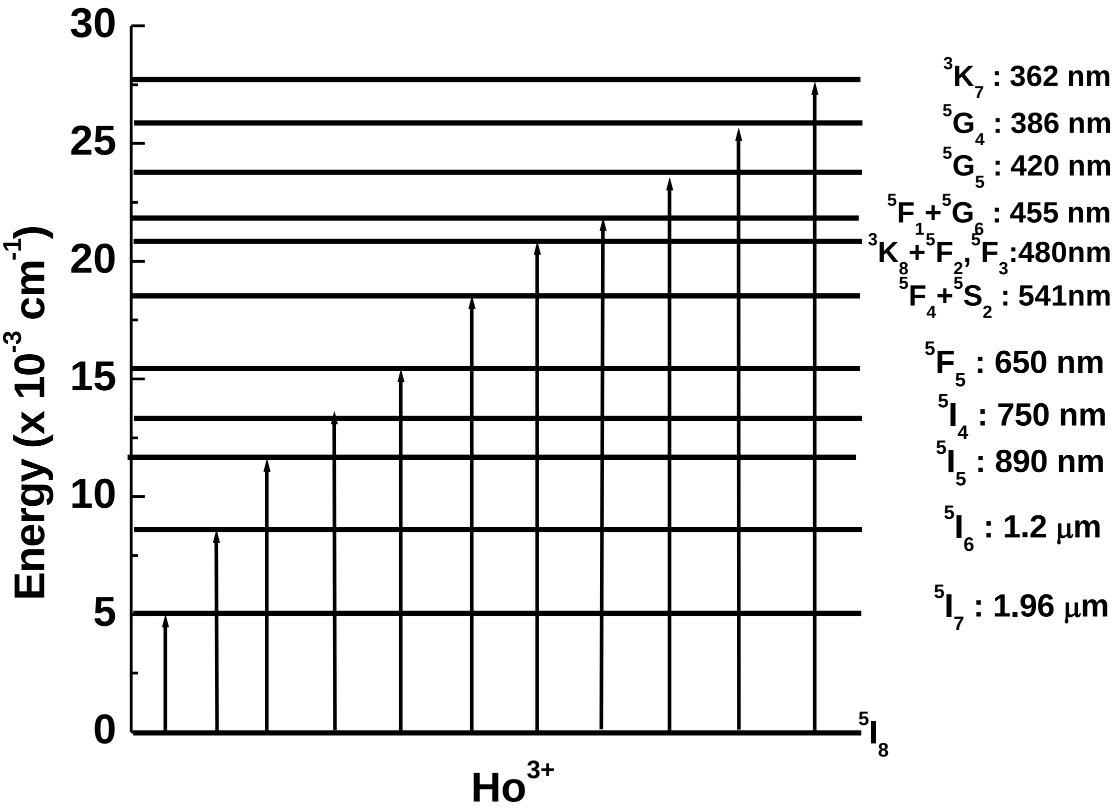

Figure 2: Energy transitions corresponding to Ho^{3+} absorption peaks.

2. Experiment

The details of the material synthesis and growth of Ho^{3+}:KPb$_2$Cl$_5$ (Ho^{3+}:KPC) have been described elsewhere (Oyebola *et al.*, 2010). The absorption peaks shown in figure 2 were obtained from transmission studies carried out with a Cary 5000 UV-VIS-NIR spectrophotometer. The observed transmission data were converted to absorption coefficients using the Beer-Lambert law. Subsequent emission studies were carried out by pumping resonantly into the $^5I_5$ level with a tunable Ti-Sapphire laser operating at ~ 907 nm. Under this pumping scheme, near infrared (NIR) emissions are observed from 1.0 – 1.8 µm using a RG 1000 filter, while mid infrared (MIR) emissions are observed from 1.8 – 3.4 µm using a LP1850 filter and from 2.7 – 4.5 µm using a LP2500 filter. The calibrated NIR – MIR emission spectra of Ho^{3+}: KPC are shown in figure 3, revealing emission bands with center wavelengths at 1.06 µm, 1.2 µm, 1.33 µm, 1.66 µm, 2.0 µm, 2.89 µm, and 3.9 µm.

