Piezoelectric properties of $Si_xGe_{1-x}O_2$ crystals

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***Abstract* — We report a first measurement of several elastic, piezoelectric, and dielectric characteristics of $Si_{0.93}Ge_{0.07}O_2$ crystals. This was made using the thickness modes of plates of several simple orientations, using normal and/or lateral excitation. Corrections accounting for energy trapping effect (finite electrode dimension and mass loading) or stray capacitances were made after the measurements when partially electroded plates were used. The most interesting features of $Si_xGe_{1-x}O_2$ crystals already demonstrated are mainly the extremely reduced OH concentration, the existence of compensated cuts, the larger piezoelectric constants and the increased temperature of the α–β phase transition.**

I. INTRODUCTION

After successful growth and characterization of α-GeO_2 single crystals with α-quartz structure [1], silicon–germanium oxide ($Si_xGe_{1-x}O_2$ or SGO) crystal growth was realized. SGO solid solution single crystals with α-quartz structure were synthesized under hydrothermal conditions [2]. The crystals of maximum GeO_2 content (38 wt. %) were obtained in ammonium fluoride aqueous solutions at temperature as high as 700°C and pressure close to 180 MPa.

In the present paper, we study the thermal stability and the elastic and piezoelectric properties of the SGO single crystals. Crystals with homogenous distribution of germanium (up to 7 mol %) were selected for these investigations. The temperature of α–β polymorph transition for α-$Si_{0.93}Ge_{0.07}O_2$ (SGO-7) is 780°C, which is 207°C higher than for the same α–β transition of quartz and the main piezoelectric constants d_{11} and d_{14} exceed those of quartz ones by 20-30 %. Infrared measurements indicate that the crystals of SGO should be considered as a material with a low OH content. This implies that several phenomena related to the presence of the OH impurity in quartz can be avoided using SGO (lowering of the Q factors and potentially causing aging effects, etc…).

Several of the elastic constants of this material were determined. They are just a little smaller than those of quartz while the density of $Si_{0.93}Ge_{0.07}O_2$ is slightly larger (by about 6 %) and the piezoelectric constants are also larger. A determination of the temperature coefficients of the constants was partially made. It was found that the thermal stability of the elastic properties were also greater than in quartz. As for $GaPO_4$, this can result, at least partly, from the higher temperature of the phase transition that has an influence on the thermal behaviour of some elastic constants. The (mean) larger distortion [3] introduced in the lattice of SGO-7 by substituting part of the Si atoms by the larger Ge ones induces as in berlinite and $GaPO_4$ a larger "distortion" of the structure, that is probably the most important factor of the favourable piezoelectric properties observed. This distortion may also be a factor of the more favourable thermal behaviour specified by stabilising of the α-quartz structure in a larger range of temperatures. The measurements have indicated that compensated cuts do also exist in this material (positive T.C. of C_{66}). Some plane resonators used in this study have displayed quite interesting Q factors On the whole, the extremely reduced OH concentration, the existence of compensated cuts, the larger piezoelectric constants and the increased temperature of the α–β phase transition make SGO a promising material, whose successful growth is already assessed.

II. THEORY

A. *Thickness and lateral field excitation measurements*

The electromechanical properties of SGO crystals were studied by resonance methods. The applied electric field induces some piezoelectric thickness modes whose properties are modeled in several kinds of theories; so, certain piezoelectric, elastic and dielectric constants could be determined [4]. In the following paragraph we recall some results of the one dimensional theory of the thickness modes of plates excited by an electric field normal to the plate using the formalism initially proposed by Glowinski [5]. This theory is most often used to extract constants from measurement of resonance frequency (from measurements of propagation delay). In this paper we consider the case of a piezoelectric

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plate totally coated with metal layers of negligible mass. For a piezoelectric solid the linear constitutive equations of the piezoelectric field (equivalent to a generalization of the Hooke's Law for piezoelectric material) are:

$$T_{ij} = C^{E}_{ijmn} S_{mn} - e_{kij} E_k \qquad (1) \qquad \text{and}$$

$$D_l = e_{lmn} S_{mn} + \varepsilon^{S}{}_{lk} E_k \qquad (2)$$

Where T=σ is the stress tensor, S is the strain tensor, E is the elecric field, the C^{E}ijmn are the elastic stiffness constants at constant electric field, the e_{ijk} are the piezoelectric constants, the ε^{S}_{lk} are the dielectric constant (at constant strain) and D is the electric displacement. In these constitutive relations, the Einstein summation convention over repeated index is employed. We use also the assumption that there is no free charges in the piezoelectric material and that the coupling of the electrical to the magnetic variables is negligible (due to the fact that the sound velocity is negligible as compared to that of the electromagnetic interactions (which is considered as infinite in this "quasistatic approximation") so that equation 3 simplify to:

$$div\vec{D} = D_{k,k} = 0 \qquad (3)$$

$$S_{ij} = 1/2(u_{i,j} + u_{j,i})$$

$$\frac{\partial T_{ij}}{\partial x_i} = T_{ij,i} = \rho \ddot{u}_j \qquad (4)$$

Equation 4 is the stress equation of motion. In a first step (problem of the eigen modes of the infinite solid or of a plate without external electric field (at V=0) we consider the propagation of electromechanical plane waves (vector wave for the displacement u or scalar plane wave for the potential in the form: $\Psi = \Psi_0 \exp(K(\vec{n}\vec{r}.\omega t))$, in the direction defined by the unit vector $\vec{n}(n_1, n_2, n_3)$ normal to the plate. In substituting the expression of the plane displacement wave (vector) and of the plane potential wave (scalar) in the previous equations and by elimination of the electric field or of the potential by a classical treatment, we obtain the piezoelectric Christoffel equation.

$$\left[C^{E}{}_{ijmn} n_i n_m u_n + \frac{e_{mij} n_m n_i . e_{lmn} n_l n_m}{\varepsilon^{S}{}_{jm} n_j n_m} u_n\right] = \Gamma_{jn} u_n + \frac{1}{\varepsilon}\gamma_j \gamma_n u_n = A_{jn} u_n = \rho \frac{\omega^2}{K^2} u_j = \rho V^2 u_j \quad (3)$$

Equation to the eigen values $\lambda^{\alpha}\ (\alpha = 1,2,3)$: $\quad A\vec{u} = \lambda \vec{u} \qquad (4)$

$with : \varepsilon = \varepsilon_{rs} n_r n_s ; \qquad \gamma_j = e_{mij} n_m n_i ; \qquad \Gamma_{jn} = C^{E}_{ijmn} n_i n_m \qquad$ A : matrice de Christoffel

$V =$ phase velocity; $\rho =$ density; $\varepsilon =$ dielectric constant in $\vec{n}$ direction; K = wave number

The Christoffel equation (3) is an eigen-values, eigen-vectors equation which has most often three distinct solutions (3 eigen values $\overline{C}\alpha$ and the 3 corresponding eigen vectors $\vec{U}\alpha$ (α=1,2,3). These solutions correspond to the longitudinal (L), fast transverse (FT) and slow transverse (ST) electro-acoustic waves propagating normally to the plate. As the Christoffel matrix is symmetrical the three corresponding acoustic plane waves have mutually orthogonal displacements. The phase velocity of these acoustic waves is related to the eigen values $\overline{C}\alpha$ of the Christoffel matrix by the relation.

$$v^{\alpha} = \frac{\omega}{K^{\alpha}} = \sqrt{\frac{\overline{C}^{\alpha}}{\rho}}$$

Where K^{α} and $\overline{C}^{\alpha}$ are respectively the wave number and the stiffened elastic constant of the mode α ($\overline{C}^{\alpha}$ generally contains non elastic terms (term containing piezoelectric constants and dielectric constants) that are added to the terms of elastic origin so as to increase their value which corresponds to a stiffening of the material by the piezoelectric effect).

From the previous equations we obtain the expression of the three piezoelectric eigen modes (for ω≠0) which are constituted of plane displacement and potential waves. The other quantities (such as for example the normal stress and normal displacement) are also plane waves

$$\vec{u}^{\alpha} = \vec{U}^{\alpha}[\lambda^{\alpha} \exp(iK^{\alpha}\vec{n}.r + i\omega t) + \mu^{\alpha} \exp(-iK^{\alpha}\vec{n}.r + i\omega t)]$$

$$\vec{T}^{\alpha} = iK^{\alpha} C^{\alpha} \vec{U}^{\alpha}[\lambda^{\alpha} \exp(iK^{\alpha}\vec{n}.r + i\omega t) - \mu^{\alpha} \exp(-iK^{\alpha}\vec{n}.r + i\omega t)]$$

$$\Phi^{\alpha} = \frac{1}{\varepsilon}\vec{\gamma}^{\alpha}.\vec{u}^{\alpha} \qquad\qquad D^{\alpha} = D^{\alpha}_{i}.n_i = 0.$$

