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Elastic characterizations of α -GaPO₄ single crystals grown by the flux method

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Abstract

Transparent gallium orthophosphate single crystals with the α -quartz-type structure, α -GaPO₄, were obtained using the high temperature solution growth technique in a Li₂O–3MoO₃ flux. A first measurement of several elastic constants C_{ijkl} of the millimeter-size α -GaPO₄ piezoelectric single crystals obtained is reported. The elastic constants were computed from the resonance frequencies of the thickness vibration modes measured, at room temperature, in plates polished in these crystals. These resonances were excited either by an electric field normal to the plates (conventional thickness excitation) or by a field parallel to the surface of the plates (lateral field excitation). As usual, the elastic constants were extracted using the formulae given by the corresponding one-dimensional theories of thickness vibration of piezoelectric plates. The measured elastic constants C_{ijkl} of the flux-grown α -GaPO₄ were generally found to be higher than those measured with α -GaPO₄ crystals grown using the hydrothermal technique. This is most probably related to the extremely weak concentration of OH impurities existing in the crystals obtained using this flux-growth method.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The α -quartz-type modification of gallium orthophosphate material (GaPO₄, space groups $P3_221$ or $P3_121$ [1]) has been intensively studied since the 1980s due to its higher piezoelectric coupling coefficient (k) and its larger thermal stability domain compared with α -quartz (α -SiO₂) [2–5]. At atmospheric pressure, the well-known α -quartz/ β -quartz phase transition which occurs at 573 °C for SiO₂, is not observed for GaPO₄. For this material, the direct transformation, upon heating, to a non-piezoelectric phase (β -cristobalite, space group $F-43m$ [6]) appears only at about 950 °C [7, 8]. This expands greatly the useful temperature range for the applications of α -GaPO₄ as compared to α -quartz. However, this phase transition does not permit us to obtain α -GaPO₄

crystals directly from the melt (1670 °C [9]) but its temperature is sufficiently high to allow a variety of growth methods.

Centimeter-size α -GaPO₄ single crystals are commonly prepared by hydrothermal methods from acid aqueous solutions in the temperature range of 150–310 °C and pressures from 2 to 150 bars [10, 11]. However, these hydrothermally grown α -GaPO₄ crystals contain most often hydroxyl groups (OH) which affect their piezoelectric properties and may limit their use at high temperature [12–14]. Equally, in the most satisfactory hydrothermal growth conditions presently known, the growth rate along the Y -direction is small, so that large crystals cannot be obtained by successive growth of nucleation but should be prepared using epitaxial growth of α -GaPO₄ on large seeds of α -quartz analogs [13].

In order to overcome these difficulties, we have developed in our laboratory the high temperature solution growth technique, also known as the flux-growth technique [15]. The

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main feature of this high temperature growth method is to use mineral fluxes as solvents for growing GaPO₄ single crystals at temperatures below their allotropic transformation. The interesting effects of both the anhydrous solvent and the high temperature used are to avoid water molecule incorporation (and hydroxyl group impurities) and to improve the crystal growth rates.

Colorless and transparent α-GaPO₄ single crystals were obtained by spontaneous nucleation using the slow cooling method in X₂O–3MoO₃ fluxes (X = Li, K) [16, 17]. From infrared measurements in the transmission mode, the millimeter-size flux-grown α-GaPO₄ crystals have been found, as expected, practically free from OH-radicals. Furthermore, these as-grown crystals present a totally reversible α-quartz ⇌ β-cristobalite phase transition from the first thermal cycle (10 °C min⁻¹) and without any annealing process [17]. To our knowledge, this phenomenon has never been reported for hydrothermally grown α-GaPO₄ crystals.

After structural and thermal characterizations [16, 17], a first determination of the elastic constants C_{ijkl} , at room temperature, was undertaken on plates obtained from as-grown α-GaPO₄ single crystals spontaneously crystallized by slowly cooling a Li₂O–3MoO₃ flux saturated with GaPO₄.

2. Theory

The application of a high frequency electric field either normal to a plate of a piezoelectric material or situated in the plane of this plate can excite piezoelectric thickness modes of the plate whose resonance and anti-resonance frequencies are more or less simply related to the piezoelectric, elastic and dielectric constants of the material [18, 19].

In the following, we recall the main results of the one-dimensional theory of the thickness modes of infinite piezoelectric plates (of thickness h) excited by an electric field normal to the plate using the formalism initially proposed by Glowinski [20]. Due to the fact that practical thickness vibration modes of finite plate are very similar to theoretical one-dimensional modes, this theory is the one most often used to extract constants from measurements of resonance frequencies (or from measurements of propagation delay). In this paper, we consider the case of a piezoelectric plate totally coated with thin metal layers (electrodes) of negligible mass. This theory is also relevant in the case of the ‘air gap’ measurements made with a negligible gap between the external electrodes and the plate.

