Origin and significance of the yellow cathodoluminescence (CL) of quartz

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Cathodoluminescence (CL) studies of quartz provide a lot of information not available by other analytical methods. The close relationship between crystal-chemical properties and luminescence characteristics can be used to visualize the defect structure of quartz and to reveal different growth generations, internal structures or distribution of trace elements within quartz. On the other hand, CL is an effective method for spatially resolved analysis of point defects in quartz by spectral measurements. In combination with EPR spectroscopy and spatially resolved trace-element analysis, the different emission bands can be related to specific lattice defects in the quartz structure (e.g., Stevens-Kalceff and Phillips, 1995; Götze *et al.*, 2001; Stevens-Kalceff, 2009; Götze, 2009).

The defects causing the different CL emissions in quartz often reflect the specific physic-chemical conditions of crystal growth and therefore, can be used as a signature of genetic conditions of mineral formation. The most common CL emission bands in natural quartz are the 450 and 650 nm band, respectively (Ramseyer et al., 1988; Götze et al., 2001). These luminescence emissions result in bluish-violet CL colours and are detectable in quartz crystals from igneous, volcanic and metamorphic rocks as well as authigenic quartz from sedimentary environments. In quartz from pegmatite, a transient emission around 500 nm (bluish-green) is characteristic (Götze et al., 2005), whereas a short-lived blue CL (emission band at 390 nm) is the typical feature of natural and synthetic hydrothermal quartz (Ramseyer & Mullis, 1990; Perny et al., 1992; Götze et al., 2001).

A conspicuous feature is the occurrence of yellow luminescent quartz, which is restricted to certain geological environments (Fig. 1). The typical yellow CL (emission band at ca. 580 nm – 2.15 eV) was up to now exclusively detected in some natural hydrothermal quartz (often related to sulfide ore mineralization) as well as cryptocrystalline chalcedony and agate. This relation to specific physic-chemical environments makes the yellow CL of quartz to an important genetic indicator (Götze et al., 1999; Götze, 2009). The recent study combines investigations by CL microscopy and spectroscopy with locally-resolved trace element analyses and investigations by electron paramagnetic resonance (EPR) to get more information about the origin of the yellow CL emission in quartz.

The observation of high intensity emission at ~580 nm (2.15 eV) is consistent with a high concentration of E' defects detected by EPR measurements in the same quartz specimens. CL studies with different electron beam parameters indicate that the ~580 nm emission can probably 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_2 host lattice. The non-radiative relaxation of the STE results in formation of defects via radiolysis (and local amorphisation of quartz). In contrast, the radiative recombination of the STE results in luminescence emission and the restoration of (i.e. radiative relaxation to) the ideal SiO_2 microstructure. A number of possible candidates for exciton defect pairs for the SiO_2-STE have been proposed and it is possible that several forms co-exist (e.g. defect pairs including E′ center and interstitial oxygen; E′ center and NBOHC, etc). High intensity emission at ~580 nm is also consistent with possible contributions from substitutional Ge associated within the quartz (detected Ge contents up to 95 ppm in agate with yellow CL) resulting in a Ge associated STE (Ge STE) in addition to contributions from a-SiO_2 (a-Si STE) associated with local amorphized regions of the quartz (Trukhin, 2000).

The close relationship between the yellow emission and high concentrations of defect centres as well as the specific geological environments lead to the conclusion that this luminescence can probably be related to processes of fast crystallization (probably from a non-crystalline precursor) in an environment with oxygen deficiency.

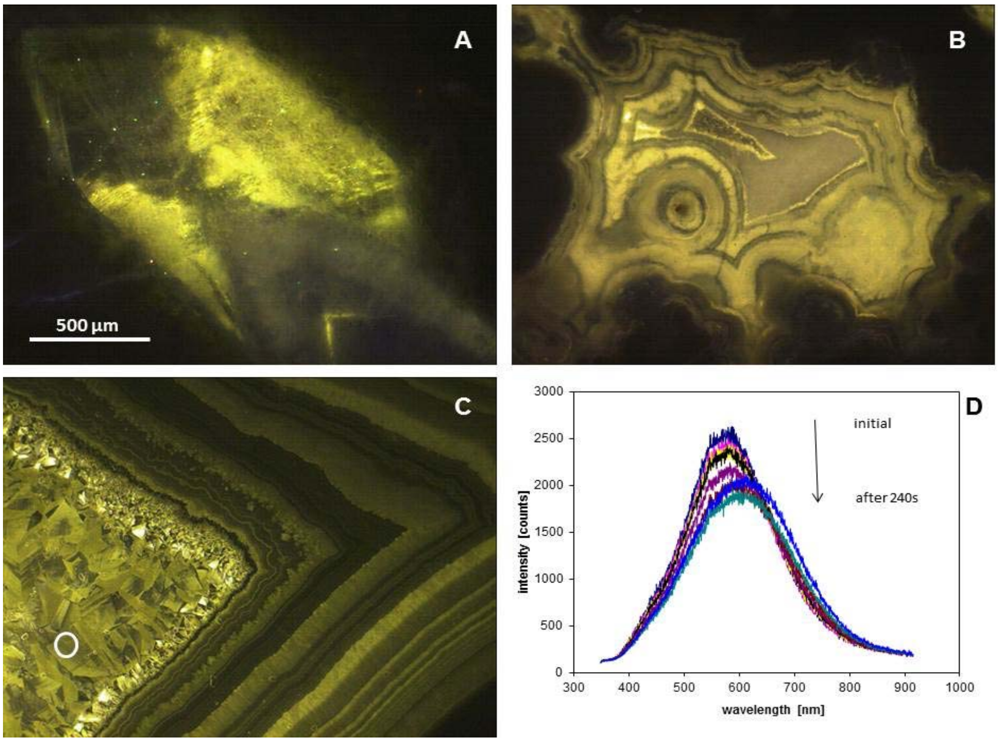

Fig. 1. *CL micrographs of quartz from different localities showing the conspicuous yellow emission; A – Sector-zoned quartz from a hydrothermal sulphide ore deposit, Freiberg (Germany); B – Colloform silica from hydrothermal environment with iron biomineralization, Matras Mountains (Hungary); C/D – Agate from ignimbrite (C), St. Egidien (Germany) and related CL emission spectrum (D).*

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