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Potential of cathodoluminescence (CL) microscopy and spectroscopy for the analysis of minerals and materials

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Abstract The present study summarizes results of cathodoluminescence (CL) microscopy and spectroscopy applied to minerals and materials. CL can be used both in a purely descriptive way to detect and distinguish different minerals or mineral generations by their variable CL colours or as an effective method for spatially resolved analysis of point defects in solids by spectral CL measurements. The cathodoluminescence emission is in all cases either related to lattice defects (e.g. electron defects on broken bonds, vacancies or radiation induced defects) and/or to trace activator ions such as $REE^{2+/3+}$, Fe^{3+}, Cr^{3+}, Al^{3+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Sn^{2+} or uranyl groups. CL spectroscopy is an outstanding method to characterize the degree of purity of materials or to detect trace elements in natural and synthetic minerals. In this way, alterations, diffusion of trace elements or formation of new phases are successfully detectable even in the case of materials with heterogeneous texture and high contents of non-crystalline phases.

Keywords Cathodoluminescence · Microscopy · Spectroscopy · Minerals · Materials

Introduction

Luminescence (luminescence glow) is a common phenomenon in inorganic and organic substances resulting from an emission transition of anions, molecules, or a crystal from an excited electronic state to a ground or other state with lesser energy [1]. According to the methods of excitation several types of luminescence can be distinguished such as photo-, cathodo-, thermo- or X-ray luminescence. Because of the wide range of individual luminescence behaviour of mineral species, luminescence techniques are used for the investigation and interpretation of the composition and structure of minerals and materials. The detection of luminescence spectra in combination with other spectral measurements (e.g. electron paramagnetic resonance, absorption spectrometry) especially allows the determination of impurity ions, molecules and other centres in solids as well as the valence of the ions, their coordination and their local symmetry. Because of these advantages luminescence techniques have developed into standard analytical techniques in different fields of science and industry, and luminescence properties of minerals have found many applications. The aim of the present work is to demonstrate the advantages of cathodoluminescence (CL) microscopy and spectroscopy in the investigation of minerals and materials.

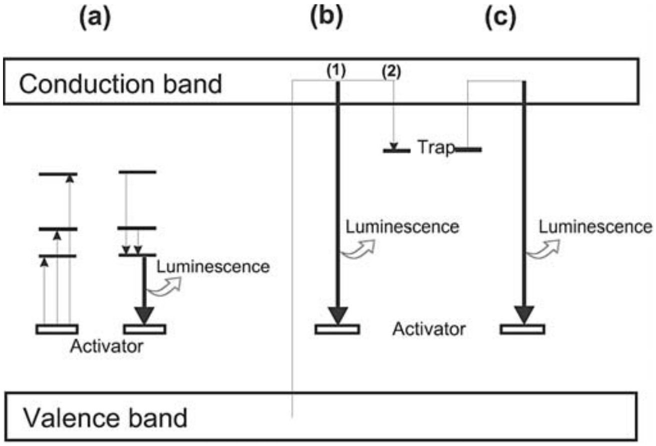

Fig. 1a–c Process of charge transfer and luminescence production in insulator crystals: **a** excitation of several energy levels by absorption of photons and resulting radiative transitions (luminescence emission); **b** excitation of an electron by high-energy particles or photons from the valence band to the conduction band and recombination with an activator resulting in luminescence emission (*1*) or trapping of the electron (*2*); **c** thermal or optical stimulation of a trapped electron to the conduction band and recombination with an activator (e.g. thermoluminescence)

