Cathodoluminescence of synthetic quartz

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Abstract. Cathodoluminescence from undoped and Ge-doped high-purity synthetic
quartz is examined over the temperature range 40 to 300 K. The undoped quartz
exhibits the well known blue (~470 nm) luminescence attributed to the decay of
self-trapped excitons. Ge-doped quartz shows green (~570 nm) luminescence at low
temperatures; it is proposed that this emission occurs as a result of exciton self-
trapping occurring at Ge substitutional sites. Line features which are considered
as resulting from molecular oxygen ions are observed in both undoped and doped
material. Evidence is presented that emission at 380 nm relates to an impurity
incorporated during growth.

1. Introduction

The luminescence of quartz provides a potentially useful monitor of the complex de-
fect structure of this material, but so far there have been few definite associations
made between the luminescence bands observed and particular defects. However, re-
cent work has provided mounting evidence for the intrinsic origin of the commonly
observed blue (~2.8 eV) quartz luminescence, seen when using ionizing radiation at
low temperatures. The results of Tanimura *et al* [1] show that there is a volume
change produced following electron irradiation, the decay time of which matches the
decay time of the luminescence at 2.8 eV (and also the decay time of absorption at
5.4 eV). This shows conclusively that transient oxygen-vacancy pairs are created by
the electron beam, probably through the self-trapping of excitons [2–4]; recombination
results in restoration of the lattice accompanied by emission of the blue luminescence,
while absorption occurs from the same excited state. Similar luminescence and ab-
sorption bands are seen in silica, and the evidence suggests that they have the same
origin [5, 6], although Tohmon *et al* [7] propose that a neutral oxygen vacancy defect
is responsible for at least part of the luminescence. For the other bands seen in quartz
(i.e. ~380 nm and 650 nm), no conclusive models are available at present. The 380
nm emission measured during thermoluminescence [8] was found to increase as the
result of heat treatment. More recently Yang and McKeever [9] have argued that the
380 nm emission is related to trace impurities incorporated during growth.

 In an effort to separate intrinsic and extrinsic features of the quartz spectrum,
this paper describes the results of cathodoluminescence (CL) measurements made on
synthetic quartz samples with differing impurity contents, including 'ultra-pure' GEC
samples having less than 1% of the Al or OH content of standard 'pure' material. Also

examined were samples of ultra-pure quartz doped with ~0.5% (by number of atoms) germanium.

Both wavelength and energy are variously quoted and in this paper the principle bands discussed are at 380 nm (3.2 eV), 440 nm (2.8 eV), 470 nm (2.6 eV), 510 nm (2.4 eV), 570 nm (2.2 eV) and 650 nm (1.9 eV).

2. Experimental

Spectra were excited by a broad (~3 mm diameter) 10 keV electron beam at current densities of ~ 50 μA cm^{-2}. The beam was incident on the sample at an angle greater than 45°, to avoid reflection of filament light emission into the collection optics, and the luminescence observed at 90° to the beam axis. Except when making lifetime
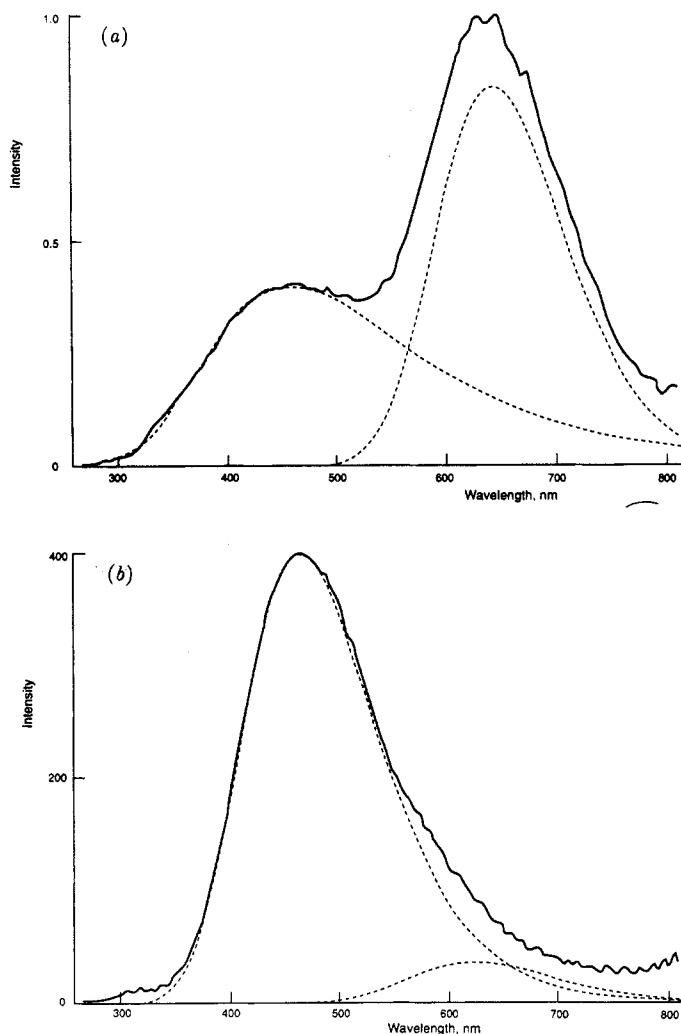

