CHAPTER 4

CONCLUSIONS

From the data and arguments presented it is reasonable to conclude that the saturation dips, first witnessed in the excitation spectrum of Eu_2O_3 nanocrystals, are due to nonlinear luminescence quenching. Of the several possible mechanisms considered, only up-conversion by energy transfer was supported by all the spectroscopic data. However, the lack of anti-Stokes luminescence, the most obvious indicator of the type of excited state interactions responsible for nonlinear luminescence quenching, makes a truly definitive assignment difficult. Also there is almost a complete lack of documented examples of up-conversion by energy transfer occurring in europium-containing compounds, certainly this must be addressed before final conclusions are drawn.

An extensive search of the literature produced numerous articles describing energy migration and luminescent properties of europium-containing compounds, however all assumed no contribution from excited-state interactions.[1-7] Even in articles concerning Eu_2O_3, excited-state interactions was not considered, and apparently nonlinear luminescence quenching went undetected.[8-11] The only examples of nonlinear luminescence quenching occurs in europium-containing compounds found were europium-doped television phosphors, such as Eu^{3+}:Y_2O_3 and Eu^{3+}:Y_2O_2S.[12, 13] The fact that the high excitation densities producible in cathode ray tubes can lead to nonlinear luminescence quenching by up-conversion has been known for some time. In the case of Eu^{3+}-doped television phosphors, energy transfer from the excited Y_2O_3 lattice is possible. If excitation densities are high, up-conversion occurs if a single Eu^{3+} ion is excited more than once. This additional excitation energy decays nonradiatively, lowering the quantum efficiency.

The Eu^{3+}-doped television phosphors provide evidence that up-conversion can occur at Eu^{3+} ions, and reasons for the lack of documented of nonlinear luminescence quenching in concentrated europium systems becomes clear from the following considerations. First, the excitation-density used in spectroscopic studies is much less than that achievable from cathode-ray excitation. Secondly, spectroscopy of concentrated europium compounds is generally done using powders. The powdered samples increase the scattering of the exciting beam resulting in a lower excitation density compared to using larger crystals. Finally, in order for up-conversion to have a noticeable effect, the rate of energy transfer must be fast enough to bring excited ions together before they decay. The rate of energy transfer in most europium compounds is simply not fast enough for this to occur, particularly at low temperatures where, in many cases, energy transfer is frozen.[14] Fortunately, for the sake of this thesis, Eu_2O_3 turned out to be the one known exception to the rule. The rate of energy transfer in Eu_2O_3 is more rapid than any other europium compound, even at very low temperatures.[14] So it can be concluded that up-conversion by energy transfer would be easier to produce in Eu_2O_3 than in any other known europium compound, and seems the most likely explanation for the saturation dips.

Chapter 4 References

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