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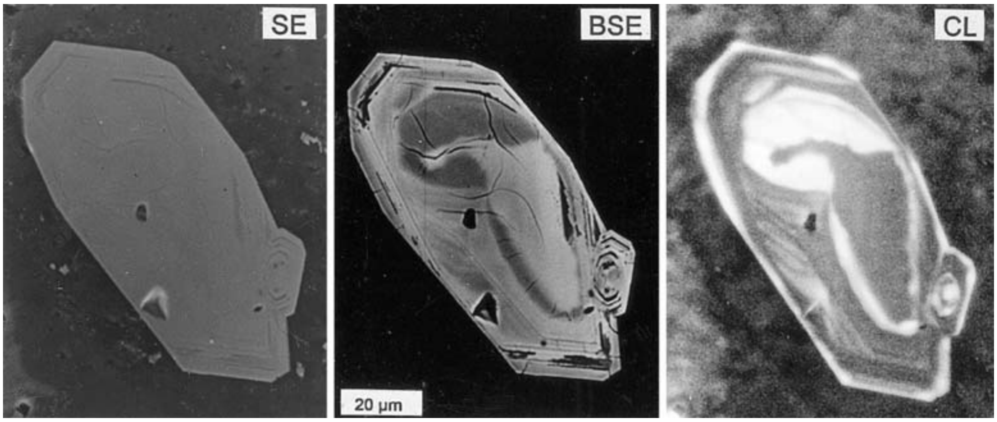

Fig. 2 SEM micrographs of SE, BSE, and CL images of a zircon grain ($ZrSiO_4$). Internal structures are only visible with BSE and CL. Note that BSE and CL intensities show a reversed correlation

Principles of luminescence

Luminescence processes can be described based on a scheme of the energy levels in a crystal. In insulators and semiconductors, a band gap (forbidden band) exists between the valence and conduction bands. A precondition for luminescence is the existence of activators (impurity ions, lattice defects), which occupy discrete energy levels in this forbidden zone between the valence and conduction bands (Fig. 1). These luminescence centres in minerals are defect centres which may be intrinsic (e.g. electron-hole centres) or impurity-related extrinsic ones, which are classified according to electronic structure: (1) transition metal ions (e.g. Mn^{2+}, Cr^{3+}, Fe^{3+}), (2) rare earth elements (REE), (3) actinides (especially uranyl UO_2^{2+}), (4) heavy metals (e.g. Pb^{2+}), (5) electron-hole centres (molecular ions S_2^-, O_2^-, F-centres) and (6) crystallophosphors of the ZnS type (sphalerite, cinnabar, realgar) [1]. More extended defects such as dislocations and clusters may also take part in the luminescence production process [1, 2].

The occurrence of luminescence can be related to three elementary processes: excitation (absorption), emission and radiationless transitions. When exciting the crystal with various kinds of energy, the ions with unfilled shells pass from the ground state to the excited state, which is attended by the appearance of an absorption band in the optical spectrum (excitation/absorption). The ions can return from the excited to the ground state by emissive transitions or through radiationless transitions (absorption or emission of lattice vibrations = phonons). In the case of emissive transition, the wavelength of the emitted light (photon energy) depends on the energy difference between excited and ground state.

Due to the interaction of the activator ion with the surrounding crystal field, some of the excitation energy is transferred to the crystal lattice resulting in a shift (Stokes shift) of the emission band in relation to the corresponding absorption band towards longer wavelengths. The activator–ligand distances in the different states and the slope of the energy levels depend on the intensity of the crystal field (expressed as crystal field splitting $\Delta=10Dq$). The stronger the interaction of the activator ion with the lattice, the greater the Stokes shift and the width of the emission line. Factors influencing values of Δ or $10Dq$ are the type of cation, the type of ligand, the interatomic distance, pressure, temperature and the symmetry of the ligand environment [3].

Natural samples commonly contain a great variety of different centres which result in complex emission spectra that are often difficult to interpret. An interaction between two or more activator ions present in a crystal can take place resulting in changes in their luminescence spectra