Figure 1. (a) Room temperature CL spectrum of Sawyer electronic grade synthetic quartz. (b) Spectrum of Sawyer electronic grade quartz at 40 K. Component Gaussian bands are shown as broken curves. The two spectra are presented using the same arbitrary intensity scale, illustrating the large increase in intensity with cooling.

measurements, the beam was chopped at a frequency of 90 Hz, and spectra taken using an $f/4$ scanning monochromator/photomultiplier arrangement followed by lock-in amplification. The temperature was varied between room temperature and 40 K using a closed-cycle refrigeration system with a heater installed at the cold end. The temperature was measured by means of a copper–constantan thermocouple with the measuring junction fixed to the sample mounting block. No instabilities due to sample charging were noted, probably because of the broad nature of the exciting beam. All spectra have been corrected for the spectral response of the whole detection system; details of the actual response of the system are given in [10]. To obtain correct band positions and shapes on the energy scale, the measured wavelength spectra were converted into energy spectra having constant energy bandwidth.

3. Results and discussion

The room temperature spectrum from a Sawyer electronic grade synthetic quartz sample is shown in figure 1(*a*). Least-squares curve fitting suggests the presence of two Gaussian-shaped bands peaking at 470 and 650 nm (2.6 and 1.9 eV). The band at 470 nm decreases rapidly in intensity with dose, while the intensity of the 650 nm feature increases. Consequently, figure 1(*a*) data were taken during a rapid spectral scan. This preserves the 470 nm feature but introduces noise on the 650 nm signal because of reduced detection sensitivity in this region. Using slower scans, the 'structure' on the 650 nm band is removed.
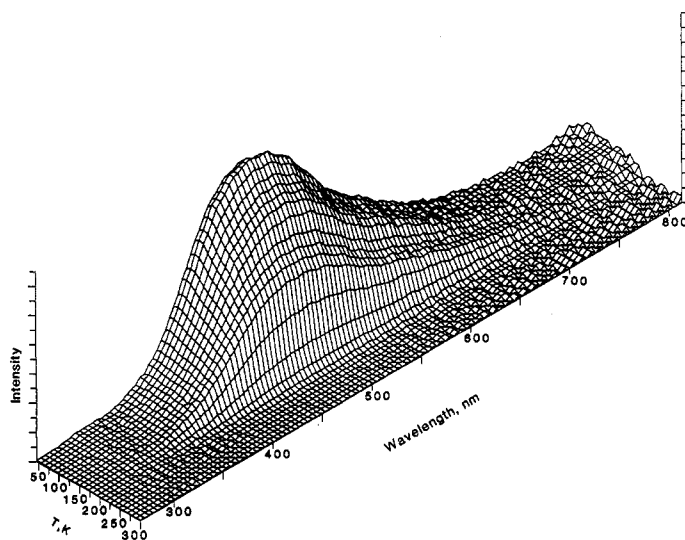

Figure 2. Isometric plot of CL intensity against wavelength and temperature for Sawyer premium quartz. Arbitrary intensity scale.