For a piezoelectric material, the linear constitutive equations of the piezoelectric field (equivalent to the stress–strain relation of elastic materials and, thus, to the generalization of the Hooke’s Law for piezoelectric material) are:

$$T_{ij} = C_{ijkl}^E S_{kl} - e_{kij} E_k \quad (1)$$

$$D_j = e_{jkl} S_{kl} + \varepsilon_{jk}^S E_k \quad (2)$$

$$S_{kl} = \frac{1}{2} \left(\frac{\partial u_l}{\partial x_k} + \frac{\partial u_k}{\partial x_l} \right) \quad (i, j, k, l = 1, 2, 3) \quad (3)$$

where $T_{ij} = \sigma_{ij}$ is the stress tensor, S_{kl} is the infinitesimal strain tensor and \vec{u} is the displacement from equilibrium

position $\vec{x} = (x_1, x_2, x_3)$, tC_{ijkl}^E is the elastic stiffness constant at constant electric field E_k ($E_k = -\frac{\partial \phi}{\partial x_k}$ where ϕ is the electric potential), e_{kij} is the piezoelectric stress constant, ε_{jk}^S constitutes the dielectric tensor at constant strain and D_j is the electric displacement field. In these constitutive relations and in the following, the Einstein summation convention over repeated index is applied. The symmetries of the tensors allow a simplified equivalent form of relations (1) and (2):

$$T_{ij} = C_{ijkl}^E \frac{\partial u_l}{\partial x_k} + e_{kij} \frac{\partial \phi}{\partial x_k} \quad (1')$$

$$D_l = e_{lmn} \frac{\partial u_n}{\partial x_m} - \varepsilon_{lk}^S \frac{\partial \phi}{\partial x_k}. \quad (2')$$

The electrical displacement obeys Maxwell’s equation (without free charges in the piezoelectric material and in the quasi-static approximation)

$$\frac{\partial D_j}{\partial x_j} = 0, \quad (4)$$

which, using (2’), can be written as

$$e_{jkl} \frac{\partial^2 u_l}{\partial x_j \partial x_k} - \varepsilon_{jk}^S \frac{\partial^2 \phi}{\partial x_j \partial x_k} = 0, \quad (5)$$

and the stress equation of motion is given by

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial T_{ij}}{\partial x_j} = C_{ijkl}^E \frac{\partial^2 u_l}{\partial x_j \partial x_k} + e_{kij} \frac{\partial^2 \phi}{\partial x_j \partial x_k}. \quad (6)$$

We consider the propagation of electromechanical plane waves in the direction defined by the unit normal to the plate $\vec{n}(n_1, n_2, n_3)$:

$$\vec{u} = \vec{u}_0 \exp(j\vec{K} \cdot \vec{r} + j\omega t)$$

$$\Phi = \Phi_0 \exp(j\vec{K} \cdot \vec{r} + j\omega t)$$

where $\vec{K} = \vec{n}K$ is the wavevector, K is the wavenumber and $\vec{K} \cdot \vec{r} = K \cdot n_j x_j$.

We have also:

$$\frac{\partial^2 u_i}{\partial t^2} = -\omega^2 u_i, \quad \frac{\partial^2 u_l}{\partial x_j \partial x_k} = -n_j n_k K^2 u_l,$$

$$\frac{\partial^2 \phi}{\partial x_j \partial x_k} = -n_j n_k K^2 \phi$$

and by replacing in relations (5) and (6), we obtain:

$$\rho \frac{\omega^2}{K^2} u_i = \Gamma_{il} u_l + \gamma_i \phi$$

$$\gamma_i u_i - \varepsilon \phi = 0$$

with $\Gamma_{ij} = C_{ijkl}^E n_j n_k$, $\gamma_i = e_{kij} n_j n_k$, and $\varepsilon = \varepsilon_{jk}^S n_j n_k$.