Where $\vec{T}^{\alpha}$ is the normal stress correspond ing to the α eigen mode ($T^{\alpha}_{i} = T_{ij} n_j$)
and D^{α} the normal electric displaceme nt correspond ing to the same eigen mode

The solution depends on two constants λ and μ that can be determined considering the boundary conditions. For the case corresponding to the excitation by a field normal to the plate we have to express that the surface of the plate is acoustically free (normal stress =0) and that a potential is applied between the two faces of the plate.

$$T_{ij} n_j = 0 \quad \text{at } z = \pm h$$

$$\Phi(+h) = Vo.\exp(j\omega t)/2$$

$$\Phi(-h) = -Vo.\exp(j\omega t)/2$$

$$2h = \text{thickness of the plate}$$

After some calculations this allow to determine λ and μ

$$\lambda^{\alpha} = -\mu^{\alpha} = \frac{E_0.\gamma^{\alpha}.}{2iK^{\alpha}\overline{C}^{\alpha}\cos\theta^{\alpha}}$$

$$\text{with } E_0 = -\frac{V_0}{2h} \quad \text{and} \quad \theta^{\alpha} = \frac{K^{\alpha}.2h}{2} = \frac{\omega.2h}{2v^{\alpha}}$$

So that we obtain the expression of the forced mode in expressing that they are a linear combination of all the eigen modes, the three eigen mode found for ω≠0 and the uniform mode which is the eigen mode when ω→0 (it is thus a quasi electrostatic mode that should be considered as the limit of the quasi-electromagnetic modes when c→∞).

$$\vec{u}(\vec{r},t) = \sum_{\alpha}\vec{u}^{\alpha} = \sum_{\alpha=1,3}\vec{U}^{\alpha}\frac{E_0.\gamma^{\alpha}.\sin(K^{\alpha}\vec{n}.\vec{r})}{K^{\alpha}.\overline{C}^{\alpha}.\cos(\theta^{\alpha})}\exp(i\omega t) \qquad (5)$$

$$\Phi(\vec{r},t) = \sum_{\alpha}\Phi^{\alpha}(r,t) - E_0(r,t).z = \frac{E_0}{\varepsilon}\sum_{\alpha}\frac{(\gamma^{\alpha})^2.\sin(K^{\alpha}\vec{n}.\vec{r})}{K^{\alpha}.\overline{C}^{\alpha}.\cos(\theta^{\alpha})}\exp(i\omega t) - E_0\vec{n}.\vec{r}\exp(i\omega t)$$

$$\vec{T}_n(\vec{r},t) = \sum \vec{T}^{\alpha} - E_0.\vec{\gamma} \qquad (\text{Normal stress of component } Tn_i = T_{ij} n_j)$$

$$D(t)_n = \vec{D}.\vec{n} = D_i n_i = \varepsilon_{ij} n_i n_j . E_0(t) \quad (\text{Normal electrical displacement}) \qquad (6)$$

The current density induced by the potential in the plate is equal to:

$$J_0 = \frac{I}{S} = \frac{\partial(-\vec{D}.\vec{n})}{\partial t} = -i\omega\varepsilon E_0 \exp(i\omega t)$$

The electrical impedance Z(ω) is obtained from the potential and the current density

$$Z(\omega)=\frac{\Phi}{J_0.S}=\frac{1}{i\omega C_0}\left[1.-\sum_\alpha (k^\alpha)^2\frac{tg\theta^\alpha}{\theta^\alpha}\right] \qquad (7)$$

with C_0 capacitance for a surface S

and : $k^\alpha=\sqrt{\frac{(\gamma^\alpha)^2}{\varepsilon.\bar{C}^\alpha}}$ (coupling coefficient)

The anti-resonance frequencies are solution of 1/Z(ω)=0 which corresponds to:

$$\theta^\alpha=(2p-1)\pi/2=\frac{\pi f_a^\alpha.(2h)}{v^\alpha}$$

$$so: \quad f_a^\alpha=\frac{(2p-1)}{2.(2h)}v^\alpha=\frac{(2p-1)}{2.(2h)}\sqrt{\frac{\bar{C}^\alpha}{\rho}} \qquad (8)$$

The resonances frequencies are solutions of Z(ω)=0. Generally the resonance frequencies are sufficiently separated so that they are solutions of simplified equations like (which is the rigorous solution when only one mode is piezoelectrically excited:

$$tg\theta=\frac{(k^\alpha)^2}{\theta}=tg\frac{\pi f_r(2h)}{v^\alpha}=\frac{(k^\alpha)^2.v^\alpha}{\pi f_r(2h)} \qquad (9)$$

From these expressions, we observe that the velocities can be deduced from the measurement of the resonance frequencies or of the anti-resonance frequencies of the corresponding vibration modes of a plate (thickness=2h). From the measurement of velocities and from the expressions given above, it is possible to determine all the elastic constants provide that a sufficient number of experiments are made.

