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

JENS GÖTZE1,*, YUANMING PAN2, MARION STEVENS-KALCEFF3, ULF KEMPE4 AND AXEL MÜLLER4,5

1Institute of Mineralogy, TU Bergakademie Freiberg, Brennhausgasse 14, 09596 Freiberg, Germany
2Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2, Canada
3School of Physics and Electron Microscope Unit, University of New South Wales, Sydney, New South Wales 2052, Australia
4Norges Geologiske Undersøkelse, Leiv Eirikssons vei 39, N-7040 Trondheim, Norway
5Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

ABSTRACT

The origin of yellow cathodoluminescence (CL) in quartz has been investigated by a combination of CL microscopy and spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and spatially resolved trace-element analysis by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The study shows that the appearance of a ~570 nm (2.17 eV) emission band can be attributed to high oxygen deficiency and local structural disorder in quartz. A proposed luminescence center model implies self-trapped exciton (STE) emission from localized amorphized regions in quartz. Although the high-intensity emission at 570 nm is in general consistent with high concentrations of $E_\Gamma$ defects detected by EPR spectroscopy, CL studies with different electron beam parameters and annealing experiments up to 600 °C show a temperature and irradiation dependence of the luminescence related defects excluding the role of $E_\Gamma$ centers as direct luminescence activators for the 570 nm emission. The evaluation of geochemical data shows that quartz with yellow CL occurs in low-temperature hydrothermal environment (mostly <250 °C) and is related to fast crystallization in an environment with oxygen deficiency.

Keywords: Cathodoluminescence (CL), yellow CL, quartz, electron paramagnetic resonance (EPR), trace elements

INTRODUCTION

Quartz is one of the most abundant minerals in the Earth’s crust and therefore, knowledge of its specific properties is indispensable for many mineralogical and geological investigations as well as for its industrial use. The great interest in luminescence studies of quartz is due to the fact that information not available by other analytical methods can be obtained. For instance, cathodoluminescence (CL) can be used to reveal internal textures, growth zoning, secondary alteration or different quartz generations, which cannot be discerned by optical or electron microscopy (e.g., Zinkernagel 1978; Ramseyer et al. 1988; Owen 1988; Ramseyer and Mullis 1990; Watt et al. 1997; Müller 2000; Götz et al. 2001a; Van den Kerkhof et al. 2004; Rusk et al. 2006, 2008; Krickl et al. 2008; Götz et al. 2009; Müller et al. 2009a; Jourdan et al. 2009a, 2009b; Lehmann et al. 2009). In addition, CL is an effective method for spatially resolved analysis of extrinsic or intrinsic point defects in quartz by spectral measurements. The combination with electron paramagnetic resonance (EPR) spectroscopy and spatially resolved trace-element analysis provides information concerning the relation between different luminescence emission bands and specific lattice defects in the quartz structure (e.g., Stevens-Kalceff and Phillips 1995; Müller 2000; Götz et al. 2001a, 2005; Van den Kerkhof et al. 2004; Stevens-Kalceff 2009; Götz 2009; Götte and Ramseyer 2012).

The ideal structure of quartz is composed of SiO$_4$ tetrahedra, where each Si atom is surrounded by four oxygen atoms, and adjacent Si atoms are bridge-bonded through a single oxygen atom (O$_4$=Si-O-Si=O$_4$). The CL emission of quartz is in general caused by various point defects including both substitutional trace elements and other lattice defects [see compilations in Stevens-Kalceff (2009) and Götz (2009)]. The defects associated with the different CL emissions in quartz often reflect the specific physico-chemical conditions of crystal growth and therefore, can be used as a signature for genetic conditions of mineral formation (e.g., Ramseyer et al. 1988; Müller 2000; Götz et al. 2001a; Van den Kerkhof et al. 2004; Müller et al. 2009a; Götz 2009).

The most common CL emission bands in natural quartz are the 450 nm (2.75 eV) and 650 nm (1.91 eV) bands (Ramseyer et al. 1988; Götz et al. 2001a), and their nature is well known. The emission observed at ~450 nm (2.7 eV) is associated with O-deficiency centers (ODC) in quartz and is more or less identical in amorphous and crystalline SiO$_2$ (Imai et al. 1988; Sakuja 1994, 1998; Pacchioni and Ierano 1997). The 650 nm (1.9 eV) emission is attributed to the so-called non-bridging oxygen hole center (NBOHC), which can be formed from different precursor defects (Stapelbroek et al. 1979; Siegel and Marrone 1981; Stevens-Kalceff 2009). The common occurrence of the luminescence emissions at 450 nm (2.75 eV) and 650 nm (1.91 eV) results in bluish-violet CL colors, which are commonly detectable in quartz crystals from igneous, volcanic, and metamorphic rocks, as well as authigenic quartz from sedimentary environments. In quartz from pegmatites, a characteristic transient emission around 500 nm (2.45 eV; bluish-green) is observed (Götte et al. 2004, 2005), whereas a short-lived blue CL emission band at 390 nm (3.18