Eliminating the electric potential between the two equations, we obtain the piezoelectric Christoffel equation:

$$\rho \frac{\omega^2}{K^2} u_i = \left(\Gamma_{il} + \frac{\gamma_i \gamma_l}{\varepsilon} \right) u_l. \quad (7)$$

Equation (7) is an eigenvalue, eigenvector equation of dimension 3 which has, usually, three distinct solutions (three eigenvalues, denoted $\bar{C}^\alpha = \frac{\rho\omega^2}{(K^\alpha)^2}$ and the three corresponding eigenvectors ($\vec{U}^\alpha \alpha = 1, 2, 3$). These solutions correspond to the longitudinal (L), fast transverse (FT), and slow transverse (ST) electro-acoustic waves propagating normally to the plane plate, the eigenvalues being the three ‘effective’ or ‘stiffened’ elastic constants related to the three modes. The three unit eigenvectors \vec{U}_0^α are the three polarizations of the modes. As the Christoffel matrix is symmetrical, the three eigenmodes have mutually orthogonal displacements. The phase velocity of these acoustic waves is by definition:

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

The forced modes (here forced by the normal field created by an electrical potential imposed between the two faces of the plate) are found to be the linear combination of plane waves propagating in the $+\vec{n}$ and $-\vec{n}$ directions that verify the boundary conditions:

$$T_{ij} \cdot n_j(\pm h/2) = 0$$

$$\Phi(\pm h/2) = \pm V_0/2$$

where h is the thickness of the plate. After some calculations, we obtain for each eigenmode:

$$\vec{U}^\alpha(\vec{r}) = \vec{U}_0^\alpha \cdot \left[-\frac{V_0}{h} \cdot \frac{\gamma^\alpha}{K^\alpha \cdot \bar{C}^\alpha} \right] \frac{\sin(K^\alpha \vec{n} \cdot \vec{r})}{\cos(K^\alpha \cdot h/2)}$$

$$\Phi^\alpha(\vec{r}) = \frac{1}{\varepsilon} \gamma_i \cdot U_i^\alpha.$$

The total field being:

$$\vec{U} = \sum_{\alpha=1}^{\alpha=3} \vec{U}^\alpha,$$

$$\Phi = \sum_{\alpha} \Phi^\alpha + \Phi_0 = \sum_{\alpha} \frac{1}{\varepsilon} \gamma_i^\alpha U_{i0}^\alpha + \frac{V_0}{h} \vec{n} \cdot \vec{r}$$

Φ^α being the potential induced by the displacement \vec{U}^α . The total potential also includes the quasi-electrostatic potential Φ_0 externally imposed. In these relations, we have $\theta^\alpha = \frac{K^\alpha h}{2} = \frac{\omega \cdot h}{2 \cdot v^\alpha}$, $\gamma^\alpha = \gamma_i \cdot U_{0,i}^\alpha$, and $k^\alpha = \frac{\gamma^\alpha}{\sqrt{\varepsilon \cdot \bar{C}^\alpha}}$; where k^α is the electromechanical coupling coefficient of the mode α . Using these results, it is possible to find the current density in the device at any frequency (from $J_0 = I/S = -\frac{\partial(D_j \cdot n_j)}{\partial t}$ and equation (2')) and to calculate the electrical impedance $Z(\omega)$ of a one-dimensional resonator having a finite surface S ,

$$Z(\omega) = \frac{\Phi}{J_0 \cdot S} = \frac{1}{i\omega C_0} \left[1 - \sum_{\alpha} (k^\alpha)^2 \frac{\tan \theta^\alpha}{\theta^\alpha} \right] \quad (8)$$

where C_0 is the capacitance for a surface S and $k^\alpha = \sqrt{\frac{(\gamma^\alpha)^2}{\varepsilon \cdot \bar{C}^\alpha}}$ is the coupling coefficient.

The anti-resonance frequencies, which are also the open-circuit eigenfrequencies, are solutions of $1/Z(\omega) = 0$ which correspond to:

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

and so to,

$$f_a^\alpha = \frac{(2p + 1)}{2h} v^\alpha = \frac{(2p + 1)}{2h} \sqrt{\frac{\bar{C}^\alpha}{\rho}} \quad (9)$$

where v is the velocity of the propagation of the acoustic wave and h is the plate thickness.

The resonance frequencies are solutions of $Z(\omega) = 0$. Generally, the resonance frequencies are separated enough so that they are solutions of simplified equations obtained considering only one term of the sum in (8),

$$(k^\alpha)^2 \tan \left\{ \frac{\pi f_r^{(n)}(h)}{v^\alpha} \right\} = \frac{\pi \cdot f_r^{(n)}}{v^\alpha}(h). \quad (10)$$

Equation (10) gives an exact solution when only one mode is electrically excited. From these expressions, we observe that the velocities v^α can be deduced from the measurements of the resonance frequencies f_r and/or of the anti-resonance frequencies f_a of the corresponding vibration modes (longitudinal, fast and slow transverses modes) of a plate. In each case, an explicit expression of \bar{C}^α as a function of the material constants (C, e, ε) and of the plate orientation (n_1, n_2, n_3) can be obtained and numerical techniques exist to extract k^α and \bar{C}^α from the measurements of the resonance and/or anti-resonance frequencies of several overtones (characterized by p in (9)) of the same mode, so that, if a sufficient number of experiments is made with plates of different orientations, it is possible to determine all the elastic and piezoelectric constants of a given material.