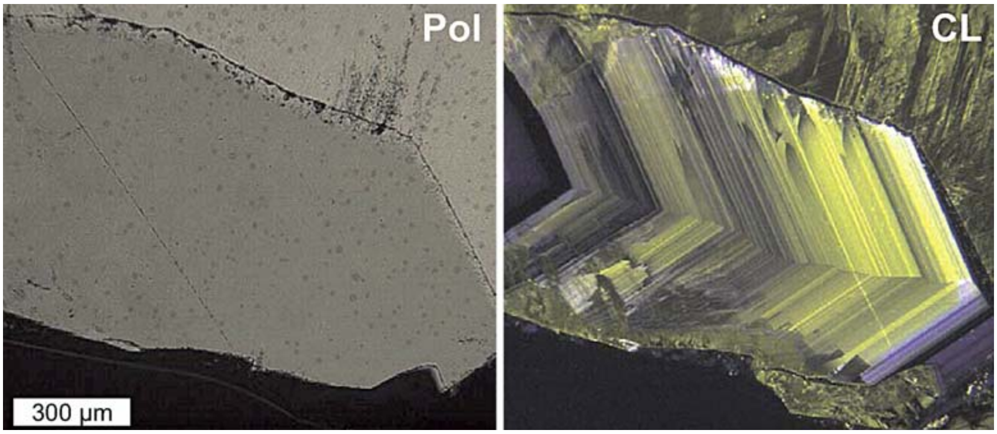

Fig. 3 A sample of hydrothermal quartz (SiO_2) imaged by polarizing microscopy (Pol) and by CL microscopy (CL) illustrating that CL reveals internal structures and growth zoning (*yellow* and *blue luminescent zones*) which are not discernible by conventional polarizing microscopy even with crossed polars

Table 1 Important analytical parameters of CL microscopy and SEM-CL

Parameter	SEM-CL	CL microscope
Sample	Polished sample surface	Polished thin (thick) section
Electron beam	Focused, scanning mode	Defocused, stationary mode
Electron source	Heated filament	Heated filament (hot-cathode) or ionized gas (cold-cathode)
Acceleration voltage	20 kV	14 kV
Beam current	0.5–15 nA	0.1–0.5 mA
Vacuum chamber	<10–6 bar	<10–6 bar
Optics	Mirror optics	Glass optics
Spectral range	200–800 nm (UV-IR)	380–1200 nm (Vis-IR)
Spot of spectral analysis	ca. 1 µm	ca. 30 µm
Luminescence imaging	Panchromatic (grey levels)	True luminescence colours
Spatial resolution	<<1 µm	1–2 µm
Analytical combination	SE, BSE, EDX (WDX)	Polarizing microscopy

due to transfer of excitation energy from one ion to another. These processes may result in sensitising or quenching of the luminescence emission and have to be particularly considered in quantitative measurements. Further details of the physical principles of the luminescence mechanisms and properties of materials are summarized elsewhere [1, 2, 3].

Instrumentation

CL can be observed on a wide variety of electron beam instrumentations due to the irradiation of a solid surface with an electron beam. The penetration depth of electrons and accordingly, the excitation depth of a crystal depends on the energy of the electrons (10–20 keV) and is in the range of 2–8 µm. The CL intensity is proportional to the acceleration voltage and current density, but is limited due to the destruction of the specimen under electron bombardment [2, 4].

First CL observations were realized using an electron probe as the exciting source. Recently, a number of different CL detectors on scanning electron microscopes (SEM) have been used. The samples may be analysed under high magnification and thus, SEM-CL equipments provide high spatial resolution of CL features (Fig. 2). The arrangement of the CL detector on a SEM allows one to compare CL investigations with BSE and SE imaging and to carry out microchemical analysis.

The combination of CL and light microscopy was first performed in the geosciences [5, 6]. The electron beam unit is mounted directly on a standard polarizing microscope, which allows one to alternate between transmitted light and CL viewing. The electron gun of the CL microscope may be performed as a "cold-cathode", in which the discharge takes place between the cathode and anode in an ionised gas, or as a "hot-cathode", in which the electrons are emitted from a heated filament [7, 8]. The hot-cathode technique provides a considerable higher CL intensity than cold-cathode instruments and is especially suitable for the investigation of weakly luminescent materials. The advantage of CL microscopy compared to the SEM-CL arrangements is that the real colours of CL emission can be detected and compared directly with transmitted light observations (Fig. 3). A compilation of important analytical parameters of CL microscopes and SEM-CL equipments is given in Table 1.