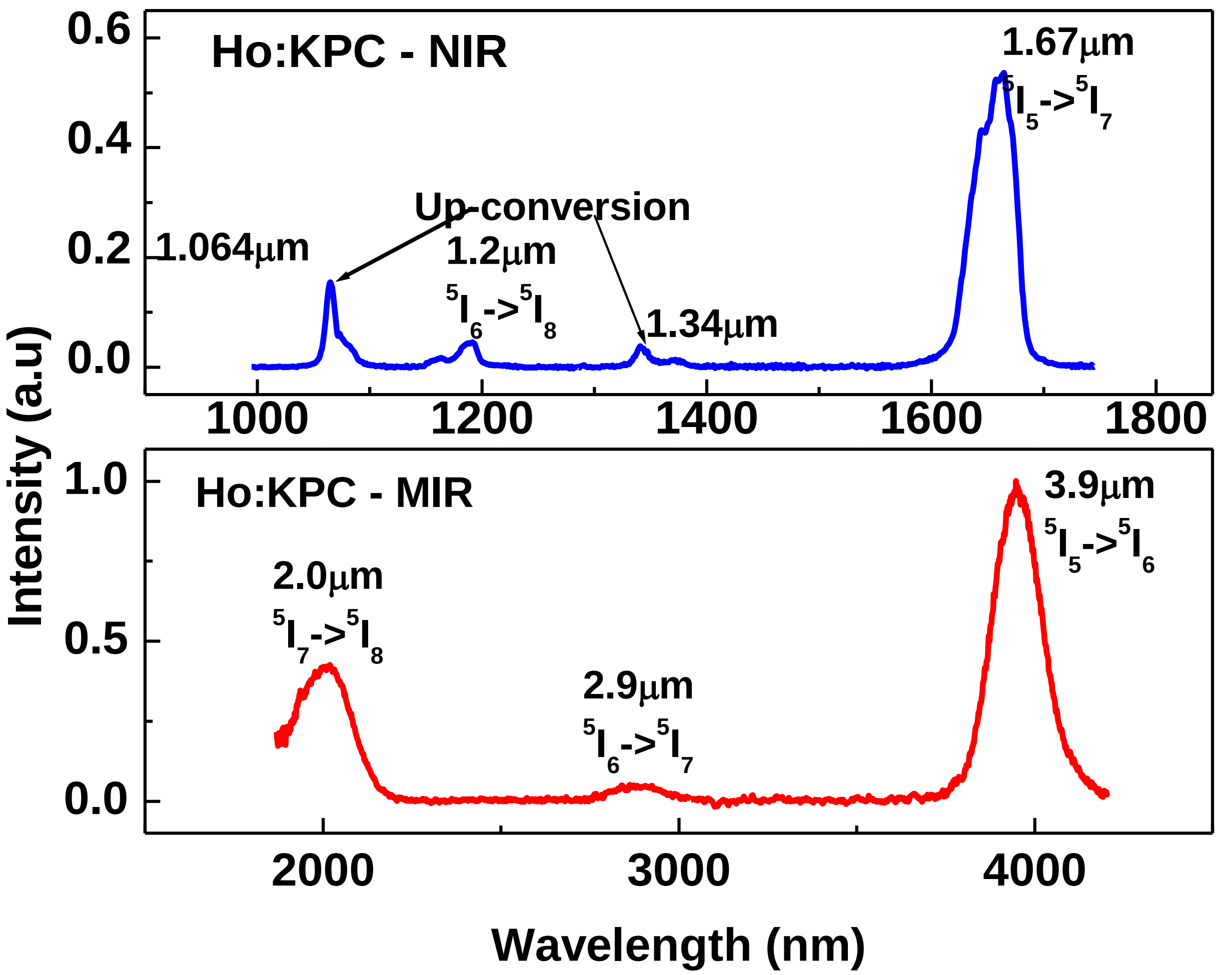

Figure 3: Calibrated near- and mid-IR emission spectra of Ho^{3+}: KPC, excited at 907 nm.