A theory relatively similar to that recalled above does exist also for the case where a field parallel to the face of a plane plate is used to excite the thickness modes (lateral field excitation) [19]. It appears that the same Christoffel equation remains valid in this case. However, the electrical boundary condition is now quite different so that the expressions of the impedance and of the coupling coefficient are different.

We will simply recall here that, for such modes, the resonance frequencies are equal to the anti-resonance frequencies obtained with a field directed in the thickness direction and, thus, are given exactly by the relation (9). So the velocity and the constants can also be derived from the resonance frequencies measured with a lateral field excitation. These resonance frequencies are, in principle, independent of the direction of the field. However, in order to maximize the ‘strength’ of the resonance and so to minimize the measurement errors, the field should preferably be applied in the direction giving the maximal value of the electromechanical coupling coefficient [11].

Table 1 gives the mathematical expressions of the velocity, v_i ($i = 1, 2, 3$), of the different plane waves which can propagate into the X- or Y-plate using the previous one-dimensional model of an infinite plate with massless electrodes.

Table 1. Mathematical expressions of the wave velocity in the case of an *X*- and *Y*-oriented GaPO₄ plates. (TE = normal field (thickness excitation), LE = lateral field excitation).

| Plate type | Orientation | Wave propagation, excitation | Wave velocity |
|-----------------|-------------|------------------------------|---|
| <i>X</i> -plate | $\perp OX$ | Longitudinal (TE) | $V_1^2 = \left(C_{11}^E + \frac{e_{11}^2}{\epsilon_{11}^S} \right) / \rho$ |
| | | Quasi-transverse (fast) LE | $V_2^2 = (C_{66}^E + C_{44}^E + \sqrt{(C_{66}^E - C_{44}^E)^2 + 4C_{14}^{E2}}) / 2\rho$ |
| | | Quasi-transverse (slow) LE | $V_3^2 = (C_{66}^E + C_{44}^E - \sqrt{(C_{66}^E - C_{44}^E)^2 + 4C_{14}^{E2}}) / 2\rho$ |
| <i>Y</i> -plate | $\perp OY$ | Quasi-longitudinal LE | $V_1^2 = (C_{11}^E + C_{44}^E + \sqrt{(C_{11}^E - C_{44}^E)^2 + 4C_{14}^{E2}}) / 2\rho$ |
| | | Quasi-transverse (fast) LE | $V_2^2 = (C_{11}^E + C_{44}^E - \sqrt{(C_{11}^E - C_{44}^E)^2 + 4C_{14}^{E2}}) / 2\rho$ |
| | | Transverse (slow) TE | $V_3^2 = \left(C_{66}^E + \frac{e_{11}^2}{\epsilon_{11}^S} \right) / \rho$ |

3. Experimental procedure

The crystal growth experiment was carried out in air in a single temperature zone, SiC resistance heater furnace with an Eurotherm temperature controller. The syntheses of both the α -GaPO₄ phase and the Li₂O–3MoO₃ flux powders, which are not commercially available, have already been reported in [17].

85 wt% of the Li₂O–3MoO₃ flux was thoroughly mixed with 15 wt% of α -GaPO₄ powder in an agate mortar. The α -GaPO₄-flux mixture was put in a platinum crucible covered with a lid, heated from room temperature to 950 °C at a ramp rate of 100 °C h⁻¹ and held at this temperature for 5 h for homogenization. The melted charge was then cooled down with a cooling rate of 0.1 °C h⁻¹ from 950 to 750 °C and with a cooling rate of 2 °C h⁻¹ from 750 to 600 °C. After, the charge was cooled to room temperature at 200 °C h⁻¹.

The crystals were separated from the growth solution by dissolving the residual flux in warm water at 30–45 °C. In this context, all secondary materials such as polyphosphate, if formed, were dissolved in water. The resultant product was sieved in order to collect only bulk materials. As-grown α -GaPO₄ crystals were carefully washed in distilled water with the help of an ultrasonic cleaner and dried at 80 °C. A four-circle x-ray diffraction spectrometer (Oxford diffraction) using Mo K α radiation was used to confirm the nature of the crystallized phase.