The hot cathode luminescence microscope used in this study (HC1-LM) works with a high-vacuum chamber ($<10^{-6}$ bar), an acceleration voltage of 14 keV and a com-

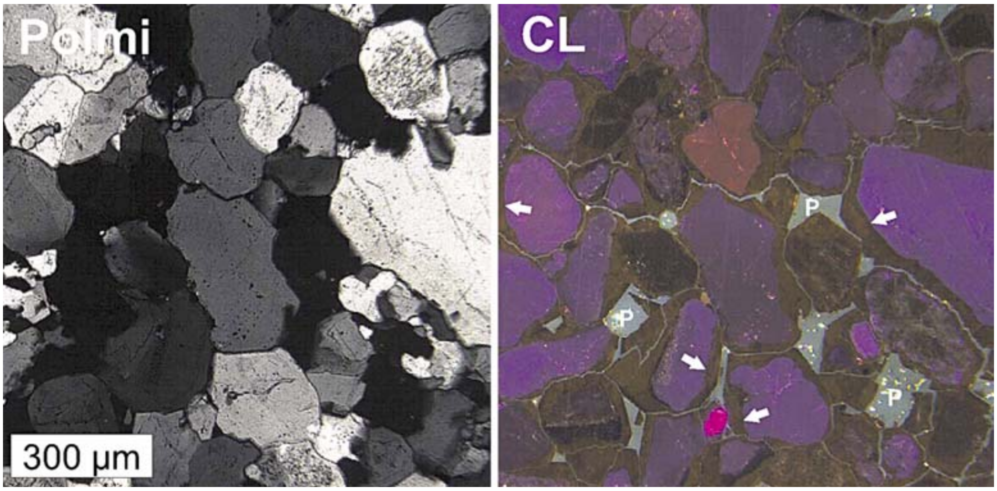

Fig. 4 A sandstone sample with brown luminescent secondary SiO_2 overgrowth (see *arrows*) on the detrital quartz grains that is only visible under CL (*P* pore space)

mon current density of approximately 10 μA mm^{-2} [9]. CL examinations are generally carried out on polished standard thin sections that are coated with carbon to prevent any build-up of electrical charge during CL operation. Colour slides of the luminescent features were taken by means of an adapted digital video camera (KAPPA 961–1138 CF 20 DXC with cooling stage). CL spectra were obtained using an EG&G digital triple-grating spectrograph with CCD detector, which is attached to the CL microscope by a silica-glass fibre-guide [9].

Applications

CL has developed into a standard technique for investigations in several fields of geosciences and material sciences [4, 7, 10, 11]. Important fields of application are the identification of minerals and the quantification of phase distribution in rocks and technical products, the analysis of real structure and crystal chemistry of solids (defects, zonal growth, internal structures, trace elements), microstructural characteristics of rocks and materials or the reconstruction of processes of mineral formation and alteration.

Identification of minerals and quantitative analysis of phase distribution

Distinct CL properties of certain minerals such as elements (diamond), sulfides (sphalerite), oxides (periclase, corundum, cassiterite), halides (fluorite, halite), sulfates (anhydrite, alunite), wolframates (scheelite), phosphates (apatite), carbonates (calcite, dolomite, magnesite) or silicates (feldspar, quartz, zeolites, kaolinite, zircon, garnet) allow a rapid identification of the different mineral constituents using CL microscopy. This is of special interest if samples consist of fine-grained material and/or of minerals with similar optical or crystallographic properties. Small grains of accessory phases can often rapidly be recognized due to bright CL, even in cases where only one grain appears in the viewed sector. These grains can then be further characterised by SEM-EDX or polarizing microscopy, respectively. In contrast, iron minerals and iron-bearing phases do not luminesce.

