

Cathodoluminescence properties and trace element signature of hydrothermal quartz: A fingerprint of growth dynamics

**THOMAS GÖTTE,^{1,*} THOMAS PETTKE,² KARL RAMSEYER,² MONIKA KOCH-MÜLLER,³
AND JOSEPH MULLIS⁴**

¹Institute for Geosciences, Goethe-University Frankfurt, Altenhöferallee 1, 69438 Frankfurt, Germany

²Institute of Geological Sciences, University Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland

³Department 3: Geodynamics and Geomaterials, Deutsches GeoForschungsZentrum, GFZ Telegrafenberg, 14472 Potsdam, Germany

⁴Institute of Mineralogy and Petrology, University of Basel, Bernoullistrasse 30, CH-4056 Basel, Switzerland

ABSTRACT

Relationships between cathodoluminescence spectra and trace element contents of hydrothermal α -quartz including hydrogen species are characterized for crystals from Gigerwald (Switzerland) and Rohdenhaus (West Germany) grown under highly different physico-chemical conditions and related to growth fabrics visualized by classical cathodoluminescence microscopy.

Distinct emission bands at 395, 448, 503, 569, and 648 nm determine the spectral characteristics of cathodoluminescence images. Aluminum, Li, and H are the most important trace elements as determined by LA-ICP-MS and IR spectroscopy, reaching up to 6000 $\mu\text{mol/mol Al}^{3+}$, 3300 $\mu\text{mol/mol Li}^+$, and 5000 $\mu\text{mol/mol H}^+$. Germanium, B, and Na are present at less than a few $\mu\text{mol/mol}$ concentrations. A large amount of H is present in structurally bound water. AlOH-defects are also common, whereas LiOH- and SiOH-defects play only a minor role.

Fast grown zones contain Li^+ and H^+ concentrations too low to compensate the charge deficit if all measured Al substitutes for Si^{4+} in the quartz structure. This indicates the occurrence of intrinsic defects such as oxygen deficiency centers, which are assumed to affect the luminescence properties. Lithium abundances correspond to $[\text{AlO}_4\text{Li}]$ -defects, correlated to the unstable intensity at 395 nm, but the correlation is different for both localities. This is inconsistent with a simple causal relationship between Al-Li-centers and the emission at 395 nm. Conversion of $[\text{AlO}_4\text{Li}]$ -defects to $[\text{AlO}_4]^0$ -defects by natural irradiation is a possible explanation for this discrepancy. The increase of the intensity at 648 nm is not proportional to SiOH concentration as suggested in the literature, indicating that other precursor defects such as peroxy-linkages are more important. The decay of the intensity at 395 nm is much more rapid than the increase at 648 nm, excluding a coupling between these processes.

Trace element incorporation in slowly grown hydrothermal quartz crystals is a direct function of fluid chemistry and temperature for a specific growth sector. Because quartz grows during extended periods of hydrothermal activity, changes in trace element inventory as visualized by cathodoluminescence may identify significant changes in growth conditions, which likely remain unrecognized during sample characterization with conventional microscopy.

Keywords: Dynamics of quartz growth, trace elements: Al, Li, H in quartz, electron microscopy, cathodoluminescence of quartz, IR spectroscopy, quartz