Hydrothermal crystal growth of α -quartz: new specificities correlated to applications

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Abstract: α -quartz is mainly used for high frequencies devices, due to its piezoelectric properties. The development of higher frequencies than before for many applications leads to new requirements concerning the material (lowest concentration of physico-chemical and structural defects) and consequently to its crystal-growth.

α -quartz, due to its piezoelectric properties has led to the development of either industrial devices and consumer equipments [1] (Table).

Industrial equipment	Radiocommunication, cable communication, electronic applications, measurement equipment, pager, security system (alarm)...
Consumer equipment	Electronic handy calculator, watch clock, timer, cable TV, color TV, video recorder, RF converter, transceiver, radio equipment, microphone, electronic appliance, microphone, electronic appliance, microcomputer and computer terminal, TV-game machine, telephone, copy machine...

Main Piezoelectric Applications of α -quartz Crystal (from Taki)

The $\alpha \rightarrow \beta$ transition taking place close to 573°C, the synthesis of α -quartz single crystals requires a low-temperature crystal-growth process. This condition has led to the development of the hydrothermal process (Fig.).

Reaction vessel used for the hydrothermal quartz growth

The use of pressure increase the solubility of the nutrient in the temperature domain selected for the crystal-growth ($T \approx 400^\circ\text{C}$). The solvents, conventionnaly used, are a molar solution of NaOH or Na_2CO_3 . A gradient of temperature ΔT between the nutrient and the seeds allows the transportation of SiO_2 as complex anions or polyanions.

Direct measurements on hydrothermal solutions in the crystal-growth conditions of $\alpha\text{-SiO}_2$ are needed to establish exactly the nature of such anionic species [2].

The cultured α -quartz single crystals are characterized by chemical and physical defects [1,2].

1. ANALYSIS OF THE DEFECTS OBSERVED IN SYNTHETIC $\alpha\text{-SiO}_2$ SINGLE CRYSTALS

Roughly such defects can be classified into two groups :

- the physico-chemical defects,
- the structural defects.

1.1. The physico-chemical defects

They are mainly induced by the nature of the nutrient of the solvent and also the chemical contamination of the solution by the metal constituting the reaction vessel.

The inclusions

They are constituted by a solid or a liquid phase inserted in the α -SiO₂ lattice.

Concerning the solid phase, the most common inclusion is the complex silicate NaFe(III)Si₂O₆ (acmite). Its formation results from the chemical attack of the reaction vessel (walls iron-alloys) by the alkaline solution (NaOH or Na₂CO₃) used as solvent.

The etch-channels

Such defects are also called etch pipes or tunnels [4-6].

The etch rate along this channel is very much higher than that characterizing the bulk-material. The formation of these defects are correlated to that of dislocations.

Chemical substitutions into the α -quartz lattice

These substitutions are induced by the similarity of cationic or anionic sizes between Si⁴⁺, O²⁻, Al³⁺ (or other trivalent cation able to accept the tetrahedral coordination) and OH⁻.

The formation of such a defect is in particular help by the basicity of the solvent (OH⁻ concentration).

Interstitial cations

In some thermodynamical conditions different cations (in particular Li⁺) can be in interstitial positions, in particular for compensating the Si⁴⁺ → M³⁺ cationic substitution into the SiO₂- α lattice.

1.2. The structural defects

The main nature of these defects are dislocations. Their origin can be generally due to foreign particles, thermodynamical parameters governing the crystal growth or hydrodynamic conditions inside the reaction vessel..

2/ QUALIFICATIONS REQUIRED FOR APPLICATIONS

In a piezoelectric resonator, electrical energy and mechanical energy are interconverted [1]. In such a schema, a resonator can be equivalent to a circuit consisting of an induction, a resistance and two capacitances.

Q is defined as : $Q = \frac{|x|}{R}$:

x is the inductive or capacitive reactance at resonance,

R is the resistance.

Q can be considered as the inverse of the fraction of the energy lost per cycle. The highest values of Q are required in order to prevent lost of energy into incoherent phonons.

The acoustic Q for natural α -SiO₂ crystal are close to 1 to $3 \cdot 10^6$ while for synthetic crystals such a value drop down to $2 \cdot 10^5$ - $1 \cdot 10^6$. The analysis of such a phenomenon has led to correlate such a Q value to infrared adsorption at 2.86 μ m corresponding to an OH stretch frequency [6-8]. This adsorption could be induced both by the presence of H₂O (as inclusion for example) or the anionic substitution $O^{2-} \rightarrow OH^-$ into the lattice, this substitution being compensated by a cationic one $Si^{4+} \rightarrow Al^{3+}$ or $Si^{4+} \rightarrow Fe^{3+}$.

During these last twenty years, the main requirement for growing α -SiO₂ single crystal was to improve Q, and to get a low concentration of physico-chemical and structural defects.

3/ NEW CONSTRAINTS FOR DEVELOPING HIGH FREQUENCY DEVICES

The development of high frequency devices (24MHz $\rightarrow$ 100 MHz and more), induces strong constraints concerning the shaping of the α -SiO₂ material.

If for 24 MHz the thickness of the sheet is close to 70 μ m, in the domain of 100 MHz such a thickness can drop down to 6-7 μ m. This requirement is important for the crystal-growth of α -quartz, the size of the defects being of the same order. Consequently for the solid state chemist, the elaboration of single-crystals with a very low concentration of defects appears to be a new goal.

3.1. Role of the defects on the applications

The existence of defects in synthetic quartz crystals leads to critical modifications of resulting devices [9].

The inclusions can be assimilated to a zone of discontinuity, the acoustic wave is propagated in another solid.

The OH concentration induce to a large decrease of the acoustic coefficient Q. The substitution $O^{2-} \rightarrow OH^-$ being coupled with the cationic one ($Si^{4+} \rightarrow M^{3+}$), the M^{3+} impurities can play an important rôle concerning the ageing process of the device and its behaviour versus ionizing radiations.

The dislocations inducing local stresses, a modification of the local electric field compared to the applied one can be observed.

3.2. New developments in α -SiO₂ crystal-growth

Considering the analysis of the main defects generally observed in α -quartz lattice, different parameters can be defined for obtaining a significative improvement of the single crystal quality :

- a) the purity of the solvent,
- b) the development of new solvents able to reduce the anionic and cationic substitutions [10,11],
- c) the increase of pressure domain [12],
- d) the strict control of the thermodynamical parameters P,T, Δ T governing the process,
- e) a reductions of the Δ T value,
- f) an optimization of all parameters governing the thermodynamical parameters and the structure of the reaction vessel [13].

CONCLUSION

The development of new devices results in the major case of the overlap of competences between solid state chemistry, physics and ingeniering. α -quartz is a old piezoelectric material if we consider the first experiments devoted to the crystal-growth of synthetic quartz [14]. The futur developments of new-devices based on high frequencies require to reach the intrinsic properties of such a material. Consequently, the improvement of single-crystals quality appears a goal in Materials Science [15].

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