The corresponding Ho^{3+} transitions are given in figure 4. The 1.2 µm and 1.66 µm emissions are the main near-IR emissions observed, arising from the transitions $^5I_6 \rightarrow {}^5I_8$ and $^5I_5 \rightarrow {}^5I_7$, respectively.

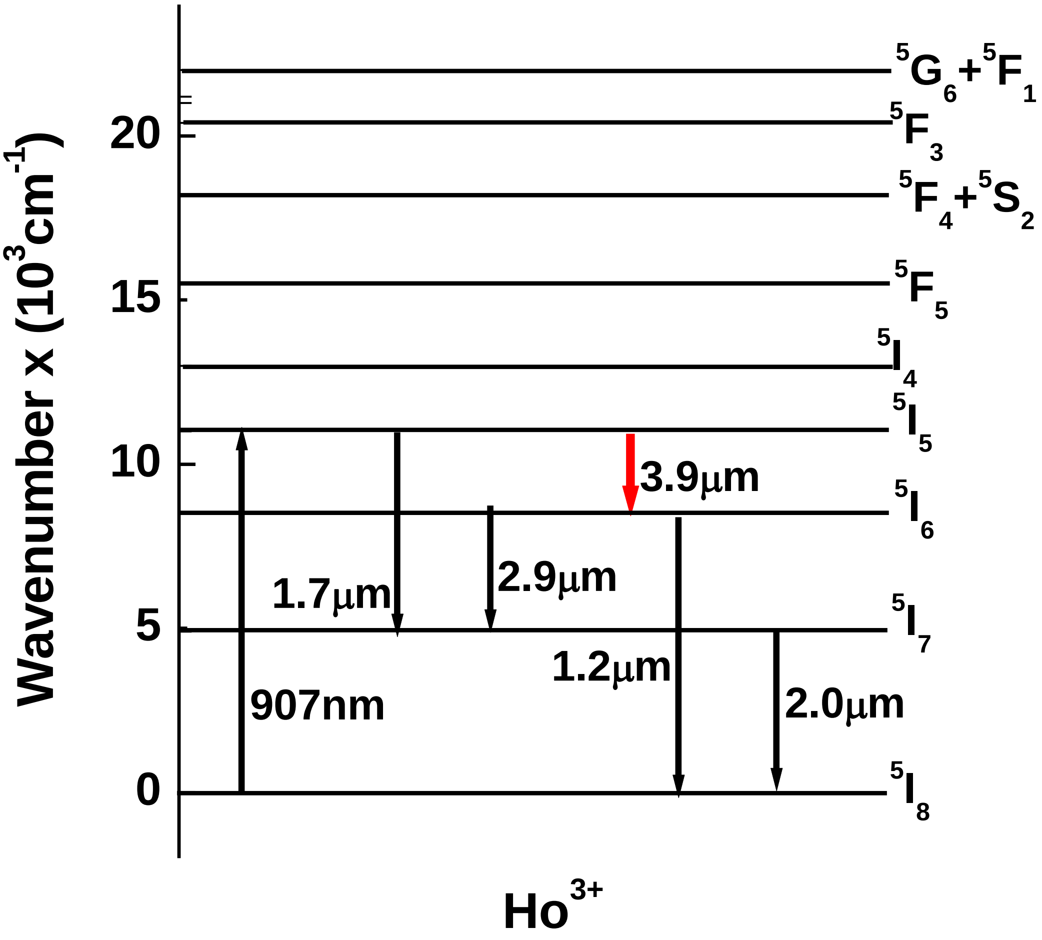

Figure 4: Energy level diagram of Ho^{3+} with emission transitions at near- and mid-IR wavelengths under 907 nm pumping.

