Optical and Photonic Glasses

Lecture 32:
Rare Earth Doped Glasses II

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As an example, let us consider the ground state of the Er\(^{3+}\) ion.

Er has the electronic configuration [Xe]4f\(^{12}\)6s\(^{2}\), so Er\(^{3+}\) has 11 f electrons ([Xe]4f\(^{11}\)).

With such a large number of electrons in its f-shell, many different values of L, S and J are possible.

For example, values of L corresponding to S, F, H, I, …etc., are possible. When L = 6 (corresponding to state I) and S = 3/2 (the total spin quantum number for 11 f electrons can be 3/2, with 3 unpaired, or 1/2, with only one unpaired), one has the following combinations leading to the possible values of J:

\[
J = L+S, \ L+S-1, \ldots, |L-S| \quad \text{or} \quad J = 15/2, 13/2, 11/2, 9/2
\]

Therefore, the four lowest energy states of the Er\(^{3+}\) ion (those with larger spin) are:

\[4I_{15/2}, 4I_{13/2}, 4I_{11/2} \text{ and } 4I_{9/2}\]

with the first (of > J) being the ground state, of lowest energy. Each \(2S+1L_J\) term is itself a multiplet, composed of \((2J+1)\) degenerate energy levels (the Stark components), which may however be split by an electric field due to ion-lattice interactions, particularly in crystals.
Electronic energy terms: \( ^{2S+1}L_J \)

where: \( L = |L| = |\sum l_i| \) \( S = |S| = |\sum s_i| \) \( J = L + S \)

this corresponds to the so-called L-S (or Russell-Saunders) spin-orbit angular momentum coupling scheme, which is generally favored for lighter atoms (including most RE ions). For the heavier atoms, the so-called j-j coupling may be used, where the individual angular momenta are first coupled, for each electron and the resultant j values of the individual electrons couple for the whole atom, in the end.

Selection rules

Selection rules are rules about the possible values of the quantum numbers of the initial and final states of a given transition, indicating whether it is allowed or forbidden. Most electronic transitions, such as those between electronic energy configurations of the RE ions, are electric-dipole in nature and, for those, the selection rules are:

- The parity of the initial and final states must be different (g \( \leftrightarrow \) u, only), sometimes called the Laporte rule
- \( \Delta L = \pm 1 \)
- \( \Delta S = 0 \) (spin conservation)
Possible RE ion dopants for glassy hosts
For RE ions, f → f transitions are electric dipole forbidden, since all states are odd (u) and the Laporte selection rule (i.e., the initial and final states must have different parity) is not obeyed. In solids, however, quantum admixing of higher lying states of opposite parity into the 4fⁿ configuration introduce a degree of electric dipole strength into the f → f transitions, as long as the ion site lacks inversion symmetry, as it usually does in glasses. However, for Er³⁺ at 1.5 µm, the electric and magnetic dipole strengths are comparable, particularly for a silica glass host.

Non-radiative transitions may be the result of interaction of the RE ions with vibrations of the host, either intrinsic or due to impurities. The ion makes a non-radiative transition to a lower electronic state through the emission of multiple phonons to conserve energy. When the non-radiative relaxation rate is comparable to the radiative one, the PL efficiency is degraded. Higher order multiphonon (MP) processes can be significant, because the electron-phonon interaction is strong and the phonon density of states is high for any solid. Yet, such transition rates fall off rapidly with increasing order of the process, i.e., with the number of phonons required to bridge the energy gap between two J multiplets. Therefore, the dominant contribution always comes from the highest energy phonons of the host.
Different types of possible non-radiative relaxation processes

concentration quenching due to ion-ion interactions

metastable levels

metastable levels

(two interm. states)

Nonradiative relaxation processes, (a) Multiphonon relaxation, (b) Cross relaxation, (c) Co-operative up-conversion. (b) and (c) → concentration quenching.

(Adapted from: Glasses for photonics, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)