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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+}, Fe³⁺, Cr³⁺, Al³⁺, Mn²⁺, Pb²⁺, Cu²⁺, Sn²⁺ 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.

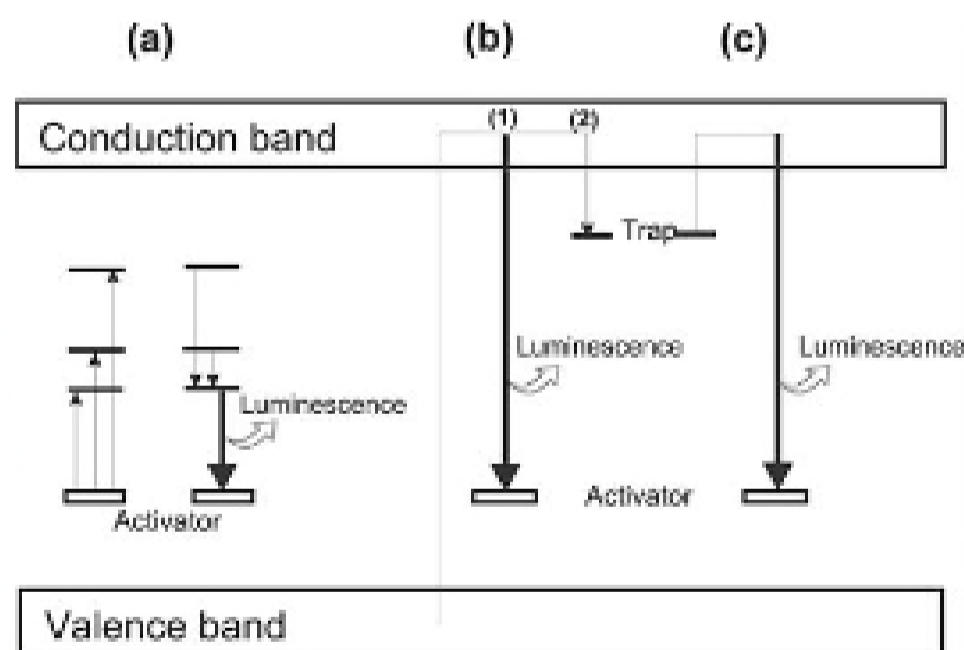
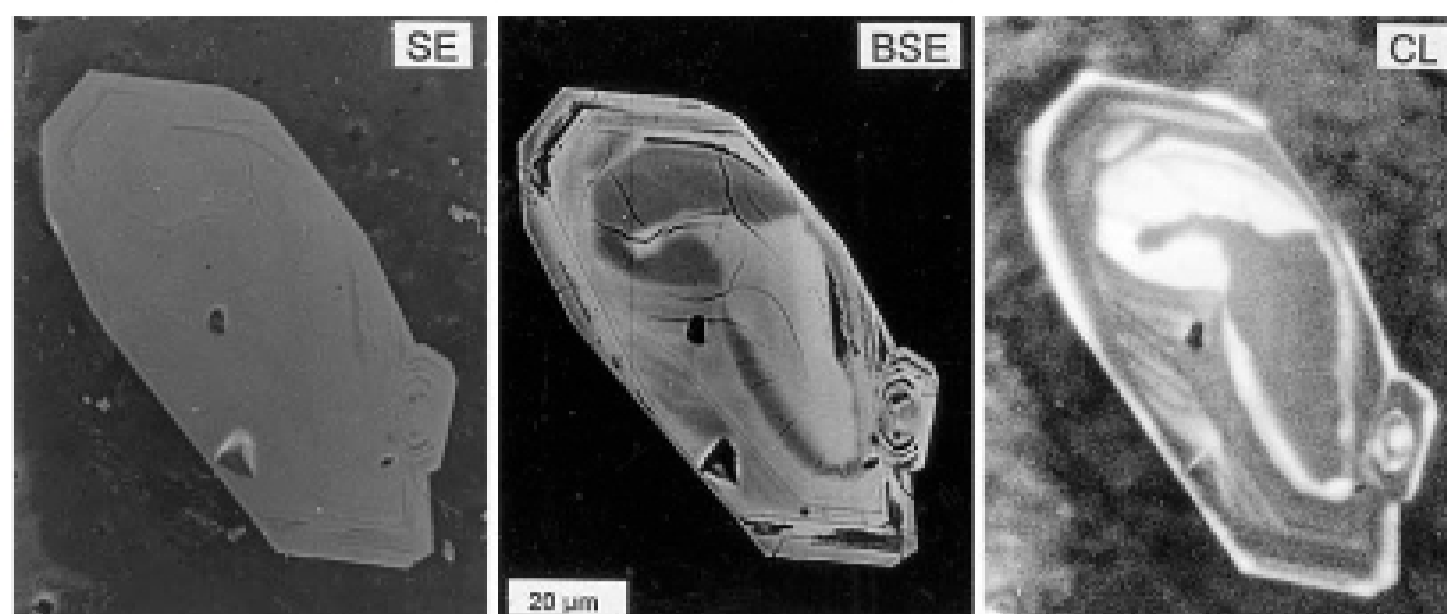


