DOCTORAL THESIS

The study of energy transfer and local field effect in lanthanide complexes with high and low symmetry

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ABSTRACT

There are lots of important applications for lanthanides (Ln) because of their unique properties. The properties are closely linked to the environment of the crystal field. Thus, two kind of crystals $Cs_2NaLn(NO_2)_6$ with high T_h point-group symmetry and $LnPO_4$ with monoclinic symmetry were chosen to study quantum cutting and Stokes shift.

Quantum cutting is a kind of down-conversion energy transfer in which one excitation ultraviolet photon is transformed into multiple near infrared photons. This phenomenon has been studied in $Cs_2NaY0_{.96}Yb_{0.04}(NO_2)_6$. The emission from Yb^{3+} can be excited via the NO_2^- antenna. The electronic transition of NO_2^- is situated at more than twice the energy of the Yb^{3+}. At room temperature, one photon absorbed at 470 nm in the triplet state produced no more than one photon emitted. Some degree of quantum cutting was observed at 298 K under 420 nm excitation into the singlet state and at 25 K using excitation into singlet and triplet state. The quantum efficiency was about 10% at 25 K.

In Chapter 3, Stokes shift which is the energy shift between the peak maxima in absorption and emission was studied. Stokes shift is related to the flexibility of the lattice and the coordination environment. $Cs_2NaCe(NO_2)_6$ with 12-coordinated Ce^{3+} situated at a site of T_h symmetry demonstrated the largest Ce-O Stokes shift of 8715 cm^{-1}. The $4f^1$ ground state and $5d^1$ potential surfaces have displaced so much along the configuration coordinate that overlap takes place above the $5d^1$ minimum, leading

to thermal quenching of emission at 53 K. A comparison of Stokes shifts with other Ce-O systems with different coordination number demonstrated larger Stokes shifts for Ce^{3+} ions with higher coordination number.

Systematic research about the energy transfer (ET) and energy migration phenomenon is still scarce, although they exist extensively among lanthanide ions. The energy migration in highly doped materials has been stated as very fast or slow, but no experimental proof was reported. In Chapter 4, the ET between Tb^{3+} and Eu^{3+} was investigated experimentally and compared with available theoretical models in the regime of high Tb^{3+} concentrations in 30 nm $LaPO_4$ nanoparticles at room temperature. The ET efficiency approached 100% even for lightly Eu^{3+}-doped materials. The use of pulsed laser excitation and switched-off continuous wave laser diode excitation demonstrated that the energy migration between Tb^{3+} ions, situated on La^{3+} sites with a 4 Å separation was not fast. The quenching of Tb^{3+} emission in singly doped $LaPO_4$ only reduced the luminescence lifetime by about 50% in heavily doped samples. Various theoretical models have been applied to simulate the luminescence decays of Tb^{3+} and Eu^{3+}-doped $LaPO_4$ samples of various concentrations. The transfer mechanism has been identified as forced electric dipole at each ion.

The control of energy transfer rate and efficiency is also an important issue. There are many chemical and geometrical factors that affect energy transfer, including the spectra overlap, the dipole orientation and the distance between the donor and acceptor. The local field of the emission center is another factor that affect the energy transfer by changing the photonic environment. In Chapter 5, the local field effect on the energy transfer between Tb^{3+} and Eu^{3+} doped in $LaPO_4$ dispersed in different solvents and solids with a wide range of refractive indexes was studied. The effects of local field (reflected by refractive index) on the ET efficiency and ET rates were clarified that the ET efficiency would decrease with increasing refractive index, while ET rates were independent of the refractive index.

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