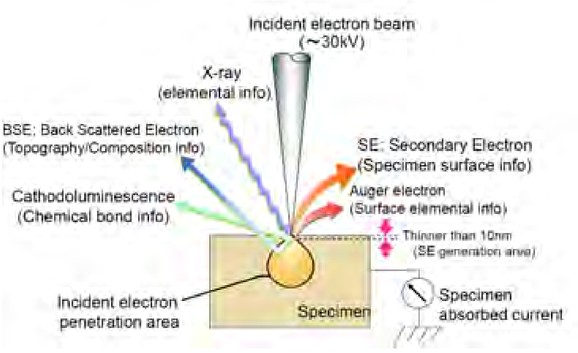
Applications note

Harnessing the power of cathodoluminescence in low vacuum SEMs & benchtop SEMs

Cathodoluminescence (CL) is a technique widely used in electron microscopy. It is frequently used in geological studies to study defect states and to support dating. It is also used in materials science to provide information on the photonic properties of semiconductors such as solar cells and in pharmaceuticals to observe the distribution of active pharmaceutical ingredients. This applications note will demonstrate how CL can be quickly and easily undertaken in Hitachi's low vacuum SEMs and benchtop SEMs.

What is CL?

Cathodoluminescence is just one of a multitude of processes which may occur when an energetic electron beam impinges on a sample. More commonly SEM's use electron signals such as secondary electrons (SE) for topographical imaging and backscatter electrons (BSE) for compositional imaging. In addition to these electron signals, a spectrum of electromagnetic radiation is generated, including x-rays which are used for elemental analysis (EDX/EDS).



Typical interactions and signals in an SEM

In some materials, photons in the infrared, visible and UV wavelengths may also be emitted. These photons can carry useful and information about subtle compositional variations, band-gap, chemical bonding, crystal structure and defects.

Undertaking panchromatic CL imaging

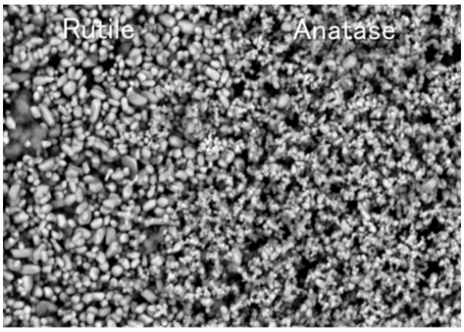
CL imaging is conventionally undertaken by adding a dedicated photon detector to a SEM. The detector simply collects photons rather than electrons. The detector may be panchromatic (detecting a wide range of wavelengths) or monochromatic (detecting specific wavelengths as required). The detector may consist of a simple light guide and photomultiplier tube orientated towards the specimen. To increase collection efficiency it may also consist of a parabolic mirror immediately above the specimen (which in turn is connected to a photomultiplier tube or a spectrometer if spectral analysis of the photon wavelength is required).

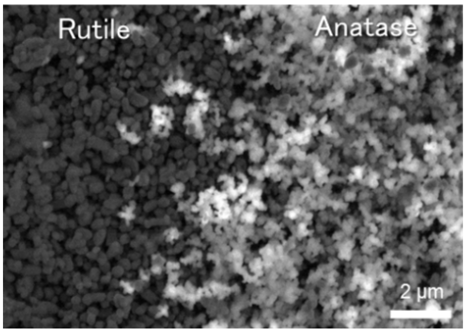
Hitachi's low vacuum SEMs fitted with a low vacuum SE detector, however, offer the capability to detect panchromatic CL without any modification. A wide range of panchromatic CL investigations quickly and easily undertaken in a low cost, readily accessible instrument such as the TM4000Plus benchtop SEM. Since Hitachi's low vacuum secondary electron detector (referred to as UVD) is based on light collection technology, CL detection can be achieved with a single mouse click. By switching off the bias which is usually applied to enhance secondary electron signal the detector functions as a photon detector, with the secondary electron signal suppressed. As the instruments also include a high performance backscatter electron detector and multi-channel image handling capability, it's possible to acquire compositional and CL information simultaneously. The datasets can be even richer if the (optional) EDX elemental mapping capability is used – providing qualitative and quantitative chemical information within minutes.

