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### ► To cite this version:

Pierre-Emmanuel Hickel, Gerard Demazeau, R. Arnaud, Rémy Chapoulie, Pierre Guibert, et al.. The hydrothermal growth of alpha-quartz and the nature of the physico-chemical defects detected in the resulting crystal. *High Pressure Research*, 2000, 18 (1-6), pp.265-269. 10.1080/08957950008200978 . hal-02556304

**HAL Id: hal-02556304**

**<https://hal.science/hal-02556304>**

Submitted on 13 Feb 2023

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# THE HYDROTHERMAL GROWTH OF $\alpha$ -QUARTZ AND THE NATURE OF THE PHYSICO-CHEMICAL DEFECTS DETECTED IN THE RESULTING CRYSTAL

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The development of  $\alpha$ -quartz for high frequencies devices leads to a strong reduction of the thickness of the piezoelectric sheet. Such a thickness is comparable to the size of the defects. Consequently, the main objective for the improvement of the performances of  $\alpha$ -quartz used as a piezoelectric material is to reduce the density of physico-chemical defects.

Our work has been focussed in two directions:

- (i) the identification of different physico-chemical defects using the overlap of different techniques (X-ray topography, IR spectroscopy, Cathodoluminescence, Thermoluminescence, EPR, ...),
- (ii) attempts at improving the correlations between the different parameters governing the hydrothermal crystal growth of  $\alpha$ -quartz and the nature or the density of defects.

**Keywords:** Hydrothermal crystal-growth;  $\alpha$ -quartz; density of defects

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## 1. INTRODUCTION

$\alpha$ -quartz was the first material tested for the hydrothermal crystal growth [1–3]. Single crystals of  $\alpha$ -quartz, due to their piezoelectric properties, have been developed for different applications (industrial electronics in particular, and radiocommunications) [4].

The strong increase of the work-frequency (to 800–900 Mhz for U.H.F. devices [5]), leads to a miniaturisation of the quartz-sheet (for a frequency of 2000 Mhz the thickness of the piezo- electric sheet is close to 1–2  $\mu\text{m}$ ). Consequently, this thickness is comparable to the size of defects.

The main defects observed in single-crystals of  $\alpha$ -quartz can be roughly divided into two categories.

(A) physico-chemical defects, including:

- (i) the cationic and anionic substitutions in the lattice ( $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$  with  $\text{O}^{2-} \rightarrow \text{OH}^-$  or with the formation of a hole  $h^+$  on the oxygen site associated with alkaline  $-$ ions in substitutional position),
- (ii) inclusions (fluid-type as  $\text{H}_2\text{O}$ , aqueous solution, gas or solid-type as acmite  $\text{NaFeSi}_2\text{O}_6$ ).

(B) structural defects such as dislocations, etch-channels. . . .

In parallel, such defects have a negative effect on the performance of electronic devices.

For all these reasons the main objective is to reduce the density of defects in  $\alpha$ -quartz single crystals. Consequently, the hydrothermal crystal growth must be carefully controlled; the role of the different physico-chemical parameters governing such a process has been investigated previously [6, 7].

One important problem is to characterize the different defects existing in  $\alpha$ -quartz single-crystals by means of physico-chemical techniques.

## 2. HYDROTHERMAL CRYSTAL GROWTH OF $\alpha$ -QUARTZ

Using a hydrothermal pilot-plant [8] with a reaction vessel volume close to 1.5 liters and an aqueous solution of 1 M NaOH as a solvent, three  $\alpha$ -quartz single-crystals were prepared for each run.

TABLE I Main crystal-growth parameters characterizing the  $\alpha$ -quartz single crystals used as samples

	AD17	AD18	AD19
Crystal growth temperature ( $^{\circ}$ C)	370	370	370
$\Delta T$ ( $^{\circ}$ C)	5–8	10	14
Pressure (MPa)	230	270	290
Crystal-growth speed (mm/face/day)	0.298	0.500	0.620
Thickness (Z axis) (mm)	34	16	7

Table I gives the different parameters characterizing their crystal-growth.

### 3. PHYSICO-CHEMICAL CHARACTERIZATIONS

Different characterizations were carried out: chemical analysis through ICPMS, Castaing micro-probe, IR. spectroscopy, cathodoluminescence.

The present paper gives the first results concerning the evaluation of the chemical impurities and the density of OH defects.

#### 3.1. Chemical Analysis of the Samples

Table II gives the main impurities observed by ICPMS ( $\mu$ g/g).

Among the impurities, aluminum – due to its role in the cationic and anionic substitutions – plays a specific role in the reduction of the performance of  $\alpha$ -quartz based devices.

