

Defect pair mechanism for quartz intermediate temperature thermoluminescence bands

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ABSTRACT

The well-known 160 °C and 220 °C intermediate temperature bands in quartz thermoluminescence are attributed to the same defect reaction pair proposed previously to explain the 110 °C predose band. In particular, the trend towards longer spectral wavelengths as the glow proceeds across the 110 °C, 160 °C and 220 °C bands is shown to be consistent with the known energy levels of the $[\text{AlO}_4^-/\text{h}^+]^0$ substitutional defect.

1. Introduction

The bands in alkali halide thermoluminescent (TL) glow curves have long been associated with known defect pairs. For example, the prominent NaCl band centred near 270 °C is associated with recombination of an electron released from an F centre (an electron trapped at a chlorine vacancy) with a hole at a nearby H centre (an interstitial chlorine atom). [Refer, for example, to Hayes and Stoneham, 1985 and Preusser et al., 2009]. The M, R, and N emission bands that appear at lower temperatures are explained respectively by the presence of two, three and four neighbouring F centres.

In contrast, quartz luminescence is often treated phenomenologically. Thermoluminescence, for example, is described as the result of thermal excitation of a trapped electron to the conduction band and subsequent radiative recombination with a hole trapped near to the valence band. [Refer, for example, to Preusser et al., 2009 and many of the references therein]. The rather large difference between the band gap energy and the emitted photon energy is largely unexplained, being loosely attributed to an increase in the vibrational energy of the lattice.

The approach of Itoh et al. (2002) has been rather different. In their physically-based defect pair model, both optically stimulated luminescence (OSL) and two of the most prominent TL bands (110 °C and 325 °C) are explained in terms of reactions involving defect species generated earlier during the ionising irradiation process. Itoh et al. did not, however, offer an explanation for the other bands in the thermoluminescence spectrum, most notably those characterised by the intermediate temperature 160 °C and 220 °C TL peaks.

In this paper we show that these bands can be included within the

same defect pair model by combining their well-known thermoluminescence properties with structural information available within the wider solid state physics literature.

2. Quartz defect pair model

The crystal structure of quartz has been well-described in the literature [e.g., Preusser et al., 2009, Götze and Möckel, 2012 and within the website description and visualisation by Akhavan (2012)]. The interested reader is referred to these sources. In its natural state, quartz crystallises as α -quartz. The α -quartz structure is built from SiO_4 tetrahedra which are linked by sharing each of their corner oxygens with other tetrahedra. In structural terms, six of the tetrahedra link to form a 6-fold helix and two such helices wind together along a common direction to form the wall surrounding an empty channel, called a c-channel. Neighbouring groups of the 6-fold helices are linked by additional tetrahedra via smaller gaps to complete the repetitive crystal structure. As presented visually by Akhavan, the complete structure surrounding each c-channel exists in the form of two intertwined but unconnected 6-fold helices of the same handedness. By simple scaling from the cross-sectional structure illustrated by Akhavan, we estimate that 3.4×10^{10} c-channels exist within a hexagonal quartz crystal characterised by 100 μm flat-to-flat distance.

It is both the c-channels and the helices that are significant to quartz luminescence. The channels are large enough for small interstitial cations such as H^+ , Li^+ and Na^+ to move when freed by ionising events. Electrons and holes also move by winding along the chain of oxygen atoms within the 6-fold helices. The holes can be trapped at oxygen

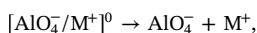
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vacancies and also by Si substitutional atoms such as Al, Ge and Ti. It is the presence both of the substitutional defects and the mobile species that underlie the luminescent processes.

As mentioned above, the defect pair model follows from the well-established alkali halide model for luminescence. In the case of quartz, many defect species have been identified, some of which are critical to the luminescent processes. [See, for example, Götze and Plötze, 1997 and Müller et al., 2012]. In particular, the aluminium ion Al^{3+} is a significant impurity that substitutes for Si^{4+} in the crystal structure. In nature, Al^{3+} is accompanied by an interstitial proton or alkali ion in order to ensure local charge balance. [See, for example, Halliburton et al., 1981]. Li^+ and Na^+ are common charge-compensating interstitial impurities.

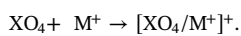
In their landmark paper, Itoh et al. (2002) explained that while the main charge species generated by β or γ ionising radiation are electron/hole pairs, the ionisation also results in the release of the interstitial charge-balancing ions into the c-channel; viz.,



where the tetrahedral AlO_4^- defect group lies within the c-channel wall and where M^+ represents the cation that is released. The cation moves along the c-channel until it is captured by one or another of several types of defects within the wall structure.

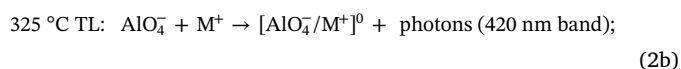
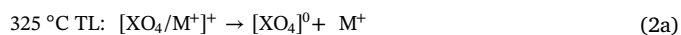
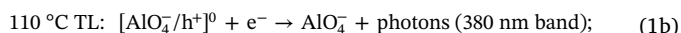
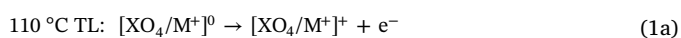
In this paper we emphasise the significance of the substitutional impurities within the 6-fold helices. In expanding the Itoh et al. nomenclature, we label as XO_4 the particular tetrahedral defect group that leads to luminescence. They suggested that XO_4 is possibly TiO_4 , although recent work has supported GeO_4 (Vaccaro et al., 2017), as we discuss below.