All data presented in this applications note has been acquired with a Hitachi TM4000Plus benchtop SEM in standard configuration

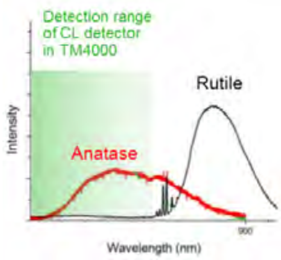
CL imaging in materials science

In materials science, CL imaging can be a powerful technique to understand the crystallographic properties or bonding state of materials. In the example below, a multi-phase TiO_2 sample was studied. No significant contrast variation can be seen in the backscatter electron image (top) since there is no compositional variation across the specimen. However, in the CL image (bottom), distinct regions are visible. These relate to the rutile and anatase phase of TiO_2.





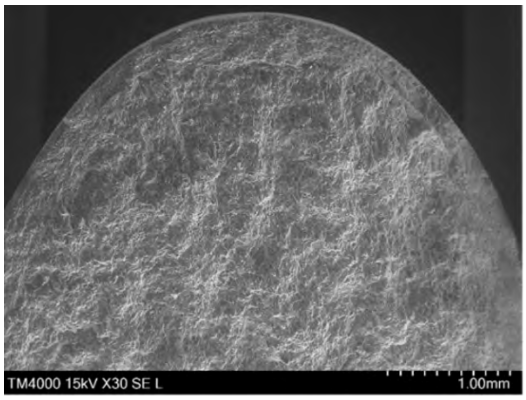
Since the CL detector used in these experiments has greater sensitivity in the shorter wavelength range, the anatase phase appears bright, whereas the rutile phase (where emitted photons have a wavelength >500nm) appears dark.

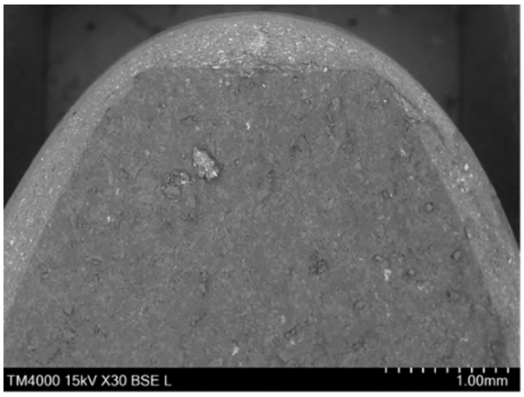


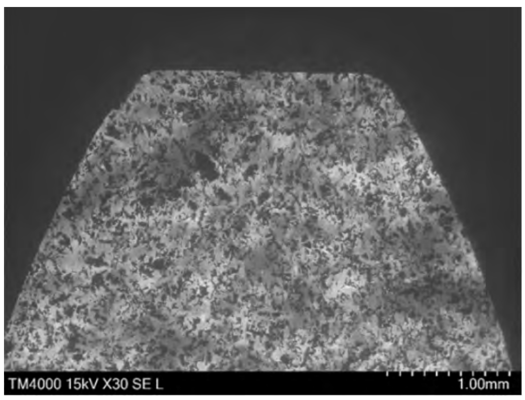
Using this quick and simple method avoids the need to undertake separate spectrophotometry or diffraction studies and gives spatially resolved information at the sub-μm scale not easily attainable from other techniques.

CL imaging in pharmaceuticals

In pharmaceutical drug delivery systems such as a simple tablet, the correct distribution of the Active Pharmaceutical Ingredient (API) is critical. The particle size and distribution of the API needs to be carefully controlled to ensure efficient uptake within the body. The example below is a cross-section through a commercial ibuprofen tablet. The secondary electron image (top) simply shows the roughness associated with the fracture of the tablet. The backscatter electron image (middle) shows the enteric (gastric resistant) coating surrounding the tablet itself. The CL image (bottom), however, shows detailed information about the distribution of the API. This information can be used for rapid process control and quality control.



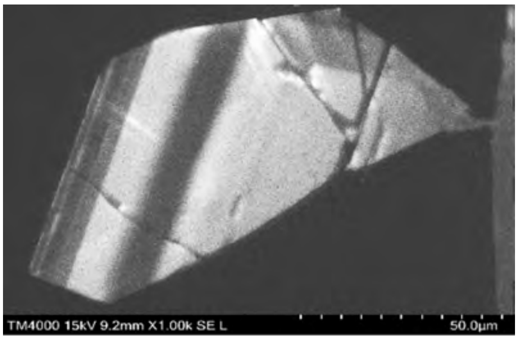




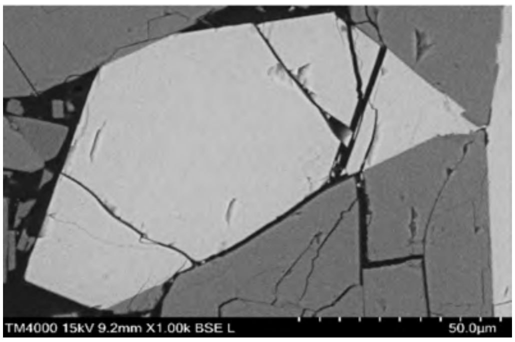
CL imaging in geology

CL is widely used in geology to study subtle variations in the formation of crystals which may not be apparent from secondary electron imaging, backscatter electron imaging or energy-dispersive X-ray analysis. In the syenite example below, the BSE image (middle) shows no brightness variation across the crystal since there is little or no compositional change, whereas the CL image exhibits strong brightness variation across the crystal due to zonation.