Numerous single crystals of millimeter-size were obtained from the flux-growth experiment described above. The biggest as-grown α -GaPO₄ single crystal was 8 × 3 × 3 mm³, figure 1(a). A *Y*-oriented parallel plate with a thickness of 1.220 mm was prepared from this crystal by polishing, figure 1(b). An *X*-oriented parallel plate with a thickness of 0.617 mm was polished from another as-grown single crystal of 4 mm length and 2.5 mm width, figure 2. The orientations of these plates were achieved to a precision of 0.06° with a Laue camera. The Laue diffraction patterns have not revealed any sub-grain structure or twins.

The values of the elastic constants C_{ijkl} of the flux-grown α -GaPO₄ single crystals were derived from the

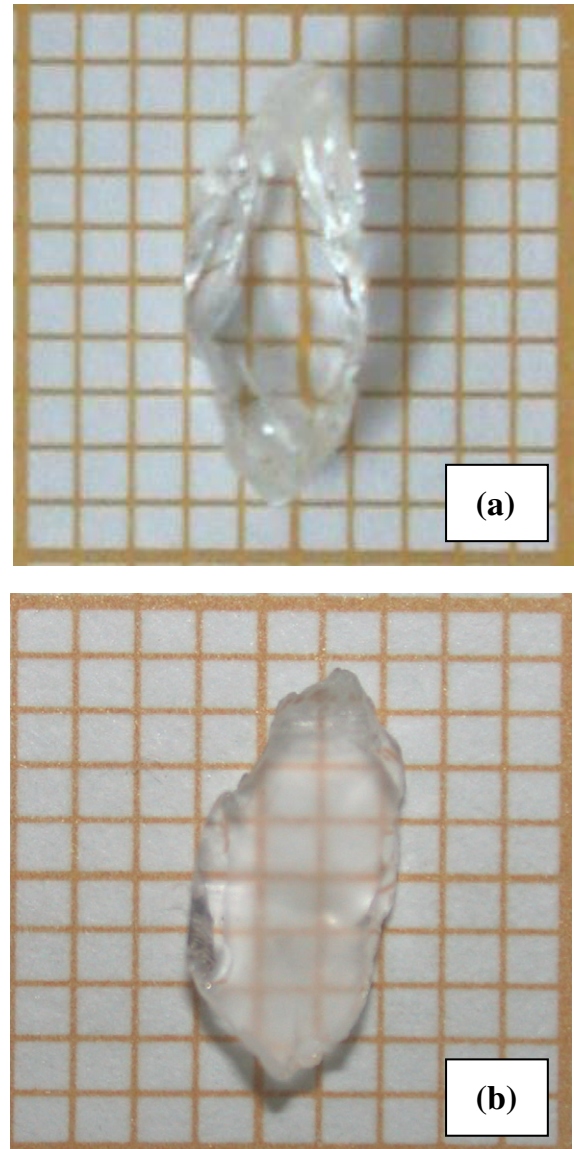


Figure 1. As-grown α -GaPO₄ single crystal (a), *Y*-oriented plate obtained by polishing (b). The smallest division of the grid is 1 mm.



Figure 2. X-oriented α -GaPO₄ plate. The smallest division of the grid is 1 mm.

measurements of their electrical resonance spectra registered at room temperature with network analyzers in the 0.9–10 MHz frequency range.

For the modes excited by a thickness field, the resonance and some anti-resonance frequencies were directly obtained from air gap measurements of the Y- and X- GaPO₄ plates. The experimental set-up mostly used has already been described in [21]. In most cases, electrodes totally covering the plate and a very small variable gap (few microns) between the electrodes and the surface of the GaPO₄ plate were used. It was previously verified (by varying the gap and extrapolating the resonance frequencies to a zero gap) that this small gap has a negligible effect on the constant extracted compared with other uncertainties affecting the measurements (principally the precision of the thickness measurements and possibly the effect of the finite dimensions of the plates and, in some cases, the degeneration of the thickness mode, etc).

Several experiments were made using a simpler set-up in which the sample was placed between a totally metalized plane silica piece and a thin plane metal plate larger than the sample. In this case, the gap was also negligible. The contact of the upper electrode has sometimes some how degraded the Q factor of the resonance and the reproducibility of the measurements, but on the whole, the resonance frequencies measured were not significantly different to those obtained with the first set-up. One measurement was made using deposited electrodes smaller than the Y-plate. In this case, corrections were used to account for the effect of the mass of the plating and of the finite dimension of the electrodes on the resonance frequency. As the anti-resonance frequencies are very sensitive to the parasitic capacitances, they were most often deduced numerically from the measurements of the resonance frequencies of one or several overtones (application of relation (10)).

