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Thermal (500 - 580 °C) stability of hydrogen in synthetic quartz

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Abstract : Thermal stability of hydrogen as it appears in the 3125- 3800 cm⁻¹ infrared spectra has been studied as a function of the annealing temperature between ~ 500 to 580°C under vacuum or air atmosphere. Thin Z-cuts show a decrease of the OH infrared absorptions which can become clear above ~ 520°C under vacuum. From these measurements we infer an increase of the diffusion coefficients for the H-outdiffusion in the range of about 10⁻¹¹ to 10⁻¹⁰ cm²/s in vacuum from ~ 520 to 560°C (~ 540 to 580°C in air). X and Y cuts do not show outdiffusion for these temperatures.

1. INTRODUCTION

It is well-known that the performances of quartz (SiO₂) piezoelectric devices are limited by impurities [1] introduced during the hydrothermal growth. Among these, hydrogen (OH centers) has been shown to play a particularly important role because : i) it gives acoustic losses - related to a broad band water like infrared absorption - ii) it acts as a charge compensator, for the aluminium impurity, when the quartz is irradiated or when it is purified [2] using high temperature electrolysis ("sweeping"). The electrolysis are usually performed in a 500-550°C temperature range to avoid the α - β transition at ~ 573°C which could induce electrical twins. It was shown [3] that it is possible to obtain, from vacuum electrolysis, synthetic quartz free of as-grown OH centers. Otherwise many authors [4,5,6] have pointed out a modification of the infrared (I.R.)-OH spectra after prolonged time at high temperature. In particular a strong reduction of the "s" peaks (typical of the OH absorption in synthetic quartz) after annealing [5] or deuterium exchange [4] at ~ 1000° was put in evidence.

Here we present the results obtained from thin X, Y and Z cuts which were submitted to heat treatments under air or vacuum atmosphere with temperatures and durations typical of electrolysis processes. The OH content was monitored by the measurement of the infrared OH absorptions usually used to qualify the synthetic quartz : the sharp "s₄" band at 3584 cm⁻¹ (2790 nm) and the 3500 and 3410 cm⁻¹ absorption coefficients to characterize the

broad band (fig. 1). It has been shown [7] that a linear relationship exists between these coefficients obtained from as grown samples.

2. EXPERIMENT

All spectra were performed at room temperature using a Lambda 9 Perkin Elmer double beam spectrometer with an I.R beam (section $\sim 2 \times 4 \text{ mm}^2$) which can be considered as practically polarized in the wavelengths investigated ($3800 - 3125 \text{ cm}^{-1}$). To improve the accuracy, a virgin quartz was used as a standard to correct the spectrometer response.

Air annealing was made with an open air furnace. Vacuum was $\sim 2.10^{-6}$ mbar during the vacuum annealings.

3. SAMPLES

All the samples were cut in a small block of synthetic quartz of medium quality taken in the pure Z zone. They are square in shape with large faces optically polished. The dimensions are about :

- X cuts : $0.75 (// X) \times 13.70 (// Y) \times 13.6 (// Z) \text{ mm}^3$
- Y cuts : $0.75 (// Y) \times 13.5 (// Z) \times 12.2 (// X) \text{ mm}^3$
- Z cuts : $0.85 (// Z) \times 10 (// X) \times 11 (// Y) \text{ mm}^3$

4. RESULTS

Fig. 2 and 3 show the evolutions of the absorption coefficients measured at the center of the samples. For the Z-cuts we give the mean of the $(\vec{E} // X + \vec{E} // Y)/2$ absorption values from two samples. For the X-and Y-cuts we give the $\vec{E} // Z$ absorptions which maximize the s_4 intensity (the $\vec{E} \perp Z$ absorptions practically show the same behavior but s_4 is negligible). s_4 intensity is given both by its peak value and the area (dashed line) of the band. We see that the different annealings, made with comparable durations on the X; Y; Z-cuts, produce on the Z-cuts a decrease of the absorption coefficients, at $\sim 520^\circ\text{C}$ under vacuum (on fig. 2 top, the thickness 0.48 mm reported in addition shows a greater effect) and slightly later under air ; on the X and Y cuts, practically no effect appears except for s_4 which peak absorption increases [5, 6] with however a nearly constant integral absorption.

Fig 4 shows the apparent diffusion coefficient D calculated assuming that the rate of decrease of the OH absorptions (Z cuts fig. 2 and 3) is governed by a one dimensional out diffusion process (verified at higher temperature: will be presented in a next paper) for hydrogen. Thus we used [see for instance 4] the formula :

$$\frac{\bar{c}}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 D \cdot t}{L^2}} \quad L : \text{thickness of the sample}$$

where we took the infrared absorptions* as a measure of the mean OH concentration $\bar{c}$ after the time t of annealing. We find diffusion coefficients between $10^{-11} \text{ cm}^2/\text{s}$ and $10^{-10} \text{ cm}^2/\text{s}$ which are in reasonable agreement with extrapolated values obtained [8] from H-D exchange at higher temperatures. A small temperature shift ($\sim 20^\circ\text{C}$) appears between

* We have subtract $\alpha = 0,021$ and $0,071 \text{ cm}^{-1}$ to account for the residual SiO_2 intrinsic lattice absorption at 3500 and 3410 cm^{-1} respectively.

Fig. 1 : quartz I.R. spectra with(—) and without(...) OH-absorptions . Example (Z-cut) of annealing effects: a: virgin; b: after 21 days at 552°C under vacuum.

Fig 4 : Arrhénius plot (Z-cuts) of the H-outdiffusion coefficients calculated from :

S4 : ▲ peak , × area ; □ 3500 cm-1; ▣ 3410 cm-1

Fig. 2 : I.R. absorption coefficients vs the annealing temperatures (vacuum):

S4 : ▲ peak , × area ; □ 3500cm-1; ▣ 3410 cm-1
0 : virgin ; 1 : 3 hours at 445 < T < 517° C
2 : 8 days ; 3 : 21 (Z) or 26(X,Y) days

Fig. 3 : I.R. absorption coefficients vs the annealing temperatures (air):

S4 : ▲ peak , × area ; □ 3500cm-1; ▣ 3410cm-1
0 : virgin ; 1 : 3 hours at 445 < T < 517° C
2 : 8 days ; 3 : 16(Z) or 26(X,Y) days ; 4 : 28 days

the values obtained from the air and vacuum experiments. Activation energies of 2.5 ± 0.6 eV is estimated, to be compared with the 1,6-2,1eV values found for the dc ionic conductivity attributed to H^+ displacement at the end of sweeping experiments [2,3].

5. CONCLUSION

Annealing effects of medium quality synthetic quartz appear very anisotropic for the OH related I.R. adsorptions measured in the $3800\text{-}3125\text{cm}^{-1}$ region. Thus we find a reduction of both the sharp s_4 (integrated) band and the broad band above $\sim 520^\circ$ under vacuum atmosphere for the Z cuts while no effect appears on the X and Y-cuts except an increasing of the s_4 peak absorption. Admitting that the OH reduction is governed by the hydrogen out diffusion we find diffusion coefficient in rough accordance with the published data along the Z direction.

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