Contrasting Emission Behaviors of YAG:V^{5+} Co-doped with Pr^{3+} or Eu^{3+}

Guohua Jia[1], Peter A. Tanner[1], and Bing-Ming Cheng (鄭炳銘)[2]

[1]Department of Biology and Chemistry, City University of Hong Kong, Kowloon, China
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

The study of the optical spectra of vanadium ions in yttrium aluminum garnet (YAG) by Weber and Riseberg [1] demonstrated that it is difficult to assign bands to specific V(i) (i = II-IV) oxidation states. Subsequent studies focused upon tetrahedrally coordinated V^{3+} [2-4] and octahedrally and tetrahedrally coordinated V^{4+} [5]. In our program to investigate the occurrence and applications of energy transfer between transition metal and lanthanide ions, we therefore decided to investigate the doping of V^{5+} and possibility of energy transfer to lanthanide ions. In this paper we report the rather different results for the additional incorporation of Eu^{3+} or Pr^{3+}, using vacuum ultraviolet (VUV) and ultraviolet-visible (uv-vis) spectroscopy.

Figure 1 shows the emission spectra of YAG:V,Pr at various temperatures and under different excitation conditions. Using synchrotron radiation excitation into the YAG conduction band (Fig. 1(a)), the broad features at highest energy correspond to $4f^1 5d^1 \rightarrow 4f^2$ interconfigurational transitions of Pr^{3+}, as in YAG:Pr. By contrast, the weaker, sharper features to low energy of 474 nm correspond to the $4f^2 \rightarrow 4f^2$ transitions, with those from the initial $^3P_0$ state being most intense. The spectrum in Fig. 1(b), with excitation directly into Pr^{3+} $4f^2$ energy levels, is similar to that in Fig. 1(a), except for self-absorption of the high energy $^3P_0 \rightarrow {}^3H_4$ transition, and in agreement with features in previous spectral studies of YAG:Pr. The 10 K emission spectrum of YAG:V,Pr, Fig. 1(c), with excitation into the Pr^{3+} $4f^2$ energy level using 438 nm excitation, is identical with our 10 K spectrum of YAG:Pr (not shown), with no additional bands. The emission spectra of YAG:V,Pr with excitation into Pr^{3+} energy levels, do not give any signature for the presence of vanadate. However, although the excitation wavelengths 310 nm and 314 nm gave rise to intense emission from Pr^{3+} in YAG:Pr, the emission was weaker under the same conditions for YAG:V,Pr, due to the participation of competitive vanadate absorption.

The room temperature emission spectra of YAG:V excited by synchrotron or ultraviolet radiation exhibit a broad vanadate band with maximum near 420 nm. The most unexpected part is the occurrence of sharp emission bands at lower energy. These are due to Eu^{3+} and are at similar locations to bands in the emission spectrum of YVO_4:Eu, but not YAG:Eu. Analysis of the YAG:V sample by inductively-coupled mass spectrometry showed that the concentration of Eu^{3+} was ~1 ppb and that its origin was from the 99.999% Y_2O_3 used in the synthesis of YAG. The synchrotron radiation excitation spectrum of YAG:V is the same whether the vanadate emission at 419 nm is monitored, or whether the trace Eu^{3+} $^5D_0 \rightarrow {}^7F_1, {}^7F_2$ emission bands are monitored. The broad excitation bands at 195, 243 nm are at the same locations as in the VUV excitation spectrum of YVO_4.

References

[1] M. J. Weber and L. A. Riseberg, J. Chem. Phys. **55** 2032 (1971).
[2] V. P. Mikhailov *et al.*, Opt. Mater. **2,** 267 (1993).
[3] K. V. Yumashev *et al.,* J. Appl. Phys. **80,** 4782 (1996).
[4] J. Ma, M. Du, and F. Miao, Phys. Stat. Sol. (b) **243**, 1785 (2006).
[5] M. Grinberg *et al*., J. Phys. I France **3**, 1973 (1993).

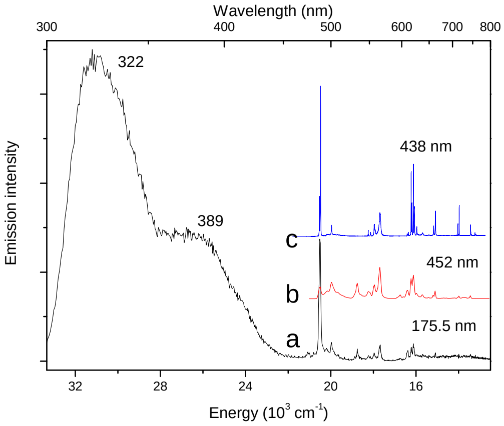

Fig. 1: Emission spectra of YAG:V,Pr (each doped at 2 at.%): (a) synchrotron radiation excitation at 175.5 nm with band pass 1.5 nm at 298 K (the spectra using 237.5 nm, 286 nm and 320.5 nm excitation are similar); (b) 452 nm excitation at 295 K; (c) 438 nm excitation at 10 K.