

New Luminescent Multiplet Terms in $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$

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Transparent crystals of erbium-doped KPb_2Cl_5 of good optical quality are readily grown and serve as an attractive material for upconversion, infrared lasing and anti-Stokes laser cooling. The chemical and mechanical stabilities of KPb_2Cl_5 are superior to those of other rare earth chloride host lattices. As shown by Raman spectroscopy, the highest energy optical phonon of the KPb_2Cl_5 lattice has an energy of only 202 cm^{-1} so that multiphonon nonradiative decay processes are slow and there are many potential luminescent states. The upconversion processes in $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$ have been investigated under 801 nm excitation into the $^4\text{I}_{9/2}$ multiplet term [1]. The upconverted emission was thought to arise from both excited state absorption and energy transfer mechanisms and was assigned to the $^2\text{H}_{9/2}$ and $^4\text{S}_{3/2}$ multiplet terms. Upconversion was also studied by pumping the Er^{3+} $^4\text{I}_{13/2}$ term using $1.55\text{ }\mu\text{m}$ radiation [2]. Tkachuk et al. [3] utilized 973 nm laser diode pumping of the $^4\text{I}_{11/2}$ multiplet of Er^{3+} and obtained green upconverted emission from $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, with a very minor red contribution from $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$.

Crystals of KPb_2Cl_5 are monoclinic, with space group $\text{P2}_1/\text{c}$. The Pb^{2+} ions occupy two distinct sites, each having C_1 site symmetry, Pb(1) and Pb(2). The Pb(1)-Pb(1') distance is $0.64\text{ }\text{\AA}$. The absorption spectra of $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$ have been recorded at low temperatures and the bands were assigned to just one site. Based upon this assumption, the derived energy levels were fitted by crystal field analyses assuming that the Er^{3+} ions occupy the Pb(2) site with a vacancy in the nearby K^+ site.

Several previous reports have been made of the room temperature visible emission spectra of $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$. The highest energy emission was reported from the $^4\text{G}_{11/2}$ multiplet term, at $\sim 26300\text{ cm}^{-1}$. The strong absorption above this energy was attributed to the matrix. Our present results using synchrotron radiation excitation at low temperature extend the luminescent levels to higher energy and the excitation spectra enable the distinctions to be made between Er^{3+} , Pb^{2+} and band to band excitations.

Figure 1 displays the 10 K luminescence spectra of dilute $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$ under various synchrotron radiation excitation lines. All of the spectra are significantly different from those previously reported and in addition, they differ from one another. Most of the observed features correspond to emission transitions of Er^{3+} . For the detailed interpretation it is necessary to investigate the excitation spectra of selected emission bands and this was performed in detail. Sharp absorption bands in the excitation spectra at 305 nm and 318 nm are assigned to transitions from the electronic ground state to the $^2\text{K}_{13/2}$

and $^2\text{P}_{3/2}$ multiplet terms of Er^{3+} , respectively. The energy gaps below these multiplets are spanned by 6-7 and >17 highest energy phonons in KPb_2Cl_5 , respectively. Thus upon exciting each of these multiplets (top two spectra, Fig. 1) emission is observed to the ladder of energy levels below. Note, as expected, the absence (e.g. lines 6, 9 in Fig. 1) of emission from $^2\text{K}_{13/2}$ under $^2\text{P}_{3/2}$ excitation. Line 2, $^2\text{K}_{13/2} \rightarrow ^4\text{I}_{13/2}$, is coincident with the $^4\text{G}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition which is observed under both 305 nm and 318 nm excitation. Thus the excitation spectrum of line 2 shows not only $^2\text{K}_{13/2}$ absorption but also that from $^2\text{P}_{3/2}$ which populates $^4\text{G}_{11/2}$ nonradiatively.

In conclusion, there are many luminescent levels of $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$ from the infrared to ultraviolet spectral regions. This emphasizes the dominance of radiative processes over multiphonon nonradiative ones for this low-phonon energy host. In particular, two new luminescent levels are reported herein which were previously considered to be above the matrix absorption. Certainly, the highest luminescent state is $^2\text{K}_{13/2}$ since nonradiative decay from slightly higher Er^{3+} energy levels (e.g. $^4\text{G}_{7/2}$) is rapid. Even higher Er^{3+} levels lie within or above the host conduction band and are therefore not luminescent.

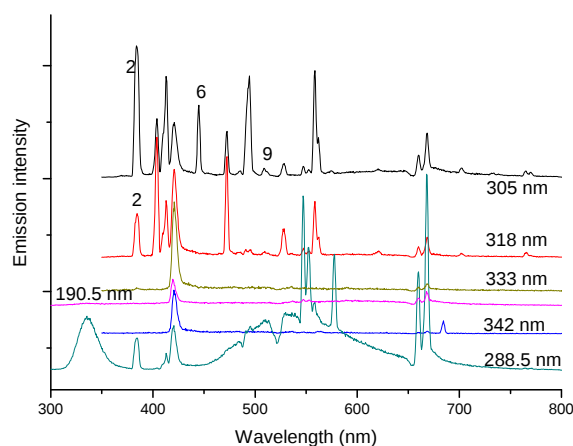


Figure 1. 10 K emission spectra of $\text{KPb}_2\text{Cl}_5:\text{Er}^{3+}$ using selected excitation lines as shown.

[1] R. Balda, A. J. Garcia-Adeva, M. Voda, and J. Fernandez, *Phys. Rev. B* **69**, 205203 (2004).

[2] R. S. Quimby, N. J. Condon, S. P. O'Connor, S. Biswal, and S. R. Bowman, *Opt. Mater.* doi:10.1016/j.optmat.2007.03.002.

[3] A. M. Tkachuk, S. E. Ivanova, M.-F. Joubert, Y. Guyot, L. I. Isaenko, and V. P. Gapontsev, *J. Lumin.* **125**, 271 (2007).