The emission bands of 2.0 µm, 2.89 µm and 3.9 µm are three mid-IR emissions arising from the $^5I_7 \rightarrow {}^5I_8$, $^5I_6 \rightarrow {}^5I_7$, and $^5I_5 \rightarrow {}^5I_6$ transitions respectively. The transitions leading to the other observed near-IR wavelengths 1.06 µm and 1.33 µm are not immediately obvious. The observed calibrated emission spectra of Ho^{3+}: KPB shown in figure 5 are similar to those of Ho^{3+}: KPC except that 1.06 µm and 1.33 µm are missing.

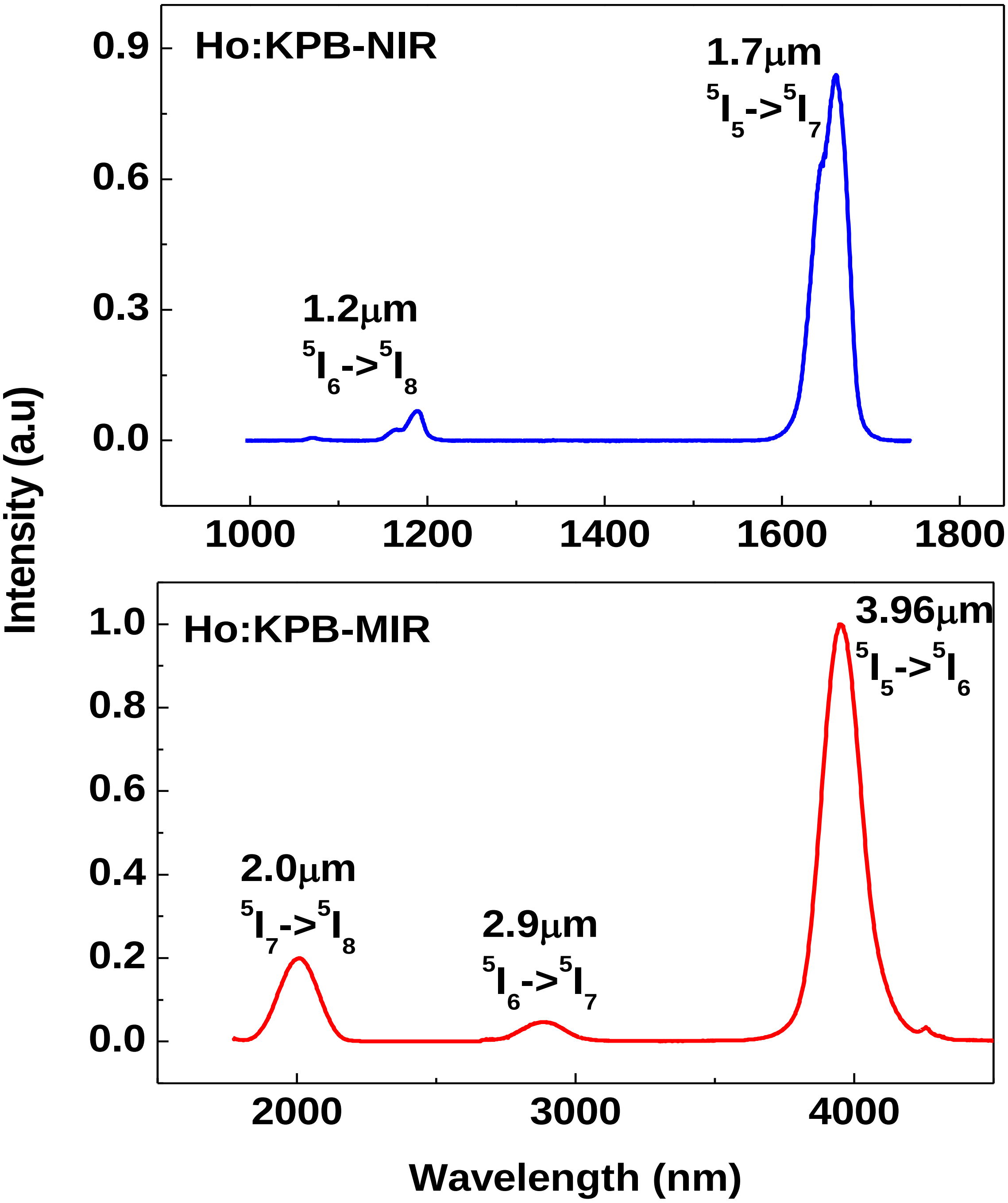

Figure 5: Calibrated near- and mid-IR emission spectra of Ho^{3+}: KPB.

