

# Preface

In the broad sense the subject of our book belongs to the Physics of Minerals field, namely, to its spectroscopic part. The main features of our experimental technique are laser excitation of minerals and time-resolved detection of resulting emission and scattering. Laser sources allow study simultaneously as events of linear optics, such as luminescence and breakdown spectroscopies, and non-linear ones, such as Raman spectroscopy and Second Harmonic Generation. Time-resolved technique, namely, signal detection only during certain time gate after certain delay following the end of the laser pulse, results in drastically improved spectroscopic sensitivity and selectivity. It enables to collect new data, which contribute greatly to our fundamental knowledge of minerals and materials and may be practically used.

The Book is arranged as follows.

The **Chapter 1** contains the basic definitions of the main scientific terms, such as *spectroscopy*, *luminescence spectroscopy*, *luminescent mineral*, *luminescent center*, *luminescence lifetime*, *luminescence spectrum* and *excitation spectrum*. The state of the art in the *steady-state luminescence* of minerals field is presented. The main advantages of *laser-induced time-resolved technique* in comparison with steady-state one are shortly described.

The **Chapter 2** contains description of the main processes involved in luminescence, such as *absorption of the excitation energy*, and *radiative return* to the ground state. The resulting luminescence is considered based on *ligand field theory*, *configurational diagrams model*, *molecular orbitals theory* and *band scheme approximation*. The main attention is paid to *luminescence decay*, consisting of radiation decay, non-radiation decay and special types of decay, such as stepwise energy transfer, cooperative sensitization and cooperative luminescence.

The **Chapter 3** describes our experimental setup with the following main parts: *laser source* (Ar, excimer, Nd-YAG, nitrogen, dye, OPO), imaging monochromator, *gated detector* (Intensified Charge Coupled Device) and computer with corresponding software. The main features of the experimental devices are described, which enable to accomplish time-resolved detection.

The **Chapter 4** contains time-resolved luminescence spectra for more than 100 minerals and synthetic analogues. The following information is presented for each one, comprising literature and original results: short description of the *crystal structure, optically active colour centres and luminescence centres*, detected by steady-state and time-resolved techniques.

The **Chapter 5** is devoted to detailed explanation of luminescence centres interpretation process, which comprises investigation of spectral and kinetic parameters of excitation and emission at different temperatures from 4.2 to 300 K. In numerous cases the interpretation is confirmed by study of synthetic mineral analogues artificially activated by potential impurities, which may serve as emission centres. The following luminescence centres have been confidently detected and interpreted:

*rare-earth elements* ( $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Yb}^{2+}$ );

*transition elements* ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Mn}^{5+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{4+}$ ,  $\text{Cr}^{5+}$ ,  $\text{V}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ni}^{2+}$ );

*s<sup>2</sup> ions* ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pb}^{+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Tl}^{+}$ ,  $\text{Sb}^{3+}$ );

*d<sup>10</sup> ions* ( $\text{Ag}^{+}$ ,  $\text{Cu}^{+}$ );

*d<sup>0</sup> complex ions* ( $\text{WO}_4$ ,  $\text{MoO}_4$ ,  $\text{TiO}_4$ ,  $\text{VO}_4$ );

*molecular centres* ( $\text{UO}_2$ ,  $\text{S}_2^-$ ,  $\text{O}_2^-$ );

*radiation-induced centres*

*diamond centres* (N3, H3, H4, S2, S3);

reabsorption lines of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{U}^{4+}$ ,  $\text{Nd}^{3+}$ .

The centres such as  $\text{Mn}^{6+}$ ,  $\text{Cr}^{4+}$ ,  $\text{Cr}^{5+}$ ,  $\text{V}^{3+}$  and  $\text{V}^{4+}$  are described, which are not found in minerals yet but are known in synthetic analogues of minerals, such as apatite, barite, zircon and corundum.

The **Chapter 6** describes of laser-induced spectroscopies, which may be used in combination with laser-induced luminescence, namely, Breakdown, Raman.

The **Chapter 7** presents several examples of laser-based spectroscopies' application in remote sensing of minerals, rocks and foliage.

The **Chapter 8** describes several examples of laser-based spectroscopies' application in radiometric sorting and process control in mining industry.

The **Chapter 9** shortly describes laser-based spectroscopies' applications in gemology, micro-element mapping, waste storage, bio-minerals and LED. It contains Conclusions, Bibliography and Subject Index.

Laser Distance Spectrometry

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