Another point of interest is that the CL of mineral phases is often highly variable depending on the specific conditions during formation. The knowledge of the typomorphic luminescence characteristics of minerals can be used to re-

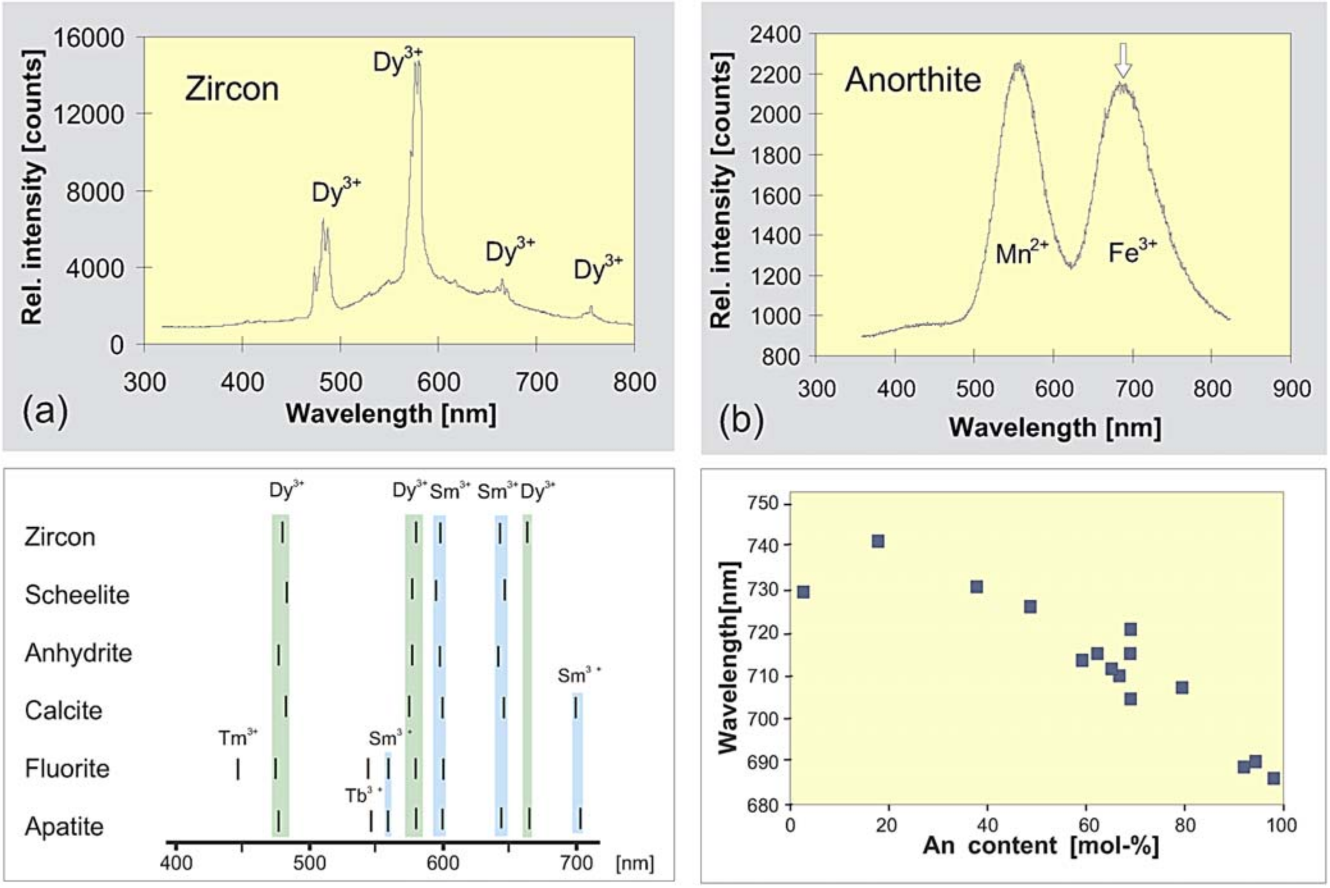

Fig. 5a,b Influence of the crystal field on the shape and position of CL emission spectra: **a** sharp emission lines with more or less constant peak positions independent on the host crystal (no influence of the crystal field); **b** broad emission bands with shift of the emission maxima depending on mineral composition (anorthite content in feldspar) due to the varying influence of the local crystal field construct the processes of mineral formation and alteration. For instance, the diversity of CL colours in detrital quartz of sediments (e.g. quartz sands) provides the basis for provenance studies in geology. Furthermore, the chronological order of crystallization can be ascertained and detrital and newly formed authigenic components are easily distinguished in addition to secondary alterations (Fig. 4).