B. Lateral field excitation of thickness modes of plates

A theory relatively similar to those recalled above for the thickness modes of plane plates excited by a field normal to the plate does exist when a field parallel to the face of the plate is used to excite the thickness modes [4]. It appears that Christoffel equation remains valid in this case (so that the 3 same thickness modes can be excited). However the electrical boundary conditions are quite different in this new case. We will simply recall here that for such modes the resonance frequencies are given exactly by relation (8) so that the velocity can be very simply derived from the resonance frequencies obtained with lateral excitation. The anti-resonance frequencies are the solution of equations relatively similar to (7) and (9), but concerning the admittance and where a new dielectric constant (in the direction of the field) and new coupling coefficients appear [4].

$$Y=\frac{i\omega\varepsilon'' S''}{d}\left[1+\sum_\alpha (k_e^\alpha)^2\frac{tg\theta}{\theta}\right]$$

$$with: \quad \theta=2\mathrm{h}.\eta=\frac{2h.\omega}{\mathrm{v}^\alpha}$$

d : distance between the electrodes generating the field

III. EXPERIMENTAL PROCEDURE

A. Measurements with use of lateral excitation

The lateral excitation shown in Fig. 1 use an electric field a parallel to the surface, generally in the direction giving the maximum coupling. In fact, the results are practically independent of the chosen direction when the modes are sufficiently excited to be accurately measured. The resonance frequencies of the different overtones are in principle in harmonics relation. However this is not always exactly observed for various reasons such as, the use of electrodes having a mass (if the plates are metallized), the non flatness of the plates; the fact that the field generated by such electrodes does is not fully compatible with the hypothesis made in the theory, etc…)). In our experiments, such cases were rather often met. This has led us to use the overtones frequencies that were the most in harmonic relation among all those measured, in general those of overtone 5 and 7 and to use corrections for several effects.

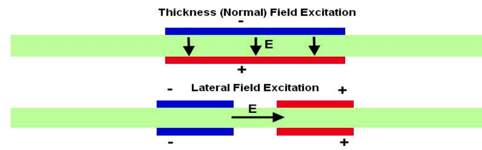

Figure 1. Thickness and lateral field excitations

We have experimental observed that a simple technique based on the method of the ratio of two overtone frequencies (used in the case of the perpendicular excitation see below) could be applied to obtain efficient corrections when the overtone frequencies were not in harmonic relation. This method is partly based on the fact that the lateral field excitation using electrodes such as those considered in figure 1 introduces other components of the field and that for a the normal component the method of the ratio can be applied to correct the frequency lowering due to this field.

From comparison with other technique of treatment of the results, it was observed that this technique introduces a correction which seems very realistic. However we did not use the results of this technique for the determination of constants because of justification of the theoretical validity of this correction is not well established (although it can result of the fact that the one-dimensional theory of the modes excited by lateral field does conduct to a relation nearly identical to the equation

$$\frac{tg\theta_p}{\theta_p}=\frac{tg\theta_q}{\theta_q}$$

established (see below) for two overtones mode p and q excited by normal excitation. In this case there is the relation Y(fap) =Y(faq) =0 that leads to a similar equation.

In the treatment of measurements, we have used the ratio of the frequencies of the overtone mode to eliminate the measurements leading to ratio frp/frq too different from p/q.

In some cases, metallized plates were used. Then we have made a correction of "mass loading" by estimating the fraction F of the surface covered by the metal film at the center of the resonator. (The correction is (1+R.F) for frequencies and (1+2R.F) for the effective elastic constants of the mode if R is the mass loading, it was always very small, a few thousandth).