3. Discussion on the 1.06 µm and 1.33 µm lines in the KPC host

The observance of the mid-IR emissions in Ho^{3+}: KPC and Ho^{3+}: KPB is due largely to the narrow phonon spectrum of the two host materials as predicted by the energy gap law

(Kaminskii, 1996). But the appearance of the 1.06 µm and 1.33 µm in only the Ho^{3+}: KPC crystal is curious. A possible reason for this may be the slight difference in the phonon spectrum of KPC and KPB, which impacts the excited state population as suggested in the following analysis.

Consider optical pumping into the $^5I_5$ level at 907 nm (~ 11000 cm^{-1}) as illustrated in figure 6. Due to the long lifetime of the $^5I_5$ level, an excited state absorption can occur from this level to populate the $^5G_6$+$^5F_1$ level (~ 22000 cm^{-1}). The depopulation from higher to lower excited states can occur through non-radiative (multi-phonon relaxation) or radiative transitions. The dominant transition between two adjacent levels is determined by the phonon spectrum of the host material. The energy gap law suggests that levels separated by a small energy difference (ΔE) are likely to exhibit non-radiative transitions. The rule of thumb is that multi-phonon relaxation processes are dominant when less than five phonons are required to bridge the energy gap ΔE (Weber, 1968). The 1.06 µm and 1.33 µm emissions appear to arise from the closely superposed $^3K_8$+$^5F_2$,$^5F_3$ level (~ 21200 cm^{-1}). In the event of an excited state absorption leading to the population of the $^5G_6$+$^5F_1$ level, the $^3K_8$+$^5F_2$,$^5F_3$ level, which is ~ 800 cm^{-1} below the former, could be populated through radiative and non-radiative feeding from the higher excited state. For KPC ($\hbar\omega_{max}$ ~ 203 cm^{-1}), less than five phonons would be required to bridge the ΔE ~ 800 cm^{-1} energy gap between these levels, whereas for KPB ($\hbar\omega_{max}$ ~ 140 cm^{-1}), the same energy gap would require more than five phonons. It thus appears that in the KPC host, the dominant mechanism for feeding the $^3K_8$+$^5F_2$,$^5F_3$ level was non-radiative branching from the $^5G_6$+$^5F_1$ level, leading to the observed IR up-converted emissions. The non-observance of these IR up-converted emissions in the KPB host suggests the dominance of radiative transitions to other levels, possibly to the ground state with an up-converted 455 nm emission, which is outside the wavelength range under investigation. Indeed, radiative transitions have been observed in KPB with energy gap of about 1000 cm^{-1} (Hommerich *et al.*, 2006) and up-converted blue emissions have been observed from higher excited states of Nd^{3+}: KPB (Balda *et al.*, 2006).