Many of the phases occurring in ceramics, glasses, refractory materials and biomaterials show distinct CL properties allowing a rapid identification of phase distribution and phase transformations. CL results are of special interest in materials in which high contents of non-crystalline components, low concentrations of mineral phases and/or extremely heterogeneous materials limit other analytical methods. Thus, CL is an effective addition to conventional analytical methods such as polarizing microscopy, XRD, SEM or microprobe analysis [11].

The combination of CL microscopy and image analysis enables to use the advantages of these two methods for the recognition and modal analysis of mineral phases in rock samples and technical products [11]. The high-contrast colour patterns produced by CL can effectively be quantified by computer-aided image analysis, and additional information can be obtained at the same time on texture, grain-size distribution or grain shape.

Real structure and trace element distribution in minerals and materials

It has been already mentioned that most mineral groups have members showing reliable CL emission. In particular, silicates, carbonates and phosphates have been intensively studied as they form the major constituents of sedimentary and igneous rocks. Furthermore, mineral phases belonging to these classes play an important role as industrial products and biomaterials. The activation of CL in these minerals is in all cases either related to substitutional trace activators like Mn^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Eu^{2+}, REE^{3+}, Pb^{2+}, Cu^{2+} or Sn^{2+} and/or electron centres closely associated with lattice defects [1].

Concerning the spectral characteristics of the trace element-related CL emissions, the following general conclusions can be drawn:

1. If the electronic energy levels responsible for much of the absorption and emission of photons are not involved with bonding to nearby atoms, the influence of the crystal field only results in small splitting of the energy levels, and the resulting luminescence emission is characterized by narrow emission lines without Stokes shift. This is the case for the trivalent ions of the REEs, in which the electron transitions within the 4f orbitals are shielded from the influence of the crystal field by the electron shells of the 5s and 6p orbitals. Accordingly, the emission spectra are specific for each REE^{3+}

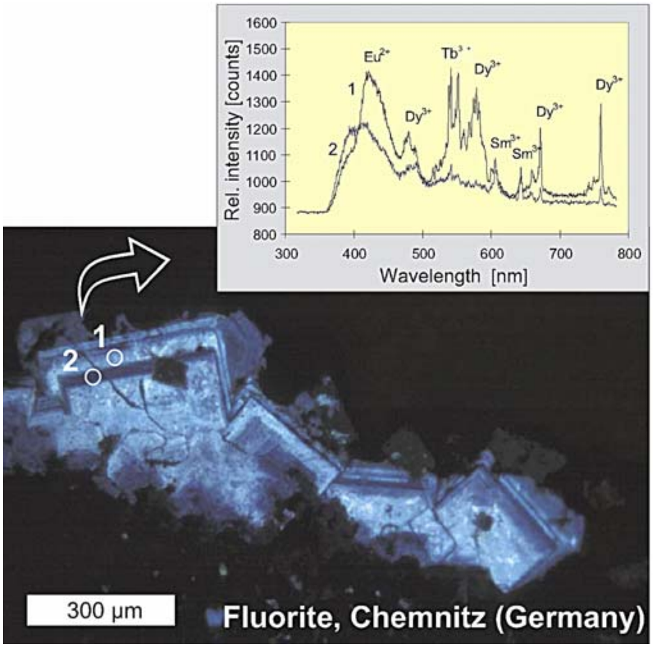

Fig. 6 CL image of a fluorite sample (CaF_2) from Chemnitz, Germany. The CL emission spectra of two zones (*1* bright greenish blue, *2* dark blue) illustrate that the differences in CL are mainly caused by different activation due to rare earth elements