TABLE II Chemical analysis using castaing micro-probe

Impurities ( $\mu$ g/g)	Reference	AD14 near the seed	AD18 near the seed	AD17 near the seed	AD17 far from the seed
Al	3.4	27.4	11.6	14.7	8.8
Li	0	2.2	0.9	0.33	0.2
Co	0	0.2	0	0	0
Ni	0.5	1.4	0.8	1.4	0.6
Na	33.8	35.5	31.6	32.8	23.1
Mg	4.4	2.6	1.9	3.5	2
K	33.2	23.9	19.8	40.7	21.7
Ca	76.4	117.7	69.8	111.1	73.1
Cr	1.2	2.2	1.6	2.8	0.8
Mn	0.1	0.2	0.2	0.3	0.1
Fe	7.2	13	10.2	16.8	8
Cu	0.3	0.8	0.3	0.4	0.3

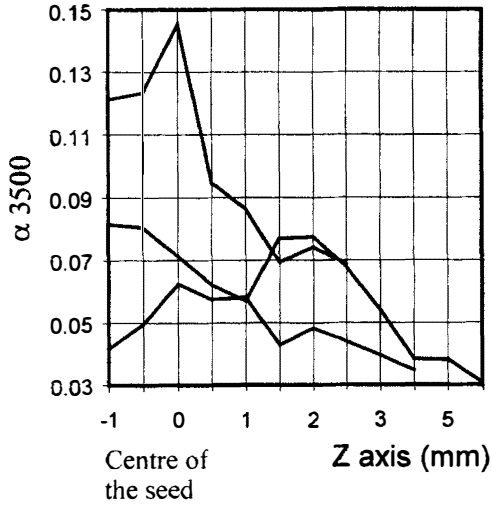


FIGURE 1 Evolution of  $\alpha$  (AD18) versus the distance from the center of the seed to the growth part.

### 3.2. IR. Spectroscopy

Infra-red spectroscopy is mainly able to evaluate the density of OH groups as chemical defect. The  $\alpha$  coefficient is defined as:

$$\alpha_{3500\text{cm}^{-1}} = \frac{A_{3500} - A_{3800}}{d}$$

with:

$A_{3500}$  = absorbance at  $3500\text{cm}^{-1}$ ,

$A_{3800}$  = absorbance at  $3800\text{cm}^{-1}$ ,

$d$  = thickness of the quartz sheet.

Figure 1 illustrates the evolution of  $\alpha$  for different the  $\alpha$ -quartz samples, and for each sample versus the distance from the seed, in order to evaluate the density of OH defects during the crystal growth process.

## 4. DISCUSSION

In ICPMS analysis, the strongest variations of the chemical composition of the sample compared to that of the seed are observed for Al, Li,

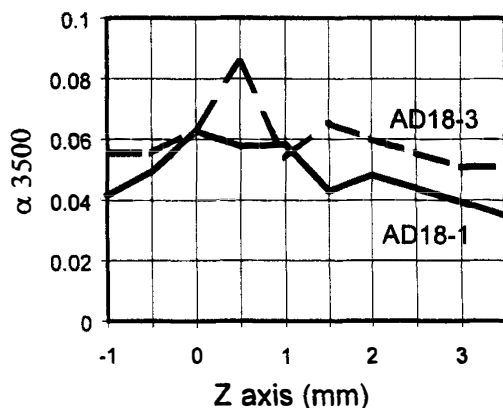


FIGURE 2 Evolution of  $\alpha$  for two samples prepared during the same experiment (AD18-1 at the top and AD18-3 at the bottom of the crystal growth zone).

Na, K, Fe, Ca. In all cases, for the sample AD17 the concentration of impurities decreases when moving away from the zone near the seed. Such a behaviour illustrates the role of the first step of the crystal-growth involving the beginning of quartz deposition.

The average proportion of impurities (Tab. I and Fig. 1) seems to be strongly dependent on the crystal-growth speed.

Moreover, the pressure and  $\Delta T$  parameters play an important role, with the sample AD18 illustrating this double effect. The position of the sample in the crystal-growth zone also appears to be an important factor (Fig. 2).

In order to characterize all the defects and to evaluate the role of the impurities on the density of defects, cathodoluminescence and thermoluminescence studies are in progress.

## References

- [1] Spezia, G. (1905). *Atti. Acad. Sci. Torino*, **40**, 254.
- [2] Bordui, P. (1987). *J. Crystal Growth*, **85**, 199.
- [3] Demazeau, G., Mroczkowski, S. and Buisson, X. (1991). *High Pressure Research*, **8**, 548.
- [4] Lafon, F. and Demazeau, G. (1997). *Matériaux et Techniques*, **3-4**, 11 and **5-6**, 17.
- [5] Detaint, J. and Schwartzel, J. (1994). *J. de Phys. IV, Colloque C2- Suppl. to J. de Phys. III*, **4**.
- [6] Lafon, F. (1996). Thesis of the University Bordeaux 1, No. 1467.
- [7] Hickel, P. E., Lafon, F., Chvansky, P., Largeteau, A. and Demazeau, G. (1997). *Annale de Chimie (Science des Matériaux)*, **22**, 571.
- [8] Hickel, P. E., Largeteau, A. and Demazeau, G., *Rev. Sci. Instr.* (submitted).