Upon cooling, the luminescence intensity increases by approximately 400 times from room temperature to 40 K. At low temperatures, the 470 nm feature dominates the spectrum (figure 1(*b*)). The rise in intensity at the red end is due to second-order scattering. No major differences were noted between the spectra from Sawyer electronic grade material and Sawyer premium grade; GEC standard purity material

also gave very similar luminescence. No significant changes were noted between samples of similar origin having different crystalline orientations. An isometric plot of CL intensity against wavelength and temperature taken during a cooling cycle is given in figure 2 for a Sawyer premium grade sample, showing the growth of the 470 nm band; however, for this particular sample, faint line features are seen superimposed on the main band. The average energy spacing of these lines is 0.09 eV. These lines are insufficiently well resolved to quote more precise energies; they have been seen in several samples and are reproducible in energy. The possible significance of these features will be discussed below.
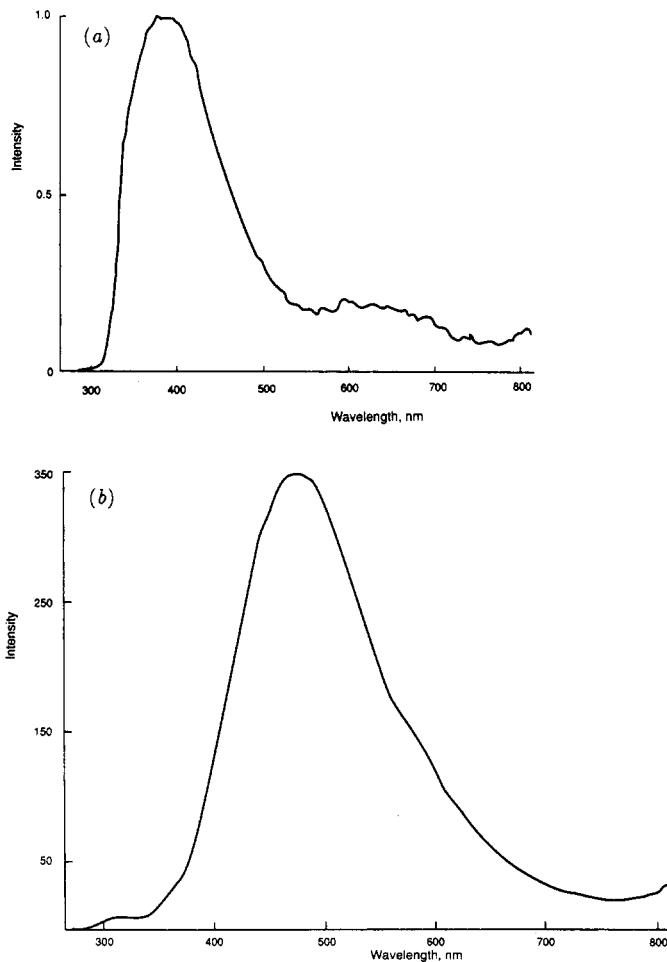

Figure 3. (*a*) Room temperature and (*b*) 40 K spectrum from GEC ultra-pure quartz (slow-growth side). The same arbitrary intensity scale is used for both spectra.

An intrinsic origin for the 470 nm emission is suggested by the spectrum obtained from GEC 'ultra-pure' grade quartz, which shows the same broad spectrum at low temperatures as the standard grade materials (figure 3(*b*)). A major problem in deciding between an intrinsic or an extrinsic process exists for this 470 nm band in the sense that if the luminescence arises from exciton decay then the same signals will be

enhanced by the presence of impurities, particularly if the defect-controlled electron–hole recombinations give 'intrinsic' 470 nm light. Electron–hole recombination at defects is well known; for example, in studies of the 100°C thermoluminescence peak [9] the 380 nm emission increases with the addition of impurities. It is demonstrated by EPR measurements that the thermoluminescence peak is linked to the reduction of electron (e.g. $(GeO_4)^-$ centres) and hole $((AlO_4)^0$ and $(H_3O_4)^0)$ defects.

