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ANELASTIC BEHAVIOUR OF SYNTHETIC α -QUARTZ

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Résumé - Q^{-1} est mesuré en fonction de la température T de 77 K à 700 K sur du quartz de haute qualité. On observe un pic P_1 à 573 K indépendant du recuit, de l'état de surface et de l'amplitude de déformation : sa hauteur dépend de l'orientation cristallographique (énergie d'activation $E_a = 1$ eV). P_1 semble dû à la diffusion d'impuretés alcalines. Entre 173 K et 373 K, on observe divers pics très sensibles au recuit. Certains de ces pics semblent liés aux défauts de surface et à la teneur en eau. Le fond continu n'est activé thermiquement qu'au-dessus de 400 K.

Abstract - Q^{-1} of high quality quartz is measured as a function of temperature T from 77 K up to 700 K. A single peak (P_1) can be observed at 573 K ; it is not sensitive to surface state, annealing and strain amplitude ($E_a = 1$ eV activation energy). The P_1 peak seems to be due to alkaline impurity diffusion. Between 173 K and 373 K one can observe various peaks very sensitive to successive temperature rises. Some of these peaks appear to be connected to surface defects and to water-impurity content. The background is thermally activated above 400K only.

1 - INTRODUCTION

Stability of the frequency of synthetic quartz resonators is mainly based on the crystalline quality of quartz. This quality is obviously limited by the intrinsic structural defects and associated impurities introduced during the hydrothermal growth process. Alpha-quartz is a piezoelectric crystal which belongs to the rhombohedral crystallographic system ; it is stable up to 846 K. The unit cell of quartz consists of three silicon ions and six oxygen ions. Quartz is a highly covalently bonded structure possessing large channels approximately 10 nm in diameter parallel to the Z axis (one per unit cell) and slightly smaller channels parallel to the X axes (three per unit cell). Such large channels are characteristic of glass-forming crystals and allow the incorporation of interstitial ions which are very often alkali ions (Na^+ , Li^+ , K^+) because the hydrothermal process uses an alkaline solution. Generally these monovalent cations are associated with Al^{3+} ions which are found in all synthetic quartz grown using natural quartz as nutrient. The Al^{3+} ions easily substitute for Si^{4+} and thus, require charge compensation which gives rise to $Al-Na^+$, $Al-Li^+$ centers.

The presence of hydrogen leads to the $Al-OH^-$ center. From ionic size considerations one would expect the mobility of interstitial impurities along the Z-channels using an electric field and thermal activation. Such electrodiffusion in air allows to sweep the compensating alkaline impurities which are replaced by H^+ ions. The same mechanism is used in order to dope a given crystal with a specific alkaline ion.

These point defects have been studied for over twenty five years by numerous workers using various techniques. A number of reviews have summarized much of this work [1-4]. About Q^{-1} , most of the results are obtained at 5 MHz.

Concerning extended defects like dislocations there are a few papers [5-6] probably because the fabrication of resonators needs a very low intrinsic dislocation density (10^2 cm $^{-2}$). However extrinsic dislocations can be introduced as surface defects during the fabrication process.

The present paper deals with the anelastic behaviour of high quality synthetic quartz (labelled as H.Q. 262) specially elaborated by SICN $\diamond$. Q^{-1} has been measured as a function of temperature T from 77 K up to 700 K. The influence on the (Q^{-1} - T) curves has been studied according to the following parameters :

- surface state of samples : as-sawed (A-S) or mechanically polished (M-P).
- annealing effect due to successive temperature rises.
- crystallographic orientation.

All the samples have been prepared by CEPE $\diamond\diamond$.

2 - EXPERIMENTAL

2.1 - Samples :

The main informations about samples are given in the Fig. 1 and its caption. The vibration frequency is about 7 kHz. The strain amplitude ϵ is about : 10^{-6} . Q^{-1} is obtained from logarithmic decrement measured by free decay oscillation. Samples have been prepared according to the same fabricating process used by CEPE for resonator blanks : i) sawing, ii) mechanical polishing, iii) chemical cleaning, iv) vacuum annealing at 400°C for 10 hours, v) gold vapor-plating on the largest faces, vi) vacuum annealing at 400°C for 10 hours.

Fig. 1 : a : dimensions of parallelepipedic blanks : $40 \times 5 \times 2 \text{ mm}^3$.

- b : samples are driven in flexural vibration (fundamental mode) by electrostatic excitation. The largest faces are gold vapor-plated.
- c : The pure Z growth zone is used for fabrication of samples. The dashed lines show the direction of channels.
- d : 2 crystallographic orientations are tested : Z-cut and X-cut samples.

2.2 - Material :

The following results of the chemical analysis (from SICN) shows a low impurity content :

	Al	Fe	Mg	Li	Na	K
ppm/Wt SiO_2	2 ± 1	$.7 \pm .1$	$.1 \pm .1$	$.5 \pm .5$	$.5 \pm .5$	$.3 \pm .1$

The infrared analysis indicates a low water content.

Concerning the dislocation density, the results of the X-ray topography study show that the seed and the pure Z-growth zone have similar density which can be roughly estimated at 10^4 cm^{-2} .