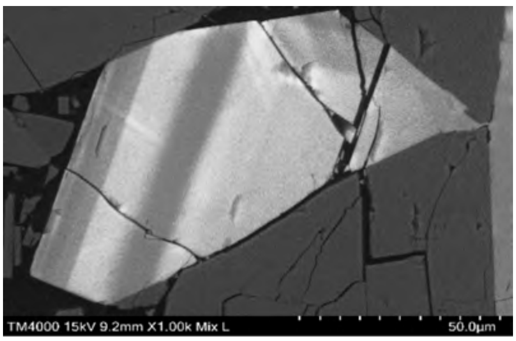
Zonation study in coarse grained syenite with alkali feldspar



CL image demonstrating zonation



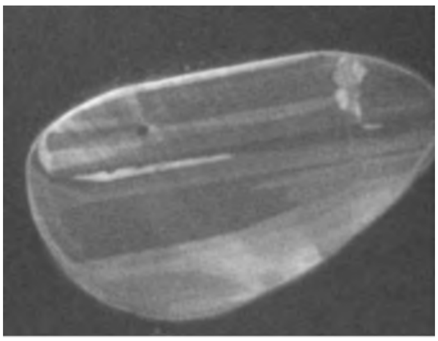
BSE image showing compositional contrast



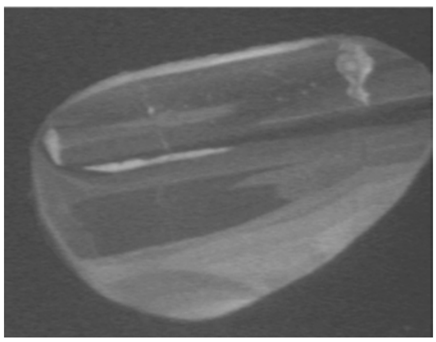
Mixed (CL+BSE) image

Another example where the technique can be readily applied is to support geological dating of zircons. Variations in U-Th-Pb ratios within zircon crystals can be used to determine the date of formation of the crystal. The small variation in U-Th-Pb ratio is smaller than can be reliably detected with chemical techniques in the SEM such as EDX. The exact ratio of the elements is determined precisely by mass spectrometry instead. The challenge, however, is that the mass spectrometer cannot quickly identify areas of interest to examine. CL in SEM, therefore, can play a powerful role in identifying areas of interest for further analysis and can significantly speed up the dating process. The "zoning" apparent in CL images of zircons gives an indication of which grains exhibit the biggest variations in U-Th-Pb ratios, helping to guide the geologist to undertake mass spectrometry on the most suitable crystals.

The example below compares CL imaging of a zircon in TM4000Plus (top) with the same crystal imaged in a conventional larger SEM with dedicated CL detector (bottom). Comparable information is present and both approaches provide the information required to select the optimum grains for subsequent mass spectrometry.



CL image of zircon from TM4000 benchtop SEM using integrated detector



CL image of zircon from full size SEM fitted with dedicated panchromatic CL detector

Conclusion

Panchromatic imaging capability can be effectively performed in a Hitachi benchtop SEM to help understand a wide range of materials systems. The ability to overlay BSE and CL data in one image provides users with accurate correlation of chemical and crystallographic or bonding information – either as standalone studies or to support further investigations such subsequent spectrometry or diffraction studies.

As these instruments require less capital investment, require less lab space, offer faster time-to-data and can be easily used by any operator regardless of previous electron microscope experience, they offer the opportunity for CL studies to be applied far more widely than in the past. This enables the power of CL to be accessible in many more labs than in the past, including for process and quality control as well as in academic environments. Additionally, the Hitachi benchtop SEMs offer the ability to undertake this type of CL work without any modification or any additional hardware investment. Coupled with secondary electron (SE) and backscatter electron (BSE) imaging, as well as EDX elemental analysis and mapping, this type of instrument provides a powerful addition to pharmaceutical labs, geoscience labs and a wide range of materials science labs.

Acknowledgments

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