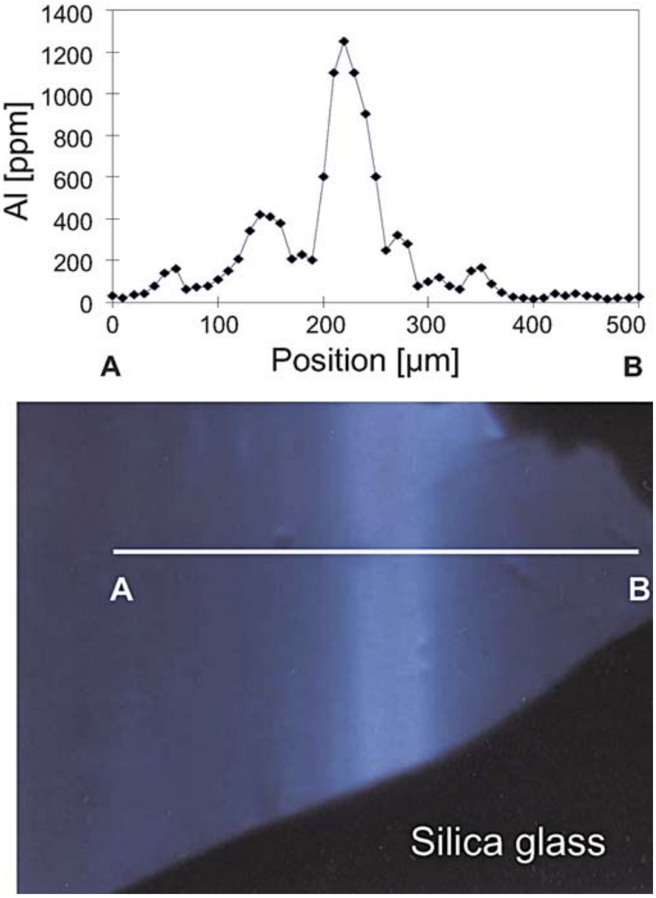

Fig. 7 CL image of a silica glass sample revealing internal heterogenities (*bright* and *dull blue luminescent zones*) that can be related to varying Al concentrations

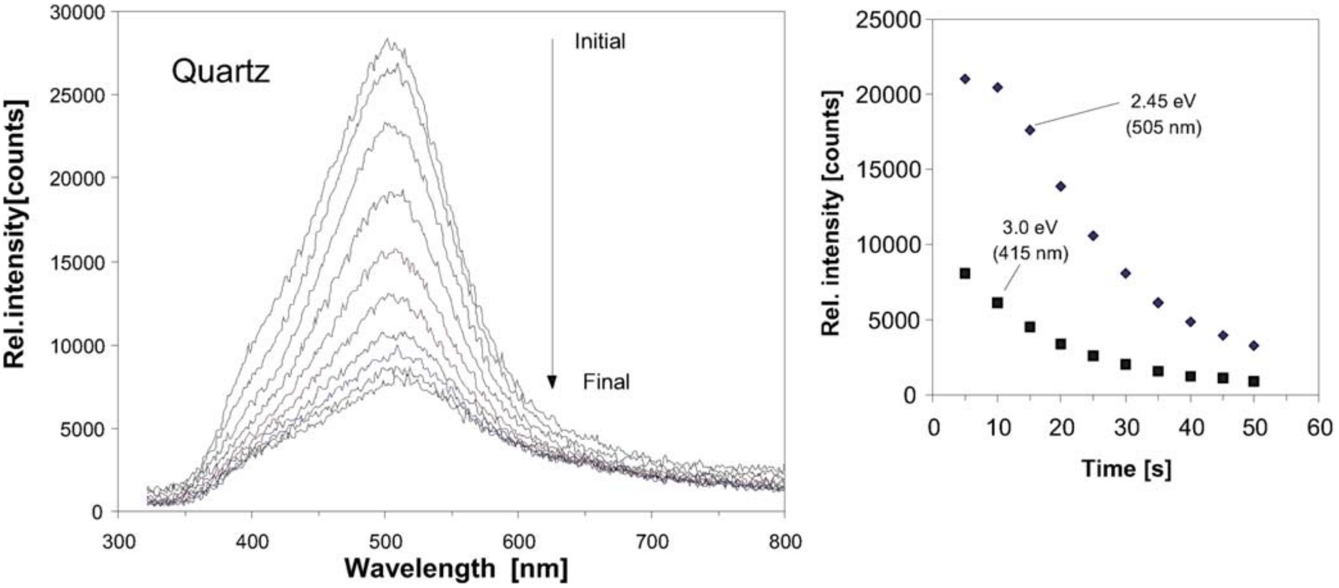

Fig. 8 Time-resolved CL emission spectrum of quartz (SiO_2) showing transient behaviour of the emission bands during to electron irradiation