Most of the measurements have concerned the extensional mode, and the fast thickness shear of the Y-cuts and the two shear mode of the X-cuts. The results were most generally very reproducible between the sample (3 X plates, 2 Y plates) and between the experiments [at least 3 experiments for each plate made using two air gap set-up (giving a lateral field), and metal films electrodes). The results obtained for the Z plates were not used for the determination of constants. For the other results we have used

fast shear	mode	Xcut	C_{trx} = 6.6452 E+10 N/m²
Slow shear	mode	X-cut	C_{tlx} = 2.8377 E+10 N/m²
Fast shear	mode	Y-cut	C_{try} = 4.9814 E+10 N/m²
Extent	mode	Y-cut	C_{tey} = 9.2982 E+10 N/m²

Determination of constants (10^{10} N/m²):

$C_{tey}+C_{try} = C_{11}+C_{44}$= A =14.2796

$C_{trX}+C_{tlx} = C_{66}+C_{44}$= B = 9.4829

$C_{tey}-C_{try} = [(C_{11}-C_{44})^2+4.C_{14}^2]^{1/2}$ = C =4.3168

$C_{trx}-C_{tlx} = [(C_{66}-C_{44})^2+4.C_{14}^2]^{1/2}$ = D =3.8075

so, $(C^2-D^2)-(A^2-D^2)=4.C_{44}*(C_{66}-C_{11})$

or $C_{66}-C_{11}=(B-A)$

Therefore $[(C^2-D^2)-(A^2-D^2)]/(4.(B-A))=C_{44}$=5.72497 E+10

$C_{11}=A-C_{44}$=8.55462 E+10

$C_{66}=B-C_{44}$=3.75792 E+10

$C^2-(C_{11}-C_{44})^2$= 4 C_{14}

$C_{14\,(11)}$= 1.63001 E+10

$D^2-(C_{66}-C_{44})^2$= 4 C_{14}

$C_{14(66)}$=1.63001 E+10

Therefore $C_{12}=C_{11}-2.C_{66}$ = 1.03878 E+10

C_{33} and C_{13} were not determined

The estimated precision of the measurements is of the order of a one percent (relative value); the extraction slightly augments this estimation (specifically for C_{12}).

B. *Measurements with use of thickness excitation*

The air gap technique was mostly used since it allows the use of large electrodes overing totally the plate. Several measurements were made using metal film electrodes covering all, or part, of the plate, a few were made using the small (parasitic) normal component generated by the electrode generating the lateral fields.

In many cases (particularly when the measurements use full metallized plates or air-gap method with larges electrodes covering nearly all the plate) we have several resonances in the neighboring of the theoretical frequency of the thickness mode. These modes takes their in origins in high order plates modes (of the finite plate) which couple with the thickness mode, an/or in the anharmonics of the thickness modes also coupled with plate modes). It is generally possible to distinguish the modes situated in the vicinity of the main mode and the coupled modes situated in the vicinity of the anharmonics of the thickness mode (except for the case of the thickness extensional mode of the X cut).

We have performed some computing by the "method of the ratio" which consists in solving equations verified by a couple of two overtone (measured) frequencies Frp and Frq (being respectively those f the pth and qth overtones):

$$\frac{tg\theta_p}{\theta_p}=\frac{tg\theta_{qq}}{\theta_q} \quad \text{or rather:} \quad r=\frac{\theta_p}{\theta_q}=\frac{tg\theta_q}{tg\theta_p}$$

with $\theta_i=\frac{\pi.fr_i}{2.fa_1}$ and r ratio of measured frequencies.

These equations are simply derived from the condition of resonance (Z(frp) = 0 = Z(frq)) of one-dimensional theory. The solution of these equations allows to find the anti-resonance frequency of the fundamental mode (fa_1). With:

$$fa_1=\frac{v}{2.2h}=\frac{1}{2.2h}\sqrt{\frac{\overline{C}}{\rho}}$$

and therefore $\overline{C}$ the "effective" elastic constant for the mode (solution of the Christoffel equation), knowing frp and frq. It is necessary to note that the direct determination of k by this method is numerically very hazardous when p or q are >3. So, the calculation of k must be done from data concerning the fundamental mode or from $\overline{C}$ and the appropriate elastic constants (C_{11} and C_{66} in our case).