Most of the experiments using lateral field were made with a very simple set-up (by simply placing the plates, in the appropriate direction, on a pair of rectangular electrodes separated by a gap and deposited on a very flat piece of

Table 2. Values of the elastic constants presented in this work and compared to values obtained from hydrothermally grown α -GaPO₄ single crystals.

| Elastic constants (10 ⁹ N m ⁻²) | This work | Ref. [23] | Ref. [24] |
|---|------------------|------------------|------------------|
| C_{11} | 64.01 ± 1.92 | 66.35 ± 0.02 | 66.58 ± 0.37 |
| C_{14} | 5.52 ± 0.17 | 4.20 ± 0.08 | 3.91 ± 0.33 |
| C_{44} | 39.39 ± 1.17 | 37.80 ± 0.01 | 37.66 ± 0.27 |
| C_{66} | 25.25 ± 0.75 | 22.35 ± 0.01 | 22.38 ± 0.32 |

fused silica). Some experiments were made using electrodes on both faces of the plate. Although they produce a more uniform lateral field inside the sample, practically no difference was observed concerning the resonance frequencies. In fact, the accuracy seems to be quite good and limited by the same factors as indicated above for the transverse modes. It is degraded for the extensional modes due to the frequent decomposition of these modes into several others (coupling to other plate modes at the edge of the plate).

In table 2 are given the resulting elastic constants at room temperature. For the calculation of these constants, the dielectric permittivity at constant strain, ϵ_{11}^S , was measured at high frequency and at room temperature. Its value, 5.83, is very close to the one reported in [22]. The value of the piezoelectric coefficient e_{11} , 0.21 C m⁻², was taken from [23]. The density, at 20 °C, calculated from our x-ray diffraction measurement is equal to 3571.4 kg m⁻³ in perfect agreement with [24].

4. Discussion

To determine all the elastic and piezoelectric constants of a crystal, it is necessary to use plates having a sufficient number of different orientations in order to have a sufficient number of relations to extract the constants.

The precision of the values of the constants is directly related to the accuracy of the frequency measurements and of the thickness measurements and it depends also on the concordance between the actual vibration mode of the real device and the model used to extract the constants. Here, the theoretical analysis is carried out under a one-dimensional assumption for the mode shapes of the thickness extension and of the thickness shear modes. This implies that the piezoelectric plate is sufficiently large (ratio of the lateral dimensions to the thickness) so that the mode is sufficiently close to a plane wave. In fact, this assumption is generally considered as good when the lateral dimensions are much larger than the thickness (a factor of about 10–20, depending on the material, is usually sufficient when the plate is totally covered by the electrodes). When the lateral dimensions of the plate (or the electrodes) are smaller, the lateral boundary conditions could have a larger influence on the vibration mode shape and thus, finally, a non-negligible influence on the value of the resonance frequency and on the accuracy of the constants. However, it should be recalled that the influence on the eigenfrequencies is theoretically much lower than that on the mode shapes. In several cases (plane or plano-convex resonators of simple shape, covered by electrodes smaller than

the plate), suitable three-dimensional theories exist that permit us to determine an accurate correction to the result obtained with the one-dimensional theory even if the lateral dimension of the plate is not very large compared to its thickness.

For this work, only two plates of simple orientations (*X*- and *Y*-plates) have been obtained from our spontaneously crystallized materials. The average small size of the as-grown GaPO₄ single crystals (typically 4–5 mm in the lateral direction) has not allowed us to get the rotated orientations which are necessary for the measurements of the whole elastic constants. In this context, only four out of six independent elastic constants were obtained from the two plates available. The four calculated elastic constants, derived from the resonances of both the *X*- and the *Y*-plates, were C_{11} , C_{66} , C_{44} , and C_{14} (C_{12} can be deduced from C_{11} and C_{66}). Their values, presented in table 2 with the uncertainty associated with them, are compared to the values extracted from measurements made on hydrothermally grown α -GaPO₄ crystals using, respectively, the Brillouin scattering [24] and the pulse-echo technique [23]. The elastic constants found by these authors are in reasonable agreement (see table 2) although an evolution of the elastic properties of the material has most probably occurred with the progress of the hydrothermal growth methods.

Compared to these published values, the experimental elastic constants obtained for our samples present some slight differences, table 2. The values of the shear constants C_{66} and C_{44} are higher than the ones registered for hydrothermally grown α -GaPO₄. On the other hand, the value of the longitudinal constant C_{11} appears to be lower than (or nearly equal to) the ones measured on hydrothermal crystals.