ion and relatively independent of the crystal structure of the host crystal (Fig. 5a).

2. If the electron transitions take place in energy levels that are influenced by the local crystal field, luminescence emission spectra show broad bands (Fig. 5b). Because of the dependence of the Stokes shift on the strength of the local crystal field, the wavelength of the luminescence emission of each activator element varies from mineral to mineral and is specific for the crystal structure of the host crystal. Hence, one type of ion (e.g. Mn^{2+}, Fe^{3+}) can produce a great variety of luminescence spectra. The varying crystal field parameters of different carbonate minerals, for instance, result in a shift of the Mn^{2+} emission band and thus, in different visible CL colours: aragonite is green (~560 nm), calcite is orange (605–610 nm) and magnesite is red (~655 nm).

The close relationship between crystal-chemical properties and the CL characteristics of minerals and materials is the basis of detailed studies of internal structures, zonal growth and distribution of trace elements within solids which are not discernible with conventional microscopy (compare Fig. 3). Such detected heterogeneities or zones can subsequently be investigated very effectively by spectral CL measurements (Fig. 6) or additional analytical methods with high spatial resolution such as microprobe (Fig. 7), PIXE, SIMS, laser ablation ICP-MS or SHRIMP for microchemical analysis or detailed isotope studies. Additionally, during the last years attempts have been made to use CL spectroscopy for direct quantitative determination of selected trace elements in minerals [12].

Cathodoluminescence is also applied to investigate defects in natural and synthetic crystals, which are not exclusively trace element related. For instance, CL is an outstanding method to reveal radiation damage in minerals due to radioactive decay. Furthermore, several studies have been made on SiO_2 minerals for electronic and optical applications, which are highly sensitive to electron defects related to vacancies or broken bonds [13]. Here, information about the real structure can be obtained by time-resolved high-resolution CL spectroscopy combined with electron paramagnetic resonance measurements (Fig. 8). The knowledge about the formation of specific luminescence centres under specific physicochemical conditions of crystallisation enables the investigator to reconstruct various mineral-forming processes.

References

1. Marfunin AS (1979) Spectroscopy, luminescence and radiation centers in minerals. Springer, Berlin Heidelberg New York
2. Waychunas GA (1988) Rev Mineral 18:639–664
3. Burns RG (1993) Mineralogical applications of crystal field theory. Cambridge University Press, Cambridge
4. Remond G et al. (1992) Scann Micr 6:23–68
5. Sippel RF (1965) Rev Scient Instr 36:556–558
6. Smith JV, Stenstrom RC (1965) J Geol 73:627–635
7. Marshall DJ (1988) Cathodoluminescence of geological materials. Unwin-Hyman, Boston
8. Yacobi C, Holt DB (1990) Cathodoluminescence microscopy of inorganic solids. Plenum, New York
9. Neuser RD, Bruhn F, Götze J, Habermann D, Richter DK (1995) Zbl Geol Paläont Teil I H 1/2:287–306
10. Pagel M, Barbin V, Blanc P, Ohnenstetter D (eds) (2000) Cathodoluminescence in geosciences. Springer, Berlin Heidelberg New York
11. Götze J (2000) Cathodoluminescence microscopy and spectroscopy in applied mineralogy. Freiberger Forschungshefte C 485, Freiberg
12. Habermann D, Neuser RD, Richter DK (1998) Sed Geol 116: 13–24
13. Stevens Kalceff MA, Phillips MR (1995) Phys Rev B52: 3122–3134