3 - RESULTS

The figures 2,3,4 and 5 show the (Q^{-1} - T) curves from H.Q. 262 quartz. These curves will be compared for discussion with those (figures 6 and 7) obtained on either High Water Content quartz (H.W.C. from SICN) or Swept High Quality quartz (S.H.Q. from CEPE).

$\diamond$ SICN : Société Industrielle de Combustibles Nucleaires, ANNECY FRANCE.

$\diamond\diamond$ CEPE : Compagnie d'Electronique et de Piézoélectricité, ARGENTEUIL FRANCE.

The experimental conditions about either cut-orientation or surface state of samples are gathered in the table I :

Figure n°	2	3	4	5	6	7
quartz	HQ 262	HQ 262	HQ 262	HQ 262	HWC SHQ	HWC
Cut-orientation	Z	Z	X	X	Z	X
Surface state	M-P	A-S	M-P	A-S	M-P	M-P

Each of the fig. 2,3,4,5 presents at least, the results of two successive temperature rises in order to observe the evolution of the (Q^{-1} - T) curves due to annealing.

One can notice that Q^{-1} remains constant at the points A (77 K), B (473 K), D (700 K) which divide the temperature range in two parts, the stability of which are completely opposite. Between A and B, there are several peaks which are very sensitive to annealing while between B and D, there is only one peak (called P_1) which is not annealing-dependent. So the results are presented according to these two temperature ranges : the low and the high temperature ranges.

3.1 - Low temperature range (L.T.R.) :

The table II shows the main results (from fig. 2,3,4,5) which allows to characterize the influence of surface state, cut-orientation and annealing on the anelastic behaviour.

From these values of Q^{-1} , the difference $DQ^{-1} = Q^{-1}(1st) - Q^{-1}(2nd)$ and the ratio $\Delta Q^{-1}/\Delta T = (Q^{-1}(473) - Q^{-1}(77))/(473 - 77)$ have been calculated. DQ^{-1} and $\Delta Q^{-1}/\Delta T$ may be considered as two so-called parameters the values of which allow to roughly characterize respectively : the Amplitude of the Annealing Effect (A.A.E.) due to the first temperature rise and the Increasing Rate of the Background (I.R.B.) along the low temperature range.

		Polished samples			As-Sawed Samples		
		Temperature rise 1st	2nd	A.A.E.	Temperature rise 1st	2nd	A.A.E.
		$Q^{-1} \cdot 10^6$	$Q^{-1} \cdot 10^6$	$DQ^{-1} \cdot 10^6$	$Q^{-1} \cdot 10^6$	$Q^{-1} \cdot 10^6$	$DQ^{-1} \cdot 10^6$
Z-cut	77 K	5	5	0	6	6	0
	273 K	5	2.5	2.5	32	12	20
	473 K	9	9	0	25	25	0
	I.R.B. K^{-1}	.01	.01		.05	.05	
X-cut	77 K	3.5	3	.5	10	10	0
	273 K	12	5.5	6.5	140	16	124
	473 K	10	9	1	33	19	14
	I.R.B. K^{-1}	.016	.015		.58	.023	

Table II : Results from (Q^{-1} -T) curves below 473 K.

The results of the Table II suggest the following comments :

3.1.1 - About anelastic peaks :

There are severals peaks mainly located between 173 K and 373 K.

The peak height depends obviously on the surface state of the sample : it is small on polished surface sample without dependence of cut-orientation. With as-sawed sample, the highest peaks are observed on X-cut samples.

All these peaks are very sensitive to the annealing effect due to the first temperature rise as it is shown by the values of A.A.E. (273 K). Such an annealing effect may be observed after the second temperature rise on as-sawed samples but the

Fig. 2 - $(Q^{-1}-T)$ curves on polished Z-cut sample of H.Q. 262 quartz.

Fig. 3 - $(Q^{-1}-T)$ curves on as-sawed Z-cut sample of H.Q. 262 quartz.

Fig. 4 - $(Q^{-1}-T)$ curves on polished X-cut sample of H.Q. 262 quartz.

Fig. 5 - $(Q^{-1}-T)$ curves on as-sawed X-cut sample of H.Q. 262 quartz.

Fig. 6 - $(Q^{-1}-T)$ curves on polished Z-cut sample of H.W.C. (Δ) and S.H.Q. ($\bullet$) quartz.

Fig. 7 - $(Q^{-1}-T)$ curves on polished X-cut sample of H.W.C. quartz.

level of Q^{-1} is still higher than those observed on polished samples.

3.1.2- About background :

The lowest level of the background is observed with Z-cut and polished surface sample at about 220 K (figure 2). This level is so low that one can suppose that the decrease of Q^{-1} from 77 K to 220 K belongs to the high temperature side of a peak located below 77 K.

The average level of the background is low (see the values of Q^{-1} for points A and B) ; it is a little bit higher for as-sawed samples.

This level and the I.R.B. are not sensitive to annealing (see the values of A.A.E.). Besides the I.R.B. is low and is not significantly thermally activated.