The "method of the ratio" allows by a kind of triangulation to make a choice among the plates mode situated around the actual thickness resonance frequency (mostly in eliminating those which are too far from the frequency of an overtone of the thickness mode). In this process, the use of ratio involving the highest overtones (p and q $\geq$ 3) is of a great help, as the ratios Fp/Fq tends to be very close to p/q. Moreover it is possible to determine approximately an interval in which the ratio Frp/Frq should be:

$$p/q< Frp/Frq< (p/q)*(1+4k^2/p^2\pi^2-4k^2/q^2\pi^2) \text{ with } p>q.$$

This method, which is derivate from the one-dimensional theory, is satisfactory for air gap measurement made with larges electrodes covering totally the plate or for totally metallized plates (if a correction of mass loading is made). It has the very useful property to be relatively insensitive to errors dues to the decomposition of the thickness mode by coupling to "plate modes". This results of the known fact that the numerical solution of this equation converges to a value of the velocity or the anti-resonance frequency which presents a very reduced sensitivity to errors of the measured frequencies frp and frq.

The effects of this coupling is still more completely eliminated if means are computed between the results obtained with several of this plate modes that are more or less regularly distributed around the thickness resonance.

The results obtained by the "ratio technique" are only a crude approximation for energy trapping resonators (with partial metallization). However, it possible to chose the parameters of the energy trapping resonators (by choice of the dimensions of electrodes and by mass loading of the electrodes) so that only a small correction has to be made that can be determined by approximate relations (use of either very small or very large electrodes). This procedure was used in some cases.

In principle, the (three-dimensional) theory of energy trapping allows a direct and a precise determination of the relative difference between the resonance frequency of the energy trapping resonator and the anti-resonance (cut-off) frequency of the infinite unmetallized plate (frp-fa1)/fa1, when the geometrical parameters of the resonators are known.

This technique which allows a very precise determination of fa1 and thus of $\overline{C}$ require the knowledge of at least a quite good approximation of most of the constants of the material and it can almost be use to refine the results when first measurement of the constants has been made. In this work it was mostly used to assess the validity of the correction made using approximate relations and to observe that the choice of small electrodes (small electrode diameter/ to thickness ratios) and of small mass loadings lead to small and predictable corrections that can be made using approximate formula. This result of the fact that in these conditions the mode take a large extension in the plate and is thus closer to the theoretical one dimensional mode of unmetallised plates. The corrections are relative to the effect of the mass of the electrode and to their electrical effect (that lower the resonance frequency). The 2nd of these corrections is dependant of the overtones rank and it tends to become negligible when the overtone rank is greater than 5 (for this material). In this case the corrections (for $\overline{C}$) are respectively the factors $(1+2\alpha R)$ and $(1+8\alpha k^2/p^2\pi^2)$ where R is the mass loading of the electrodes (αR was directly measured by deposing the same metal films on quartz of the similar designs same during the metal deposition), α is a factor representing the fraction of the surface of the plate covered with metal).

Determination of $\overline{C}_{66}$

1) Lateral field excitation (use of the small component of a normal residual of the field) with correction of coupling (reduced in this configuration) (average between two measurements is very consistent).

$\overline{C}_{66}$.= 3.8767 E+10 N/m^2
k_{26} = 17.78 %

This is a tentative measurement which has demanded the estimation of a residual coupling k' induced by the residual normal field. The precision of this estimation is low.

2) Thickness field excitation by a large electrode without mass loading (air-gap technique with a zero gap and large electrodes). Exploitation of the results by the “ratio technique”

Y plate	$\overline{C}_{66} = C_{66}*(1+k_{26}^2)$ = 3.89593 E+10 N/m^2
	C_{66} = 3.75792 E+10 N/m^2
therefore,	k_{26} = 19.16% ± 1.5%

This result is an average over 44 results obtained by the “method of ratio” which present a low dispersion. The results point out that k_{26} is very probably in the interval 18.4-20.5 %.

The results obtained with another sample are

Y plate	$\overline{C}_{66} = C_{66}*(1+k_{26}^2)$ = 3.89128 E+10 N/m^2
with	C_{66} = 3.75792 E+10 N/m^2
Therefore,	k_{26} = 18.84% ± 2%

In both cases the precision of values is probably restricted mostly by the precision of thickness ($2*10^{-3}$), density and errors of model to about 1% for C and 2% for k.

3) Use of the higher overtone modes of resonator with small electrodes and low mass loading (energy trapping with (weak) corrections of electrical lowering and mass loading). Average between the higher overtones of two samples:

Y plate	$\overline{C}_{66} = C_{66}*(1+k_{26}^2)$ = 3.89071 E+10 N/m^2
with	C_{66} = 3.75792 E+10 N/m^2
therefore,	k_{26} = 18.79 %

Note: the results have a quite small sensitivity to the k value used for the corrections

4) Use of the method of ratio between high overtones of metallized plates with elimination. (In fact the computation without elimination gives identical results when the average of all calculated C is taken).

