

## Cathodoluminescence Microanalysis of Amorphised Quartz

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Cathodoluminescence (CL) microanalysis techniques which are highly sensitive to trace levels of impurities, have been used to investigate and compare the defect structures of natural and synthetic silicon dioxide (SiO<sub>2</sub>) polymorphs. Quartz (natural crystalline SiO<sub>2</sub>) is an important and abundant mineral in the lithosphere. Defects in the SiO<sub>2</sub> microstructure may result from impurities (e.g. substitutional and interstitial impurities, inclusions, etc.) or imperfections (e.g. self-interstitials, vacancies, dislocations, etc.). [1] Tetrahedrally coordinated silicon dioxide is a relatively pure material in the natural state. Impurities are not easily incorporated into the  $\alpha$ -quartz tetrahedral structure in high concentrations [2]. The substitution of impurity ions for silicon is limited by the high valency (Si<sup>4+</sup>) and the relatively small atomic radius (0.42 Å) of silicon. Microscopic localised amorphization of natural quartz may occur due to incorporation of impurities during growth or due to subsequent defect inducing processes (e.g. the effects of radiation, pressure, temperature, etc). Thus localised amorphous environments may occur within natural crystal quartz. The trace defect dependent CL emissions from natural quartz are of particular interest because they often reflect the specific conditions of crystal growth and therefore, can be used as a signature of genetic conditions of mineral formation.

In this investigation, valuable insights into the defect structure and possible identification of intrinsic and extrinsic CL emissions observed in spectra from natural quartz/ agate (see Figure 1) are provided by comparative investigations of crystalline and amorphous pure synthetic silicon dioxide. A single broad unresolved multi-component emission (FWHM 0.4 eV) at ~1.9 eV (650 nm) is initially observed from a-SiO<sub>2</sub> and is attributed to the Non-Bridging Oxygen Hole Centre (NBOHC) with contributions from at least two precursors. For higher electron beam irradiation doses, local defect concentration increases such that the irradiated quartz is damaged/ amorphized. The CL spectrum from a-SiO<sub>2</sub> is modified by the electron beam irradiation and resolved CL emissions are observed at 1.88 eV (~660 nm) associated with the NBOHC; at 1.93 eV (~640 nm) associated with the NBOHC with OH precursor; at 2.7 eV (~460 nm) associated with the radiative recombination of the a-SiO<sub>2</sub> self trapped exciton (STE) and at ~4.5 eV (~275 nm) associated with Oxygen Deficient Centers (ODC). Following higher irradiation doses which induces amorphization of a-SiO<sub>2</sub>, (as evidenced by the swelling of the irradiated quartz surface) a broad ~2.3 eV (~540 nm) emission associated with the radiative recombination of the STE in amorphised-SiO<sub>2</sub> is observed.[1]

Broad electron beam irradiation sensitive CL emissions from quartz/ agate are also found to be associated with trace levels of substitutional impurities (e.g. Al, Fe, and Ge).. A electron radiation sensitive CL emission at ~3.2 eV (385 nm) is attributed to the analogous substitutional Aluminium impurity defect Al<sup>3+</sup>:M<sup>+</sup> defect in  $\alpha$ -SiO<sub>2</sub> where M<sup>+</sup> is typically Na<sup>+</sup> or H<sup>+</sup>. A electron radiation sensitive CL emission at ~1.65 eV (750 nm) is attributed to the a substitutional Iron impurity defect Fe<sup>3+</sup>:H<sup>+</sup> defect in  $\alpha$ -SiO<sub>2</sub>. Finally a distinctive broad yellow CL emission (580 nm/ 2.15 eV) is observed from agate, chalcedony and some natural hydrothermal quartz (related to ore mineralization). The specific association of this yellow CL emission to particular physical and chemical environments is an important

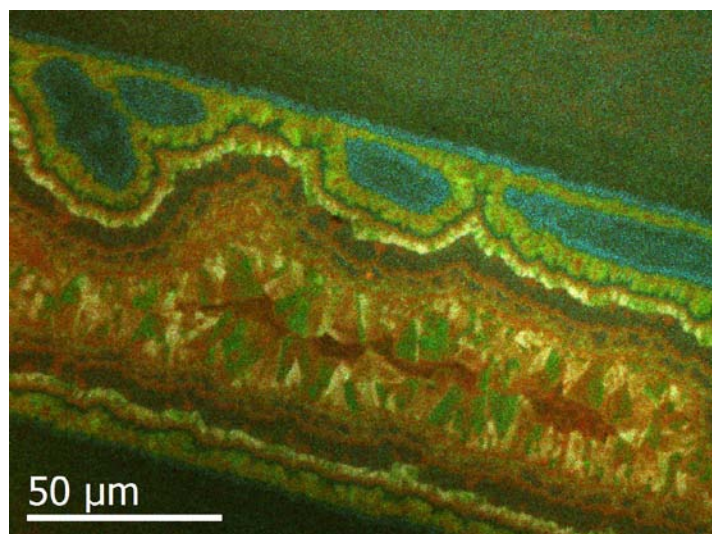
genetic indicator.[3] CL microanalysis with locally-resolved trace element analyses has therefore been used to aid in the investigation of the origin of this distinctive yellow CL emission in quartz/ agate.

The CL investigations indicate that the ~580 nm (2.15 eV) emission may be attributed to self-trapped exciton (STE) emission. Self-trapping occurs when the excited electron-hole pair (i.e. the exciton) creates a localised distortion in the SiO<sub>2</sub> host lattice. A number of possible candidates for the SiO<sub>2</sub> exciton defect pairs for the have been proposed and it is possible that several forms co-exist (e.g. STE defect pairs including 'Ecenter and the non-bridging oxygen hole centre, etc). The non-radiative relaxation of the STE results in formation of defects via radiolysis (and local amorphization of quartz). In contrast, the radiative recombination of the STE results in luminescence emission and the restoration of the SiO<sub>2</sub> microstructure.[4],[5] High intensity CL at ~580 nm is also consistent with the presence of substitutional Ge impurities in quartz/ agate (Ge < 95 ppm) adjacent to a STE resulting in a Ge associated STE (Ge STE). The observation of high intensity emission at ~580 nm attributed to radiative recombination of STE associated defects is consistent with a high concentration of E' defects detected by EPR measurements in the same quartz specimens.

#### References:

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**Figure 1.** CL RGB color composite image of St E Egidien agate. Spatial segregation of the overlapping 580nm/650nm CL emission (R), 460nm CL emission (G) and 280nm CL emission (B) is shown.