After the M^+ is released it moves along the c-channel until it is captured by a defect, perhaps at the XO_4 group of interest; viz.,



We note from Itoh et al. that while the $[\text{XO}_4/\text{M}^+]$ complex is expected to be positively charged, it also can absorb an electron and exist in the $[\text{XO}_4/\text{M}^+]^0$ charge-neutral form. Within the Itoh et al. model, the latter is suggested as the source of the 110 °C thermoluminescence band. We contend here that the $[\text{XO}_4/\text{M}^+]^0$ complex exists in several different states, each of which is the source of a different TL band.

It is the formation of the different forms of the $[\text{XO}_4/\text{M}^+]$ complex that leads to the quartz thermoluminescent properties described by Itoh et al. In particular, they suggest that subsequent defect reactions are capable of describing both the 110 °C and 325 °C TL emission bands; viz.,



Itoh et al. suggest additional defect pair mechanisms to explain a number of well-known luminescent effects in quartz, including OSL, photon transferred thermoluminescence (PTTL) and the predose effect. We refer to their paper for detail, as we do for the literature that influenced their developments.

We note that the analysis presented here is independent of the specific identity of the XO_4 defect. Nevertheless, it is valuable to provide passing comment. Recently, Vaccaro et al. (2017) have presented measurements that show that the EPR signal from $[\text{GeO}_4]^-$ decays at the same rate as the 110 °C band and have concluded that the relevant defect group is $[\text{GeO}_4]^-$. We note, however, the earlier study by McEachern and Weil (1994) which showed that an isomorphous relationship exists between the centres $[\text{GeO}_4]^-$ and $[\text{GeO}_4/\text{Li}]^0$ in α -

quartz, and also between $[\text{GeO}_4]_{\text{II}}^-$ and $[\text{GeO}_4/\text{Li}]_{\text{A}}^0$; that is, the compensating Li^+ has little effect on the electronic structure. Only within the second pair of centres are pairs of oxygen ions symmetry equivalent. McEachern and Weil stated further that warming a cold-irradiated sample (or irradiating at room temperature) resulted in conversion of $[\text{GeO}_4]_{\text{II}}^-$ into the compensated centres $[\text{GeO}_4/\text{M}]_{\text{A,C}}^0$ ($\text{M} = \text{Li, Na, Ag}$), depending on the availability of cations M^+ . With this information, the TL centres following room temperature irradiation are perhaps better explained in terms of the compensated forms. Such forms are consistent with the Itoh et al. (2002) thermoluminescence reactions we have replicated above.

The Vaccaro et al. (2017) study is interesting in that it links the decay of the Ge-based EPR signal with the 110 °C band decay. We note, however, that the higher-concentration titanium defects were not addressed. [Refer, for example, to the comprehensive treatise on quartz by Götze and Möckel (2012), within which Plötze et al. (2012), for example, have commented on the low concentrations of $[\text{GeO}_4/\text{M}]^0$ in their samples, compared to the titanium equivalent.] It would be valuable if similar titanium-based EPR and 110 °C band decay measurements could be conducted in order to investigate whether or not Ti centres display the same behaviour as observed for Ge. While such information is unavailable, we have therefore chosen to retain the generic XO_4 label.

3. Defect pair model extension

In this paper we concentrate on the 110 °C TL reaction pair and argue that it is common to the 110 °C, 160 °C and 220 °C TL bands. For illustrative purposes, we display in Fig. 1 a typical ultraviolet-emission TL glow curve, measured in this laboratory immediately following 1 Gy beta irradiation of a previously-glowed South-East South Australian Woakwine quartz sample. Note the characteristic high intensity of the 110 °C band (which decays within a few hours). We note further that only the ubiquitous nature of the three bands is of current interest, rather than their relative amplitudes or exact locations. We commonly observe the presence of the three bands amongst glow curves recorded from a wide variety of natural and laboratory-irradiated quartz samples within our possession.

The sample was prepared by application of standard processing techniques to remove clays, carbonates, feldspars and fluoride components, as has been described in detail by Moffatt (2014). After grinding and sifting, grains in the range 125–180 μm were chosen for the present study. The grains were loaded onto a stainless steel disc previously sprayed with silicone oil through a 7 mm diameter mask.

The glow curve shown in Fig. 1 was recorded using a Risø DA-20 automated reader equipped with 7 mm thick Hoya U340 filter and an in-built EMI 9235QB photomultiplier tube. The filter passes ultraviolet radiation in a 300–390 nm band centred about 340 nm.

Although it has been long-known that the three bands share similar properties [see, for example, Franklin et al., 1995], no mechanism has

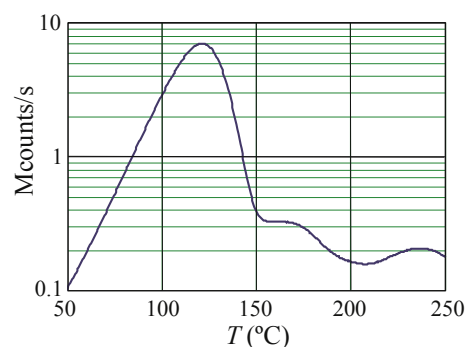


Fig. 1. Example of a quartz UV thermoluminescence glow curve (U340 band filter, 5 °C/s heating rate).

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