At room temperature there is a CL emission band at ~380 nm (3.2 eV) in the ultra-pure material, as shown in figure 3(a). This spectrum is taken from the slow-growth side of the sample; the spectrum from the fast-growth side shows a considerably reduced intensity for the 380 nm feature at room temperature. The intensity of the 380 nm feature initially increases, then decreases with beam dose. The differences in signal between different cystals and from the two sides of a sample suggest that the 380 nm emission arises from a defect incorporated during growth. It should be noted that in other studies 380 nm emission from silica has been ascribed to vacuum-related contaminants condensing on the sample at low temperature [11]. The presence of the signal at room temperature, the differences between the two growth faces, and the lack of signal from the mounting block, all discredit this suggestion in the present work. Note also that the experiments were conducted with a moderately good vacuum of $< 10^{-7}$ mbar.

No evidence was obtained to suggest that the blue feature is a composite, as reported by previous authors following polarization measurements [12, 13]. Here, polarization measurements were performed at 40 K on y-cut samples with the z axis perpendicular to the centre line of the collection optics; light was viewed at an angle of ~30° to the y axis. No significant change in the peak position of the blue feature was seen upon examination of light polarized parallel and perpendicular to the z axis, although there was some decrease of the intensity of emission at 470 nm with respect to emission at 650 nm for light observed parallel to the z axis, indicating some polarization of the blue emission.
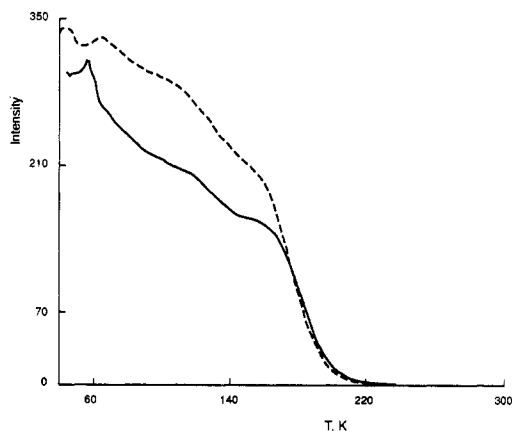

Figure 4. Ultra-pure quartz: temperature variation of CL intensity at 470 nm during cooling (full curve) and heating (broken curve) cycles. The intensity units used are those of figure 3.

The temperature variation of the CL intensity at 470 nm for the ultra-pure quartz (which according to Gaussian fits is entirely that of the 470 nm band) is shown in

figure 4. The variation shows the same general features for all grades of quartz. The presence of the feature seen in the range 170–120 K in the ultra-pure grade material suggests that it is not due to the quenching of hidden intrinsic bands as proposed previously [14,15], but rather is due solely to the temperature dependence of the competition between radiative and non-radiative decay routes within the emitting centre. Decay lifetime data for the 470 nm luminescence from a GEC standard purity sample are given in figure 5(a). The measured values are identical to those for the 470 nm emission from the Sawyer and ultra-pure material. The values are in good agreement with those given [1, 2, 16] for blue luminescence. A plot of $\ln(1/\tau - 1/\tau_r)$ against $1/T$ is given in figure 5(b), where τ_r is the lifetime at 40 K; over the range 290–170 K the behaviour is seen to obey the Mott equation, with an activation energy of +0.33 eV.
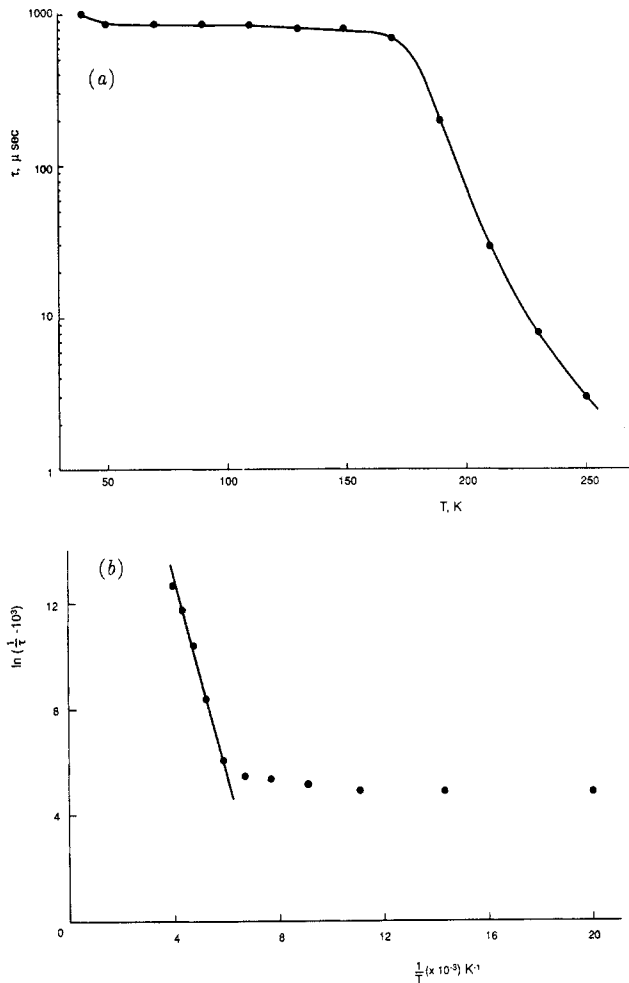