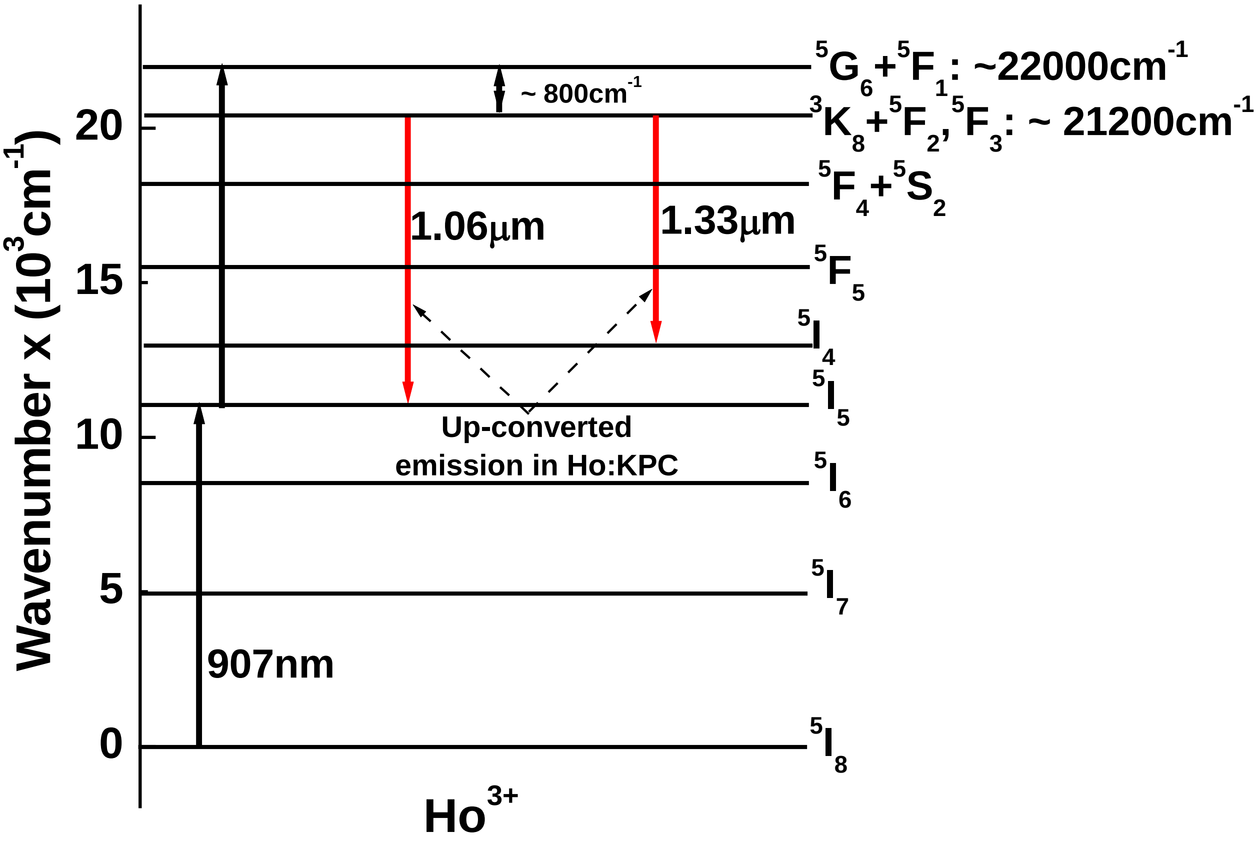

Figure 6: Explanation of up-conversion: present in Ho^{3+}: KPC; absent in Ho^{3+}: KPB.

4. Conclusion

Upon appropriate diode pumping, spontaneous emissions at various IR wavelengths have been observed in both Ho^{3+}: KPC and Ho^{3+}: KPB crystals with the Ho^{3+}: KPC crystal showing two additional wavelengths 1.06 µm and 1.33 µm, which are not found in the Ho^{3+}: KPB crystal. These emissions have been traced to emanate from the $^3K_8+^5F_2$, $^5F_3$ level, which was non-radiatively populated from the upper $^5G_6+^5F_1$ level in the case of the Ho^{3+}: KPC crystal. These amount to up-converted transitions arising from the population of the $^5G_6+^5F_1$ level through excited state absorption. In the case of the Ho^{3+}: KPB crystal, the populated $^5G_6+^5F_1$ level is capable of producing radiative transitions, possibly to the ground state. The 1.06 µm emission is particularly interesting as it coincides with the wavelength of the popular and versatile Nd:YAG laser. It is yet to be seen whether the holmium doped potassium lead chloride can produce a laser at this wavelength. Under the same pumping scheme, it will also be interesting to monitor emissions from both Ho^{3+}: KPC and Ho^{3+}: KPB crystals in the visible wavelength region to see how many visible up-converted signals actually arise from the excited state absorption of higher energy levels.

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