Excitation and Emission Spectra of $Cs_2NaLnCl_6$ Crystals Using Synchrotron Radiation

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The visible emission and vacuum ultraviolet excitation spectra of the series $Cs_2NaLnCl_6$ (Ln = Y, Nd, Sm, Eu, Tb, Er, Yb) and Cs_2NaYCl_6:Ln^{3+} (Ln = Sm, Er) have been recorded using synchrotron radiation at room temperature, and in some cases at 10 K. The excitation spectra comprise features associated with charge transfer, excitation from the valence to conduction band, and impurity bands. No d - f emissions are observed for these Ln^{3+} ions, so that the emission bands comprise intraconfigurational $4f^N$ - $4f^N$ transitions and various impurity bands. A selection of the spectra is shown in Figs. 1, 2. Theoretical simulations of the f - d absorption spectra have been included. The comparison with data from the synchrotron at Desy enables a comprehensive account to be given of the ground (or vibrationally excited ground for Ln^{2+}) states of the Ln^{3+} $4f^N$, Ln^{3+} $4f^{N-1}5d$, and Ln^{2+} $4f^{N+1}$ configurations relative to the valence and conduction bands of $Cs_2NaLnCl_6$, for which the band gaps are between 6.6-8.1 eV.

Fig. 1: Emission spectrum of $Cs_2NaTbCl_6$ excited at 186 nm (a) and excitation spectrum monitored at 547.25 nm. The initial luminescent state in (a) is $^5D_4$, and the ground state in (b) is $^7F_6$. Some terminal states are marked in both spectra. Some peak maxima are given in nm in (b) and the solid lines represent calculated spin-allowed absorption zero-phonon lines, whereas dashed lines are the positions of calculated spin-forbidden absorptions.

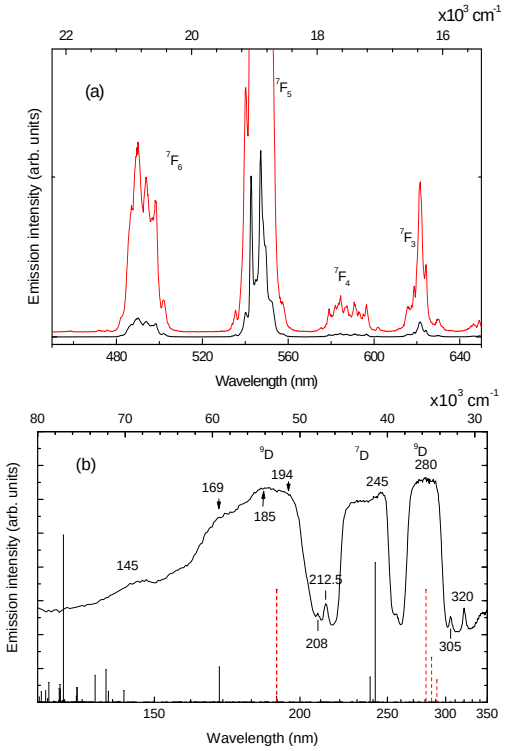

Fig. 2: Room-temperature and 10 K emission (a) and excitation (b) spectra of three samples (i), (ii), (iii) of $Cs_2NaEuCl_6$. In (a) the transitions $^5D_1 \rightarrow {}^7F_{J'}$ and $^5D_0 \rightarrow {}^7F_0$ bands are marked by J and J'.

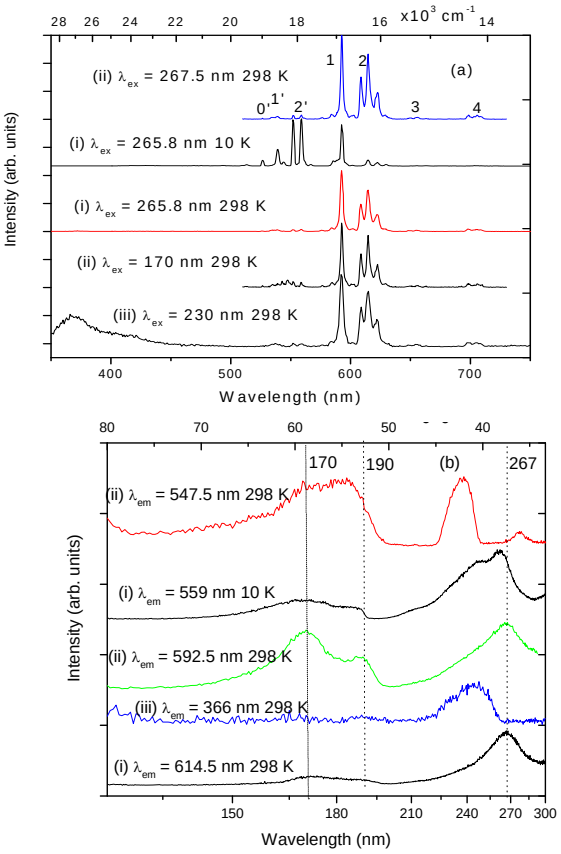

Fig. 3: Energy diagram for $Cs_2NaLnCl_6$ relative to the top of the valence band. (a), (b) absolute positions of the Ln^{3+} $4f^N$ ground state and lowest Ln^{3+} $4f^{N-1}5d$ state, respectively; (c) the absolute position of the Ln^{2+} $4f^N$ vibrationally excited ground state; (d) band gaps.