

## Spectroscopy and orange-blue frequency up-conversion in $\text{KPb}_2\text{Cl}_5:\text{Pr}^{3+}$ crystal

R. Balda<sup>a,b</sup>, M. Voda<sup>a</sup>, M. Al-Saleh<sup>a</sup>, and J. Fernández<sup>a,b</sup>  
<sup>a</sup>Dpto. Física Aplicada I y <sup>b</sup>Centro Mixto CSIC-UPV/EHU, Escuela Superior de Ingenieros, Alda Urquijo s/n 48013 Bilbao (Spain)  
email: [wupbacrr@bi.ehu.es](mailto:wupbacrr@bi.ehu.es)

The luminescence of rare-earth (RE) ions has been intensively investigated in different crystalline hosts, due to the important applications in lasers and nonlinear optics. To develop more efficient optical devices based on rare-earths doped materials, hosts with low phonon energies are required. The low phonon energy leads to low nonradiative transition rates due to multiphonon relaxation and high radiative transition rates, which increase the quantum efficiency from excited states of active ions. Sulfide and chloride based hosts have been studied due to their phonon energies lower than in fluoride crystals. However, these materials usually present poor mechanical properties, moisture sensitivity and are difficult to synthesize. Recently,  $\text{KPb}_2\text{Cl}_5$  crystal has been studied as a promising host for RE ions [1,2]. This crystal is non-hygroscopic and has a maximum phonon energy of  $199\text{ cm}^{-1}$ . Among rare-earth ions, trivalent praseodymium is an attractive optical activator which offers the possibility of simultaneous blue, green, and red emission for laser action as well as IR emission for optical amplification at  $1.3\text{ }\mu\text{m}$  [3].

In this work we report the optical properties of the visible luminescence from  $\text{Pr}^{3+}$  in the low phonon crystal  $\text{KPb}_2\text{Cl}_5$ , together with the results of orange-to-blue up-conversion by pumping the  $^1\text{D}_2$  state.

Praseodymium doped  $\text{KPb}_2\text{Cl}_5$  crystals were grown in our laboratory by the Bridgman technique. The crystal used in this study was doped with 2 mol% in the melt and was cut and polished to a thickness of 3.1 mm. Conventional absorption spectrum was obtained in the 400-2600 nm range with a Cary 5 spectrophotometer. The spectrum consists of several bands corresponding to transitions between the  $^3\text{H}_4$  ground state and the excited multiplet belonging to the  $4f^2$  configuration of the  $\text{Pr}^{3+}$  ion.

Figure 1 shows the steady-state emission spectrum obtained under excitation with an argon laser at 454 nm. As can be seen the emission corresponds to level  $^3\text{P}_0$ . The emission lines are related to the transitions  $^3\text{P}_0 \rightarrow ^3\text{H}_{4,5,6}$  and  $^3\text{P}_0 \rightarrow ^3\text{F}_{2,3,4}$ . In addition to these lines the spectrum at room temperature shows some peaks corresponding to transitions from the thermally populated  $^3\text{P}_1$  level.

The decays from the  $^3\text{P}_0$  and  $^1\text{D}_2$  states were obtained between 10 and 295 K. The lifetime value for the  $^3\text{P}_0$  level is  $11\text{ }\mu\text{s}$  and is independent on temperature, whereas the lifetime value of the  $^3\text{P}_0$  state decreases from  $88\text{ }\mu\text{s}$  at 10 K to  $67\text{ }\mu\text{s}$  at 295 K.

Anti-Stokes fluorescence from the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition has been observed between 10 K and 295 K under excitation of the  $^1\text{D}_2$  state. Fig. 2 shows the spectrum at 11 K. This blue emission shows a quadratic dependence with the laser intensity which indicates that two photons participate in the process. This up-

converted emission can occur non radiatively by an energy transfer up-conversion (ETU) or radiatively by an excited state absorption (ESA). In the first mechanism two ions are involved whereas a single ion is involved in the second one. Lifetime measurements allow to discern which is the dominant mechanism. ETU leads to a decay curve for the up-converted emission which shows a rise time and a longer lifetime than that of the  $^3\text{P}_0$  under direct excitation. The ESA process occurs within the excitation pulse width, leading to an immediate decay of the up-converted luminescence after excitation. The temporal evolution of the blue emission in this crystal follows the former behavior. The decay curves show a rise time around  $10\text{ }\mu\text{s}$  and a decay with a lifetime around  $52\text{ }\mu\text{s}$ , which is much longer than the lifetime of the  $^3\text{P}_0$  level ( $11\text{ }\mu\text{s}$ ) under direct excitation. This behavior supports that the mechanism responsible for the up-conversion process is energy transfer.

### Acknowledgements

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### References

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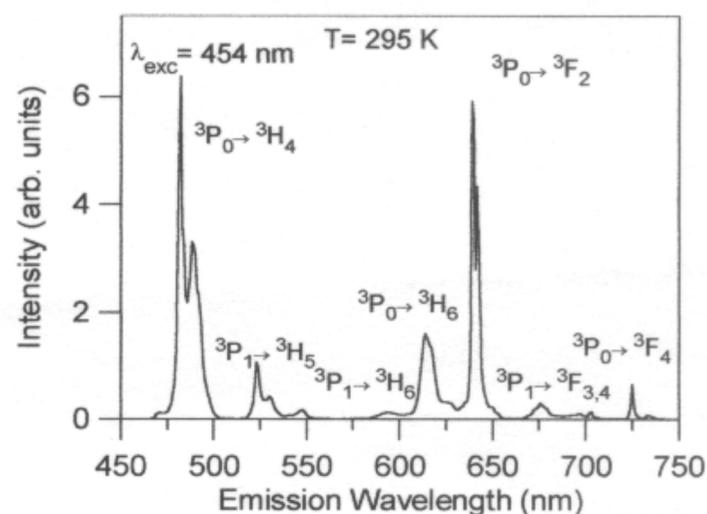


Fig. 1.- Steady-state emission spectrum obtained at 295 K by exciting at 454 nm.

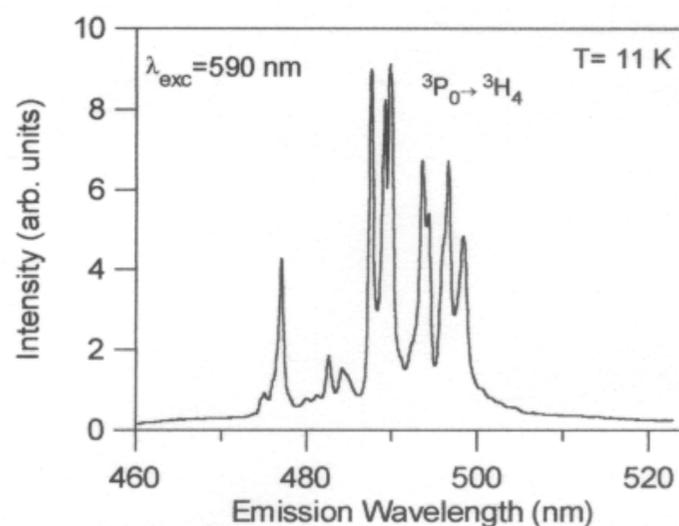


Fig. 2.- Fluorescence spectrum corresponding to the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition obtained at 11 K under excitation at 590 nm.