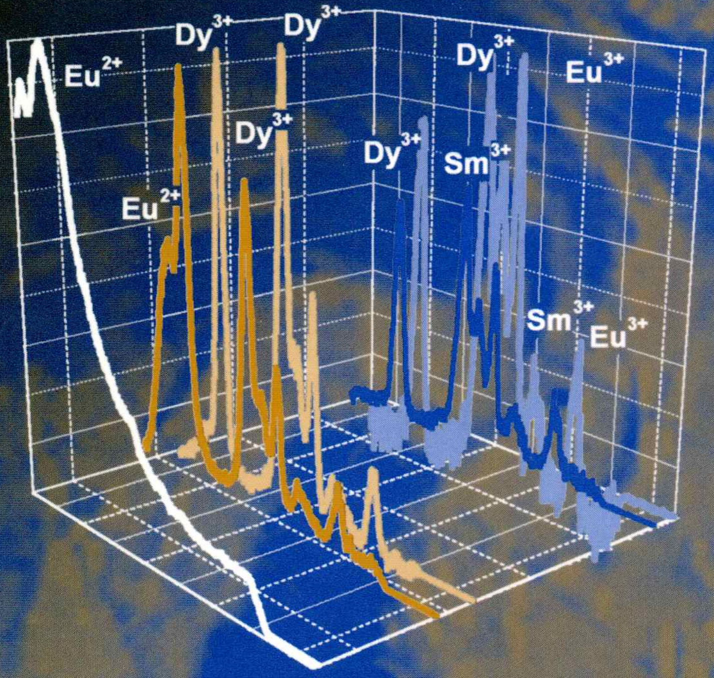
Luminescence Spectroscopy of Minerals and Materials

Michael Gaft
Renata Reisfeld
Gérard Panczer



Springer

Conclusions

In the proposed book there is an emphasis on luminescence lifetime, which is a measure of the transition probability and non-radiative relaxation from the emitting level. Luminescence in minerals is observed over a time interval of nanoseconds to milliseconds. It is therefore a characteristic and a unique property and no two luminescence emissions will have exactly the same decay time. The best way for a combination of the spectral and temporal nature of the emission can be determined by time-resolved spectra. Such techniques can often separate overlapping features, which have different origins and therefore different luminescence lifetimes. The method involves recording the intensity in a specific time "window" at a given delay after the excitation pulse where both delay and gate width have to be carefully chosen. The added value of the method is the energetic selectivity of a laser beam, which enables us to combine time-resolved spectroscopy with powerful individual excitation. The book deals mainly with the theoretical approach, experimental results and their interpretation of laser-induced time-resolved spectroscopy of minerals in the wide spectral range from 250 to 2,000 nm, which enables us to reveal new luminescence previously hidden by more intensive centers. Artificial activation by potential luminescence centers has been accomplished in many cases, which makes sure identification possible. The mostly striking example is the mineral apatite, which has been extremely well studied by many scientists using practically all known varieties of steady-state luminescence spectroscopy: photoluminescence with lamp and laser excitations, X-ray excited luminescence, cathodoluminescence, ionoluminescence and thermoluminescence. Nevertheless, time-resolved spectroscopy revealed that approximately 50% of the luminescence information remained hidden. The most important new information is connected with luminescence of trivalent rare-earth elements in minerals, such as Eu^{3+}, Pr^{3+}, Ho^{3+}, Tm^{3+}, Er^{3+}, and Nd^{3+} (Table 12.1).

Luminescence information on transition elements is substantially improved. Besides well known Mn^{2+} centers, emission of Mn^{5+} was found and Mn^{4+} proposed as a possible participant in minerals luminescence. Luminescence characteristics of Mn^{6+}, Cr^{5+}, Ti^{3+}, V^{2+}, V^{3+}, Ni^{+}, Sb^{3+} are presented and their possible role in minerals luminescence is considered. Luminescence of Pb^{2+}, Bi^{3+}, Bi^{2+}, Ag^{+}, Cu^{+} has been found. Reabsorption lines of molecular H_2O and O_2 in apatite and diamond have been identified.

Table 1.3. Luminescence centers found in steady-state spectra of minerals

Luminescence center	Transition	Decay time
Rare earth ions (line emission): Nd^{3+}, Sm^{3+}, Sm^{2+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Yb^{3+}	$4f$–$4f$	The parity does not change and the life time of the excited state is long ($\sim$ 10 µs–1 ms)
Rare earth ions (band emission): Ce^{3+}	$5d$–$4f$	Transition is parity allowed and spin selection is not appropriate ⇒ fully allowed (10–100 ns)
Eu^{2+}		Emitting level contains octets and sextets, whereas the ground state level ^8S is an octet, so that the spin selection rule slows down the optical transition rate ($\sim$ 1 µs)
Yb^{2+}, Sm^{2+}		The spin selection rule is more important and decay times are of (100 µs–1 ms)
Transition metal ions:	d–d	Decay time is long
Cr^{3+}	^2E–$^4A_2$ line	The parity selection rule as well as the spin selection rule apply ($\sim$ 1 ms)
	$^4T_2$–$^4A_2$ band	The parity selection rule ($\sim$ 10–100 µs)
Mn^{2+}, Fe^{3+}	$^4T_1$–$^6A_1$ $^4T_2$–$^6A_1$	The parity selection rule as well as the spin selection rule ($\sim$ 1 ms)
d^0 Complex ions: $(VO_4)^{3-}$, $(WO_4)^{2-}$, $(MoO_4)^{2-}$, $(TiO_4)^{4-}$	Charge-transfer	Emitting state is a spin triplet and decay time is long (10–100 µs)
$(UO_2)^{2+}$	Charge-transfer	Considerably long decay time ($\sim$ 0.1–1 ms)

value overweighs such deficiencies. It is important to note that there is simple relationship between steady-state and time-resolved measurements. The steady-statespectrum is an integral of the time-resolved phenomena over intensity decay of the sample, namely:

$$I_{(\text{steady-state})} = \int I_0 \, e^{-t/\tau} \, dt = I_0 \, \tau \,, \tag{1.1}$$