3.2 - High temperature range (H.T.R.) :

It is characterized by the P_1 peak and the background the main features of which are summarized in the table III.

The A.A.E. parameter is not presented because the (Q^{-1} - T) curves remain constant after the first temperature rise.

			Polished samples	As-sawed samples
Z-cut sample	P_1 peak	T (P_1) K H (P_1). 10^6 $Q^{-1}(C).$ 10^6	555 380 400	573 395 400
	Background	$Q^{-1}(B).$ 10^6 $Q^{-1}(D).$ 10^6 I.R.B. 10^6 K $^{-1}$	9 100 .41	25 150 .57
X-cut samples	P_1 peak	T (P_1) K H (P_1). 10^6 $Q^{-1}(C).$ 10^6	565 15 30	573 20 30
	Background	$Q^{-1}(B).$ 10^6 $Q^{-1}(D).$ 10^6 I.R.B. 10^6 K $^{-1}$	9 27 .09	19 19 .36

Table III : Results from (Q^{-1} - T) curves above 473 K. (H_{P_1} :peak height)

The results from Table III suggest the following comments.

3.2.1 - About the P_1 peak : i. Influence of cut-orientation : On Z-cut samples only P_1 takes place all along the high temperature range : $H_{P_1}(Z\text{-cut})$ is at least 20 times higher than $H_{P_1}(X\text{-cut})$. ii. Influence of surface state : On Z-cut samples, H_{P_1} and $Q^{-1}(C)$ are not affected by the surface state ; T_{P_1} is slightly shifted towards high temperature with as-sawed samples. On X-cut samples, the same features remain valid with less accuracy.

3.2.2 - About background : The background can be estimated with good enough accuracy only on X-cut samples because on Z-cut samples the point D, which is the limit of the temperature range, is still on the high temperature side of the P_1 peak. So, no comment can be proposed about the influence of cut-orientation.

Influence of surface state : on as-sawed samples the level of $Q^{-1}(B)$ is a little bit higher than the level of $Q^{-1}(B)$ on polished samples. However the I.R.B. on as-sawed samples is about four times higher than the I.R.B. on polished samples.

3.3 - Influence of homogenization thermal treatment :

All the (Q^{-1} - T) curves shown in the present paper were obtained on thermally treated samples (vacuum annealing at 673 K for 10 hours before and after gold-plating).

Without such thermal treatments, (Q^{-1} - T) curves are translated towards higher Q^{-1} values of about one order of magnitude. Besides, concerning the P_1 peak, its height becomes so high that Q^{-1} measurements are no more possible.

4 - DISCUSSION :

Two points are discussed : the P_1 peak and the loss peaks located along the low temperature range (L.T.R. peaks).

4.1 - About the P_1 peak :

The results about the P_1 peak suggest the following comments :

- The P_1 peak is due to a "directionnal" defect.
- It is not related to surface defects.
- it remains constant after successive temperature rises.
- the evaluation of the activation energy E_a leads to 1.04 eV with $\tau_0 = 10^{-14}$ s.
- it is not water-content-dependent (Fig. 6 and 7) ; it is important to notice that the P_2 peak located at 653 K is not linked with the P_1 peak (because the level of $Q^{-1}(C)$ for P_2 is lower than $Q^{-1}(C)$ for P_1).
- it is not observed on S.H.Q. quartz (Fig. 6) ; so, it is probably related with the alkaline impurities removed by electrodiffusion along the Z-axis channels.

All these comments allow to connect the P_1 peak to the loss peak reviewed by FRASER [2] in the kHz range. This peak was found near 573 K, on an exponentially increasing background ($E_a = .93$ eV and $\tau_0 = 2.10^{-14}$ s). The same peak was observed by dielectric loss measurements when the electric field was in the Z direction only ; in the perpendicular direction an exponentially increasing dielectric loss with temperature is only observed. An enhancement of the peak height is observed with lithium doped quartz. So, the P_1 peak should be attributed to the motion of impurity ions along the Z-axis channels.

4.2 - About the L.T.R. peaks :

On polished samples, there are several peaks probably due to bulk defects (mainly point defects). On as-sawed samples, there is the addition of others peaks (higher heights) due to the surface defects (mainly extrinsic dislocations). All these peaks are very sensitive to successive temperature rises already above 400 K. Some of these peaks are probably connected with water content as it is shown by the P_3 peak in H.W.C. quartz (fig. 7). FRASER [1-2] showed that peaks linked to water-content can occur at about 370 K.

About the contribution of dislocations to anelastic loss, we have performed preliminary Q^{-1} measurements in the strain amplitude dependent range ; we have observed an hysteresis effect at room temperature which disappears at 470 K.

5 - CONCLUSION

The anelastic behaviour of H.Q. 262 quartz is mainly characterized by the P_1 peak and the L.T.R. peaks. In order to suggest mechanisms which control these peaks, other experiments are performed at the present time.

Concerning the influence of these peaks on the stability of resonator frequency, one can suggest that the L.T.R. peaks affect the short-range frequency shift, while the P_1 peak seems rather to induce the long-range frequency shift. Such a suggestion is justified by the high sensitivity of L.T.R. peaks to successive temperature rises.

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