Plate Y1	C = 3.8867
with correction of mass loading	C = 3.9000
Plate Y2	C = 3.8774
or after correction of mass loading	C = 3.8907

Average between both samples:

$\overline{C}_{66} = C_{66}*(1+k_{26}^2)$ = 3.89535 N/m^2;
with C_{66}=3.75792
Therefore, k_{26} = 19.12 %

5) The direct measurements of resonance and anti-resonance frequencies of resonators gave a value close to 19 % for the partial 5 of the plate Y1 (all others values of coupling measured for the other modes being lower than this value).

In summary, it seems that the coupling coefficient of slow thickness shear mode of the Y-cut is in range from 17.8 to 20.5%; the most probable value, according to our measurements, being around 19% (18.8-19.1).

SGO-7 is a material with rather similar coupling from this point of view to $GaPO_4$ (but with velocities significantly higher). Moreover, Q factors in the range from 80.000 to 100.000 were measured for the overtones of the thickness mode modes, in air and in disadvantageous conditions (sometimes placed onto a support of metallized silica).

Determination of $\overline{C}_{11}$ *value*

Two methods were used for determination of $\overline{C}_{11}$.

1) Thickness field excitation by a large electrode without mass loading (air-gap at null gap null, with large electrodes), the results were exploited by the “ratio technique”.

The obtained results are less than C_{11}, and are typically $\overline{C}_{11}$ =8.542-8.545xE+10 N/m^2. The results are dispersed for each sample and between the samples. Computing has shown couplings between 10 and 13 % and C_{11} value in an order of 8.45E+10 N/m^2.

The main reason of this dispersion is that the response of the thickness extensional mode of X cut is very intricate with a very great number of modes over a large frequency range around the thickness mode. It is also suspected that the air gap set up could lower the frequency of this mode and constitute a source of error.

2) Lateral field excitation (use of the small residual component of normal field with a correction of the reduced coupling existing in this configuration). The exploitation of the results by the method of ratio and correction for the residual coupling on the higher overtones conduct to value of $\overline{C}_{11}$ = 8.54E+10 N/m^2 with also dispersed results for the same sample and between the samples.

Another determination of k_{11} was used: is based upon the relations:

$$k_{26}^2 = e_{11}^2/\varepsilon_{11} * C_{66} (1+k_{26}^2)$$
$$k_{11}^2 = e_{11}^2/\varepsilon_{11} * C_{11} (i+k_{11}^2)$$
so, $$k_{26}^2 (1+k_{26}^2)/k_{11}^2 (1+k_{11}^2) = C_{11}/C_{66} = 1.5087^2$$
therefore $$k_{11} (1.+k_{11}^2) = k_{26}^2(1.+k_{26}^2)/ 1.5087^2$$

if the values of k_{26} are in the order of 19%, the solution of the previous equation conduct to k_{11} which is in the order of 12.7%.

Comparison with pure quartz

We have observed a moderate increase of density, and in general a moderate reduction of constants, the increase of C_{12} could be more reduced than pointed out (small accuracy of this constant). The electromechanical coefficients of coupling are very distinctly superior to those noticed for quartz.

The benefit in electromechanical coupling results partly to the small reduction of the elastic constants shown in Table 1 but also the increase of piezoelectric constants. This differentiates this material of other analogues of quartz for which the increase of coupling is always accompanied by a more notable reduction of the elastic constants.

TABLE I. MEASUREMENTS OF CONSTANTS AND COMPARISON WITH QUARTZ

		Quartz constantes		**SGO-7**
		James	Bechmann	present
ρ	g/cm³	2.64838	2.6482	2.76
c_{11}		0.8690	0.8674	0.855
c_{12}		0.06790	0.0699	0.1038
c_{13}		0.12009	0.1191	nd
c_{14}		+0.18116	+0.1791	+0.163
c_{22}		0.8690	0.8674	0.855
c_{23}	10^{11}	0.12009	0.1191	nd
c_{24}	N/m²	-0.18116	-0.1791	-0.163
c_{33}		1.0579	1.072	nd
c_{44}		0.58212	0.5794	0.572
c_{55}		0.58212	0.5794	0.572
c_{56}		+0.18116	+0.1791	+0.163
c_{66}		0.40000	0.3988	0.375
e_{11}		+0.1711	+0.171	positive
e_{12}		-0.1711	-0.171	negativ
e_{14}	C/m²	+0.0406	+0.0403	nd
e_{25}		-0.0406	-0.0403	nd
e_{26}		-0.1711	-0.171	negative
ε_{11}	10^{-11}	3.916	3.921	4.11
ε_{22}	F/m	3.916	3.921	4.11
ε_{33}		4.104	4.103	4.19