The changes in the values of the elastic constants with the growth technique are generally associated with some slight modifications of the α -GaPO₄ lattice by intrinsic point defects, impurities, dislocations, etc. It is well known that the propagation velocity into a medium is governed by the atomic bond strength and that each structural defect produces some distortions of the lattice which may modify its rigidity. It is well demonstrated that hydrothermally grown α -GaPO₄ single crystals most often contain hydroxyl radicals which enter the lattice during crystallization via the growth medium [12–14]. These OH groups, and sometimes water molecule inclusions, reduce the elastic constants and increase the acoustic dissipation of the material [12–14].

The Brillouin experiments described in [24] were undertaken on hydrothermally grown α -GaPO₄ samples with OH impurity concentrations between 200 and 400 ppm. The pulse-echo study was realized on α -GaPO₄ crystals with an average OH concentration of 50 ppm [23] deduced from infrared (IR) spectroscopy. A typical transmission infrared spectrum, measured at room temperature, of a hydrothermally grown α -GaPO₄ presents a large absorption band between 3700 and 3000 cm⁻¹ (O–H infrared region) superposed to three well-separated peaks at 3167, 3290, and 3400 cm⁻¹ [23]. The literature [25, 26] attributes the peaks at 3167 and 3290 cm⁻¹ to third order lattice vibrations and the large band to the presence of OH groups. Always from the literature, a weak part of the absorption of the third peak (3400 cm⁻¹) is intrinsic

to the GaPO₄ lattice vibrations and the other part to O–H stretching vibrations [25, 26]. This is why the authors [25] have proposed to calculate the extinction coefficient, α , at 3400 cm⁻¹, from the expression $\alpha = 1/d[\log(T_{3800}/T_{3400})] - \alpha^*$, where d represents the sample thickness in cm, T the % IR transmission at, respectively, 3800 and 3400 cm⁻¹, and α^* is an intrinsic contribution resulting from lattice vibrations of pure GaPO₄. It has also been proposed that the OH concentration could be extrapolated from the determination of the extinction coefficient using the simple relationship $[\text{OH}(\text{ppm})] = 65\alpha$.

A transmission infrared study made at room temperature on some of our flux-grown α -GaPO₄ crystals is reported in [17]. The collected infrared spectra did not contain the large absorption band from 3700 to 3000 cm⁻¹ that is characteristic of a noticeable OH content. In our results only the three peaks at 3167, 3290, and 3400 cm⁻¹ were registered in this wavenumber domain. As already mentioned, the flux-grown α -GaPO₄ crystals were obtained from slow cooling from 950 to 600 °C. Considering this temperature range and the nature of the flux, the incorporation of O–H radicals during the crystallization is very improbable. In this context, the presence of the very small 3400 cm⁻¹ vibration peak could hardly be attributed to O–H stretching vibrations but quite certainly to intrinsic lattice vibrations. The high temperature flux-growth method seems to be a performing technique to produce transparent and H₂O-free α -GaPO₄ crystals. Then, we could assume that both the *X*- and the *Y*-plates studied in this work had a negligible OH-group content. Compared with hydrothermally grown GaPO₄ crystals, the strong reduction of the OH concentration in the lattice of flux-grown α -GaPO₄ is believed to have induced an improvement of the lattice rigidity and, consequently, an increase of the wave velocities. This would be the main effect acting for the higher values of the elastic constants measured with our GaPO₄ samples, table 2. A similar augmentation of the elastic constants was already observed with berlinite AlPO₄ when the OH concentration was reduced by modification of the hydrothermal growth conditions [27].

This was the first attempt at elastic constant measurements at room temperature of α -GaPO₄ single crystals grown by the flux method at high temperature. Nevertheless, the very interesting elastic behavior of these crystals needs to be confirmed by other measurements. Such a confirmation should particularly be concerned with the value found for C_{11} , which is the only constant found slightly lower for the flux-grown material than for the hydrothermal crystals. It should be noticed that this constant corresponds to frequency measurements made for an extensional mode which tends to degenerate into several others in practical devices. This leads to a larger uncertainty in the frequency measurements and consequently in the constant value (table 2).

More generally, due to the small ratio of the lateral dimensions of our plates to their thickness, a more or less important part of the moderate accuracy obtained in several measurements may take its origin in the difference between the actual mode shape existing in the plates and the plane wave model. This point has to be examined with larger samples (centimeter size) which will, anyway, give a much

better accuracy in the frequency measurements due to a lower impedance level and an equal or slightly lower resistance.