Figure 5. GEC quartz: (a) decay lifetimes at 470 nm, (b) plot of $\ln(1/\tau - 10^3)$ against $1/T$ giving an activation energy of 0.33 eV.

The peak position of the intrinsic blue feature reported here (470 nm, 2.6 eV) is only in rough agreement with the position reported by other authors. For example,

Tanimura *et al* [1] report luminescence peaking at 440 nm (2.8 eV), though Trukhin and Plaudis [2], using x-ray and UV excitation, give the peak as 477 nm (2.6 eV). However, the lifetime evidence suggests that it is indeed the same luminescence as seen by these various authors, attributed to the decay of self-trapped excitons. The discrepancy in exact position (and also the apparent presence of only a single band) may be a result of the differing excitation conditions used, though the suggestion has been made that some of the component bands that have been reported have extrinsic origins [12, 13], and therefore may not be present in the samples used here. It is of interest to note that a theoretical calculation carried out by Shluger [17] on the self-trapped exciton in quartz results in a value of 2.6 eV for the energy of the radiative transition.
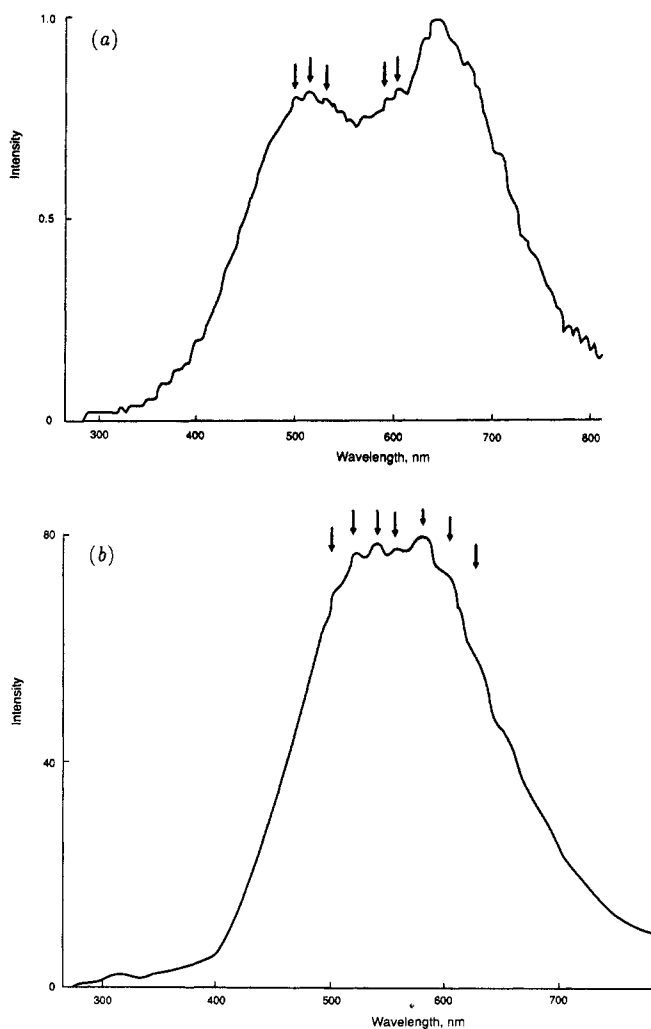

Figure 6. Spectrum from Ge-doped quartz (*a*) at room temperature, (*b*) at 40 K. The arbitrary intensity units used are the same for both spectra. Line features are clearly visible at 40 K; at room temperature, noise (amplified at the red and blue ends by the spectral response corrections) is also present. However, the features marked by arrows are reproducible and are observed more clearly with decreasing temperature.