C. *Thermal behaviour of resonators*

Positive and negative temperature coefficients were observed for the two shear modes, thus, as in quartz, the temperature compensated cuts must be existed for the slow and the fast shear modes. The temperature coefficients observed for SGO-7 for the same modes of the simple cuts have the same sign but a quite lower magnitude than for quartz. This implies that compensated cuts must exist for the thickness shear modes in SGO-7 (and most probably for many other kinds of modes of bars and plates). The temperature coefficient of Y-cut shown in Fig. 2 is a positive, and lower ($72\text{-}74*10^{-6}$) than for quartz ($91*10^{-6}$), and X-cut shown in Fig. 3, 4 is low and negative.

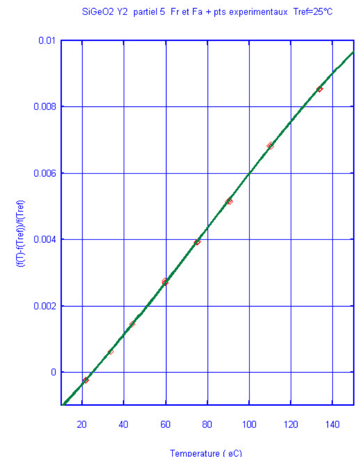

Figure 2. Piezoelectric (slow) shear mode of the Y-cut plates

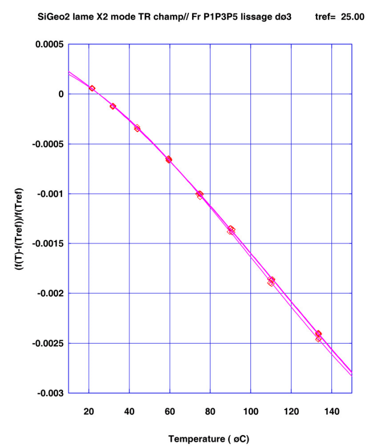

Figure 3. Fast thickness shear mode of the X-cut plates

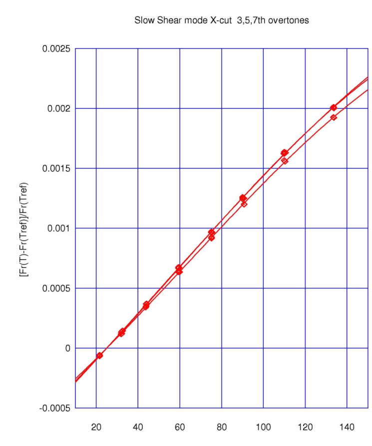

Figure 4. Slow thickness shear mode of the X-cut plates

IV. Discussion and Conclusions

The first characterization of SGO crystals results to some observation which is a T-O-T angle formed by the tetrahedrally coordinated cations. The T-O-T angle shows decreasing from 143.7° α-SiO_2 to 142.6° SGO-7, and determinines, as it was predicted by Etienne Philippot [3], the possible changes in the electromechanical properties of quartz-like materials. So, the investigation of piezoelectric constants has demonstrated values of d_{11}=2.45*10^{-12} C/N and d_{14}=0.92*10^{-12} C/N which are a bit higher that those of quartz. Also, some elastic constants of SGO-7 have shown a good correlation with a shift of the bridge angles in the quartz structure family. Thus, the comparison of some properties of SGO-7 with pure quartz shows:

1. elastic constants of SGO-7 are slightly lower than those of pure quartz,
2. piezoelectric coefficients are higher than those of pure quartz,
3. electromechanical coupling coefficients are higher than those of pure quartz. The present results are close to 19 % (k_{26}) and 12.7 % (k_{11}).

Important parameters of materials for frequency control application are the available temperature compensated cuts. The temperature characteristics of some vibration modes of SGO-7 samples were studied. The resonance frequency of the thickness mode of Y-cut plates shows a very weak positive temperature variation. The fast thickness shear mode of the X-cut plates is low and negative. These fact to high probability of temperature compensated cuts existence.

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