Luminescence of Solid State Inorganic Materials

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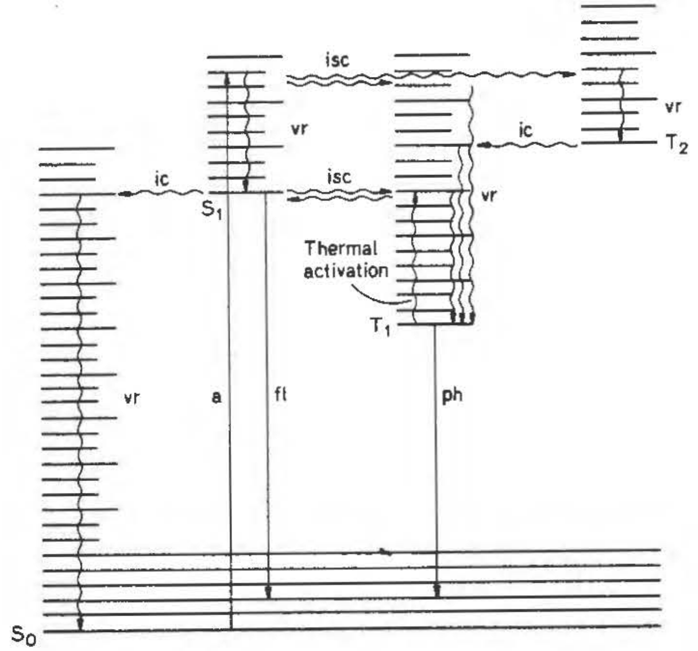
In the last ten years, the study of luminescent materials by chemists, physicists and mineralogists has led to the publication of more than 3000 papers in the scientific literature. The study of luminescence in its simplest form involves the use of some energy source to excite a luminescent center from its electronic groundstate to an excited electronic state, and then observing the emission as the system relaxes back to the groundstate. The study of solid state inorganic systems has led to an increased understanding of the localized electronic structure of luminescent centers as well as the delocalized electronic band structure of many solids. Many of these results have been summarized in recent reviews [1]. The energy diagram below depicts the electronic and vibrational structure of a molecule which is excited from a singlet groundstate S_0 to an excited singlet state S_1.



Once the molecule has been excited to S_1, it may relax back to S_0 by several different competing pathways including fluorescence (fl) from S_1 to S_0 or intersystem crossing (isc) to a triplet state T_1 followed by phosphorescence (ph) to S_0. Besides providing information about the electronic structure, a great deal of knowledge about the transfer of energy in the solid state has also been gained [2,1d].

Photoluminescence, which involves the use of an ultraviolet or visible light source to electronically excite the system of interest, has been used to probe the electronic structure of many oxo-anions such sa WO_4^{2-}, VO_4^{3-} and TiO_6^{8-}. This experimental work has been well complemented by a wealth of electronic structure calculations [3]. The electronic structures of the permanganate and chromate ions have been studied by theoretical methods for many years and these studies all predict the luminescence of the two anions. While luminescence of the chromate ion has been observed at 1.4 K, observation of permanganate luminescence has not been observed [4].

By using short pulse width laser techniques, one is able to study the dynamics of many solid state processes by monitoring the rate at which the luminescence of a particular system decays. The basis for such investigations originates from the classic work on solid state energy transfer by Forster and Dexter [5]. for an electronically excited molecule, relaxation to the ground state may proceed not only by radiative fluorescence and phosphorescence, but also via the nonradiative transfer of energy to other molecules in the lattice through dipole-dipole, dipole-quadrupole or quadrupole-quadrupole interactions. Many solid state processes provide nonradiative relaxation pathways, and by monitoring the quenching of luminescence as a function of time one is able to monitor the dynamics of such processes. Examples of such processes include electronic exchange interactions [6], localization of excitons in disordered systems [7] and temperature dependent phenomena [8].

References

1. (a) Blasse, G., "Luminescence of Inorganic Solids Trends and Applications," Rev. Inorg. Chem. 1983, 5, 319.
   (b) Golovina, A. P.; Zorov, N. B.; Runov, V. K., "Chemical Luminescence Analysis of Inorganic Substances," Structure and Bonding 1981, 47, 53.
   (c) Blasse, G., "The Luminescence of Closed-shell Transition-Metal Complexes. New Developments," Structure and Bonding 1980, 42, 1.
   (d) Powell, R. C.; Blasse, G., "Energy Transfer in Concentrated Systems," Structure and Bonding 1980, 42, 43.

2. Toyozawa, Y., "Elementary Process in Luminescence," J. Luminescence 1976, 12/13, 13.

3. (a) Van Oosterhout, A. B., "An ab initio calculation on the WO_6^{6-} octahedron with an application to its luminescence," J. Chem. Phys. 1977, 67, 2414.
   (b) Ziegler, T.; Rauk, A.; Baerends, E. J., "The Electronic Structures of Tetrahedral Oxo-Complexes. The Nature of the "Charge Transfer" Transitions," Chem. Phys. 1976, 16, 209.

4. Miller, R. M.; Tinti, D. S., "Luminescence and ODMR of The Spin-Triplet State in $CaCrO_4$ and $SrCrO_4$ at 1.4 K," J. Luminescence 1986, 36, 143.

5. (a) Forster, T., Ann. Phys. 1948, 2, 55.
   (b) Dexter, D. L., "A Theory of Sensitized Luminescence in Solids," J. Chem. Phys. 1953, 21, 836.

6. (a) Joubert, M. F.; Jacquier, B.; Linares, C.; Chaminade, J. P., "Electronic Exchange Interaction Effect on the Fluorescence Properties of Terbium Magnetic Insulators," J. Luminescence 1987, 37, 239.
   (b) Wrobleski, J. T.; Dziobowski, C. T.; Brown, D. B., "Reanalysis of the Thermal, Magnetic, and Spectral Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$ on the Basis of an Intercluster Spin-Exchange Model," Inorg. Chem. 1981, 20, 684.
   (c) Ferguson, J.; Gudel, H. U., "Spectroscopic Study of the Trinuclear Complex Salt $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$," Chem. Phys. Lett. 1972, 17, 547.

(d) Schenk, K. J.; Gudel, H. U., "Low-Temperature Structural and Spectroscopic Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$," Inorg. Chem. 1981, 21, 2253.

7. Shevel, S.; Fisher, R.; Gobel, E. O.; Noll, G.; Thomas, P., "Picosecond Luminescence of Excitons Localized by Disorder in CdS_xSe_{1-x}," J. Luminescence 1987, 37, 45.

8. Neff, H.; Bachmann, K. J.; Lay, K. Y.; Kotz, R., "Temperature Dependent Photoconductivity and Photoluminescence of $Cd_{1-x}Mn_xTe$," J. Luminescence 1987, 36, 347.