In amorphous silica similar emission bands are discussed at 460 nm (2.7 eV) as a neutral oxygen vacancy defect [7] or an excitonic transition [13]. Unfortunately, a similar 2.7 eV emission is noted at low temperature under poor vacuum conditions [11]; the 3.1 eV band is linked to Ge impurities.

The reproducible line features seen in figure 2 are possibly due to O_2 molecules either already present in the material or formed as a result of electron bombardment (perhaps as a part of the self-trapping process [13]), since the energy spacing of 0.09 eV is broadly consistent with the spacing of lines from molecular oxygen ions seen in the alkali halides [18]. Evidence for the presence of these lines was seen in most quartz samples examined, though generally not as clearly as for the particular sample shown. Much more evident line features were seen in the spectrum of Ge-doped ultra-pure quartz samples (figure 6). The energy spacing of the lines is 0.08 eV, close to that of the features seen in undoped quartz. The broad peak on which the lines are superimposed is at ~570 nm at low temperatures, but is nearer 510 nm at room temperature. Visually, the luminescence is green at low temperatures. The 650 nm feature also seen in undoped quartz is again only prominent at room temperature. If it is assumed that self-trapping in Ge-doped quartz occurs preferentially at sites where Ge has substituted for Si (the Ge–O bond is relatively weaker than the Si–O bond), then this could account for the wavelength shift of the main low-temperature band from its position in the undoped material. The line features, similarly due to molecular oxygen, may have also undergone a shift in position due to the differing environment around a Ge site.
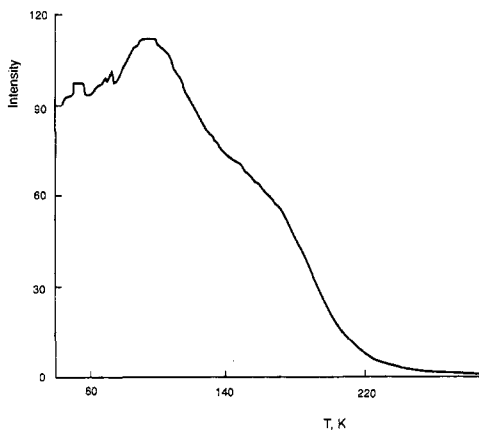

Figure 7. CL intensity variation at 570 nm for Ge-doped quartz. The intensity units used are those of figure 6.

The CL intensity variation with temperature at 570 nm for Ge-doped quartz is shown in figure 7. The variation is similar to that for the undoped quartz samples except for a drop in intensity occurring at around 90 K. Measurement of decay lifetimes at 570 nm gave similar values to those measured for the blue luminescence of undoped quartz (figure 5) from room temperature down to 100 K, although the Mott equation is not obeyed over any part of this temperature range. Below 100 K, there was a decrease in lifetime from a value of 600 μs at 100 K to a value of 450 μs at 40 K.

The origins of the features at 380 nm and 650 nm are uncertain. Both features are seen in ultra-pure grade quartz. The 380 nm band may arise from growth impurities

but the 650 nm feature is possibly related to oxygen vacancies. At room temperature, the 650 nm band is seen to grow with dose; this damage is not recoverable once the electron beam is removed, indicating the formation of permanant defects such as oxygen-vacancy centres.

4. Conclusions

The results presented in this paper show that the cathodoluminescence spectrum of quartz is dominated by intrinsic features. The main blue luminescence reported here as consisting of a single band centred on 470 nm (2.6 eV) is identified with the self-trapped exciton. Similar self-trapping occurring following the breaking of a Ge–O bond is proposed as the origin for the observed green luminescence in Ge-doped quartz. A band at 380 nm is associated with impurities incorporated during growth. The observation of line features provides evidence for the presence of molecular oxygen ions in both undoped and Ge-doped quartz.

Acknowledgments

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