The 450 nm (2.8 eV) cathodoluminescence emission in quartz and its relation to structural defects and Ti contents

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Abstract

The origin of the common blue 450 nm (2.8 eV) cathodoluminescence (CL) emission in natural and synthetic quartz has been investigated using a combination of CL microscopy and spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and trace-element analysis by electron microprobe analysis as well as inductively coupled plasma-mass spectrometry (ICP-MS). The study shows that the appearance of the ~450 nm emission band can be attributed to two different defects in quartz. First, a transient luminescence can be explained by structural defects in oxygen deficient quartz. The luminescence model implies self-trapped exciton (STE) emission related to oxygen vacancies. This type of CL emission is frequent in high-purity synthetic quartz and natural quartz of hydrothermal origin. Second, in Ti-rich quartz from natural samples (e.g., quartz phenocrysts in rhyolites) and synthetic quartz of Ti-diffusion experiments, an additional 450 nm (2.8 eV) emission was detected, which is stable under the electron beam. The intensity of this ~450 nm emission band correlates with the concentration of trace Ti in quartz, and substitutional Ti4+ at the Si4+ position was proved by EPR spectroscopy. In quartz crystals with elevated Ti concentrations both intrinsic and extrinsic blue CL emissions at ~450 nm can coexist, hindering a thorough characterization and quantification of the CL signal. A reliable distinction of the two different CL emission bands is possible by fitting the peaks of the CL spectra, and the peak width of the 450 nm emission can be used to differentiate the STE from the Ti4+ emission. However, the definitive technique is through the observation of CL peak shape change over time at a point by collecting a time series of CL spectra in conjunction with EPR spectroscopy and trace-element analysis of the Ti concentration.

Keywords: Cathodoluminescence (CL), hyperspectral CL, quartz, blue CL emission, electron paramagnetic resonance (EPR), Ti concentration

Introduction

Quartz (low-temperature α-quartz) is the most important SiO2 polymorph in nature, which occurs as a frequent constituent in almost all rock types and also represents an economically important silica raw material. Therefore, the knowledge of specific properties of quartz is indispensable for many mineralogical and geological investigations. Cathodoluminescence (CL) studies of quartz constitute a powerful method, which enables the visualization of the defect structure and reveals internal features, which are not discernible by other analytical methods (Ramseyer et al. 1988; Götze et al. 2001; Götze 2012).

The CL emission of quartz is variable and in general caused by various point defects including both pure lattice defects (e.g., related to oxygen and silicon vacancies) and substitutional trace elements. The relation of specific luminescence emission bands to different defect centers causes a diversity of CL characteristics and visible CL colors in dependence on the processes of mineral formation or alteration (Ramseyer et al. 1988; Götze et al. 2001, 2021). Therefore, the knowledge about the origin of different luminescence centers can help to reconstruct geological processes and to reveal different growth generations or secondary alteration, which cannot be discerned by optical or electron microscopy (e.g., Zinkernagel 1978; Ramseyer et al. 1988; Ramseyer and Mullis 1990; Watt et al. 1997; Götze et al. 2001, 2005, 2013, 2015, 2017b, 2021; Van den Kerkhof et al. 2004; Müller et al. 2002, 2005; Landtwing and Pettke 2005; Rusk et al. 2006, 2008; Krickl et al. 2008; Götze 2009; Jourdan et al. 2009; Lehmann et al. 2011; Götze et al. 2011; Cerin et al. 2017; Götze and Hanchar 2018).

The most common CL emission bands in natural quartz are bands with maxima at ca. 450 and 650 nm (Ramseyer et al. 1988; Götze et al. 2001, 2009). The visible luminescence colors of quartz in most igneous and metamorphic rocks as well as in some authigenic quartz depend on the relative intensities of these two dominant emission bands. Because of the ubiquitous occurrence of the blue 440–450 nm (2.75–2.8 eV) CL emission in synthetic and natural quartz of all rock types, there is an ongoing discussion concerning the defects responsible for this