Fig. 1a–c Process of charge transfer and luminescence production in insulator crystals: **a** excitation of several energy levels by absorption of photons and resulting radiative transitions (luminescence emission); **b** excitation of an electron by high-energy particles or photons from the valence 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 at-

tended 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

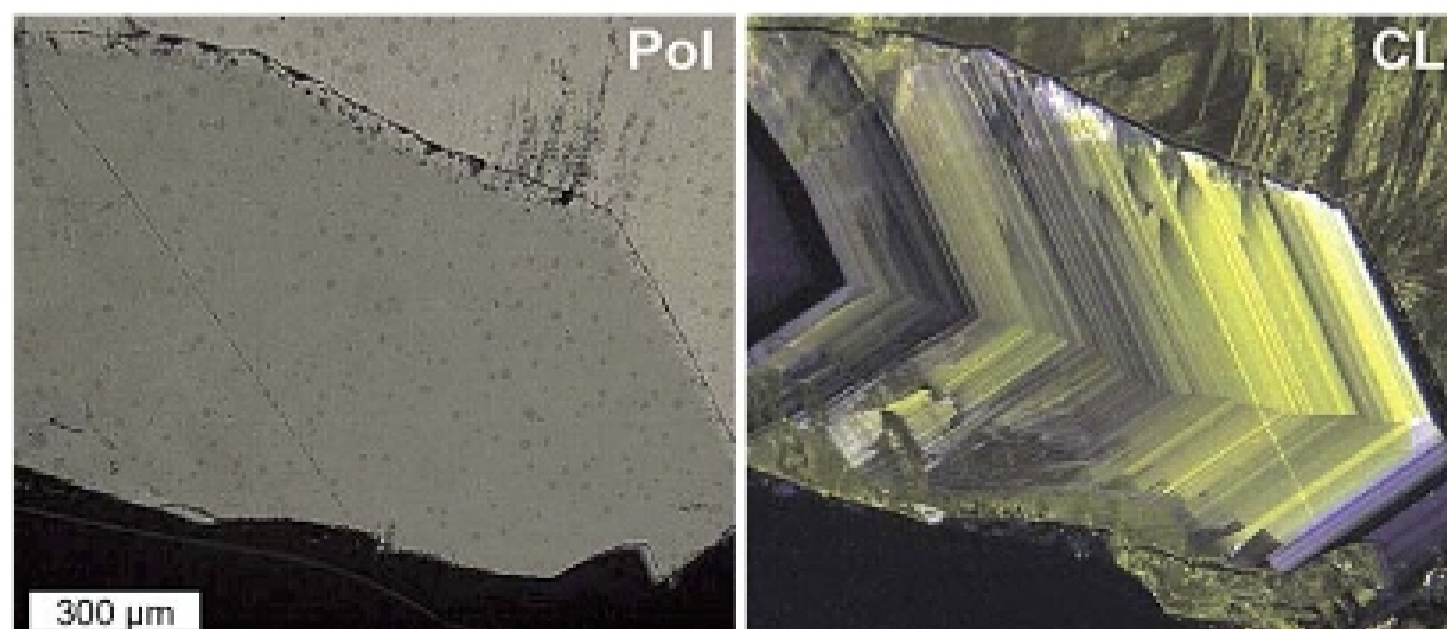


Table 1 Important analytical parameters of CL microscopy and SEM-CL.

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 μ m	ca. 30 μ m
Luminescence imaging	Panchromatic (grey levels)	True luminescence colours
Spatial resolution	<<1 μ m	1–2 μ m
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 μ m. 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 (HCL-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 SiO₂ overgrowth (see arrows) on the detrital quartz grains that is only visible under CL (P pore space)