5. Conclusion

Clear and transparent GaPO₄ single crystals of the α -quartz structure were grown using the high temperature solution growth technique by cooling from 950 to 600 °C. A first approach of their elastic constant determination was undertaken using the resonance of the piezoelectric thickness modes that can be excited in plane and parallel *X*- and *Y*-oriented plates by a thickness or a lateral electric field. It seems that the negligible OH impurity in the as-grown crystals induces a larger stiffness of the lattice, as shown by the values of the elastic constants. However, these results should be regarded as preliminary indications for pure α -GaPO₄. The opposite tendency observed for the *C*₁₁ elastic constant, the fact that we were not in the best experimental conditions to use the one-dimensional model, and several other hypotheses, lead us to conclude that extra elastic constant measurements are necessary to confirm this promising elastic behavior found for flux-grown α -GaPO₄ crystals.

References

- [1] Goiffon A, Jumas J-C, Maurin M and Philippot E 1986 *J. Solid State Chem.* **61** 384
- [2] Philippot E, Ibanez A, Goiffon A, Cochez M, Zarka A, Capelle B, Schwartzel J and Détaint J 1993 *J. Cryst. Growth* **130** 195
- [3] Krempl P, Schleinzner G and Wallnöfer W 1997 *Sensors Actuators A* **61** 361
- [4] Détaint J, Capelle B, Cambon O and Philippot E 2001 *Ann. Chim. Sci. Mater.* **26** 151
- [5] Balitsky D B, Sil'vestrova O Yu, Balitsky V S, Pisarevskii Yu V, Pushcharovsky D Yu and Philippot E 2000 *Cryst. Rep.* **45** 145
- [6] Haines J, Cambon O, Prudhomme N, Fraysse G, Keen D A, Chapon L C and Tucker M G 2006 *Phys. Rev. B* **73** 014103
- [7] Jacobs K, Hofmann P, Klimn D, Reichow J and Schneider M 2000 *J. Solid State Chem.* **149** 180–8
- [8] Angot E, Le Parc R, Levelut C, Beaurain M, Armand P, Cambon O and Haines J 2006 *J. Phys.: Condens. Matter* **18** 4315
- [9] Shafer E L C and Roy R 1956 *J. Am. Ceram. Soc.* **39** 330
- [10] Balitsky D V, Philippot E, Papet Ph, Balitsky V S and Pey F 2005 *J. Cryst. Growth* **275** 887
- [11] Motchany A I, Chvanski P P and Leonyuk N I 2000 *J. Cryst. Growth* **211** 506
- [12] Yot P, Cambon O, Balitsky D, Goiffon A, Philippot E, Capelle B and Détaint J 2001 *J. Cryst. Growth* **224** 294
- [13] Palmier D, Goiffon A, Capelle B, Détaint J and Philippot E 1996 *J. Cryst. Growth* **166** 347
- [14] Marinho E, Palmier D, Goiffon A and Philippot E 1998 *J. Mater. Sci.* **33** 2825
- [15] Laurent Y 1969 *Rev. Chim. Miner.* **6** 1145
- [16] Shvansky E, Armand P, Balitsky D, Philippot E and Papet Ph 2006 *Ann. Chim. Sci. Mater.* **31** 97
- [17] Beaurain M, Armand P and Papet P 2006 *J. Cryst. Growth* **294** 396
- [18] Royer D and Dieulesaint E 1997 *Ondes Élastiques dans les Solides, Tome 1: Propagation Libre Et Guidée* (Paris: Masson)
- [19] Yamada T and Niizeki N 1970 *J. Appl. Phys.* **41** 3604
- [20] Glowinski A 1972 *Ann. Telecommun.* **27** 147
- [21] Détaint J, Carru H, Schwartzel J, Joly C, Capelle B and Zarka A *Proc. 43rd Ann. Frequency Control Symp. (June 1989)*
- [22] Détaint J, Feldmann M, Henaff J, Poignant Y and Toudic Y 1979 *Proc. 33rd Ann. Frequency Control Symp.* p 70
- [23] Palmier D 1996 *Doctorat Thesis* UMII, Montpellier, France
- [24] Wallnöfer W, Krempl P W and Asenbaum A 1994 *Phy. Rev. B* **49** 10075
- [25] Krempl P W, Krispel F, Wallnofer W and Leuprecht G 1991 *Proc. 9th European Frequency and Time Forum* p 143
- [26] Krispel F, Krempl P W, Knoll P and Wallnofer W *Proc. 11th European Frequency and Time Forum (March 1997)* p 233
- [27] Philippot E, Goiffon A, Maurin M, Détaint J, Schwartzel J, Toudic Y, Capelle B and Zarka A 1990 *J. Cryst. Growth* **104** 713