Characterizations of piezoelectric GaPO$_4$ single crystals grown by the flux method

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Abstract

Hexagonal gallium orthophosphate crystals have been obtained by spontaneous nucleation using the slow cooling method from X$_2$O–3MoO$_3$ fluxes with X = Li, K. Compared to GaPO$_4$ crystals grown by hydrothermal methods, infrared measurements have revealed flux-grown samples without hydroxyl groups and thermal analyses have pointed out the total reversibility of the phase transition α-quartz GaPO$_4$ ↔ β-cristobalite GaPO$_4$. The elastic constants of these millimeter-size flux-grown α-GaPO$_4$ piezoelectric crystals were experimentally determined from their Brillouin scattering behaviour at room and high temperatures. The room temperature results were in good agreement with the published ones concerning hydrothermally grown samples and the two longitudinal elastic constants measured versus temperature until 850 °C have shown a monotonous evolution.
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1. Introduction

Our laboratory has been interested in the single-crystal growth of piezoelectric materials with the α-quartz structures such as α-AlPO$_4$ and α-GaPO$_4$ since the early 80s [1,2]. Since the low-quartz structure of GaPO$_4$ presents an electromechanical coupling coefficient ($k = 16\%$) better than that of α-AlPO$_4$ ($k = 11\%$) and α-SiO$_2$ ($k = 8\%$), much attention has been reported on the gallium-orthophosphate material. Furthermore, at low-temperature GaPO$_4$ does not present the displacive transformation α-quartz/β-quartz as found for α-AlPO$_4$ and α-SiO$_2$ phases [3].

Via the hydrothermal methods in acidic medium, hexagonal-like α-GaPO$_4$ crystals have been successfully synthesized in the retrograde solubility range [2]. Because, the growth rate along the Y-direction of the hydrothermally grown α-GaPO$_4$ crystals is very low, large crystals

cannot be obtained. Moreover, these crystals present a quite important hydroxyl-group (OH) contamination originating from the growth media [4,5], which reduces the mechanical quality factor Q and deteriorates their thermal behavior. In this context, it appeared that another growth technique could be applied for the crystallization of α-GaPO$_4$ single crystals to obtain hydroxyl-free crystals with a higher Q factor. The high-temperature solution or flux-growth technique seemed to be a possible alternative for this purpose.

Using X$_2$O:3MoO$_3$ fluxes (X = Li, K), colorless and transparent GaPO$_4$ single crystals with the α-quartz structure were synthesized. This paper will present an overview of the main results obtained from several physical characterizations undertaken on these flux-grown α-GaPO$_4$ piezoelectric crystals. Infrared transmission data and differential scanning calorimetric (DSC) results will be discussed in some details in the view of the observations made on hydrothermally grown α-GaPO$_4$ crystals. High-resolution Brillouin scattering measurements conducted at

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room and high temperatures to determine several elastic constants of flux-grown α-GaPO$_4$ single crystals will also be reported for the first time.

2. Experimental procedure

2.1. Sample preparation

Both the potassium and lithium tri-molybdate were synthesized as powder following solid-state reactions already described in Ref. [6]. The GaPO$_4$ powder compound with the α-quartz structure, used as the starting material for the growth experiments, was obtained by dissolving 4 N Ga metal in nitric acid followed by precipitation with phosphoric acid [6].

Crystallization of α-GaPO$_4$ single crystals was obtained by slow cooling of high-temperature solutions from 950 to 600 °C in air. The solutions were a mixture of α-GaPO$_4$ and X$_2$O:3MoO$_3$ fluxes (X = Li, K) in different ratios contained in Pt crucibles covered with a lid. The temperature control of the SiC resistance heater furnace was operated by a Eurotherm controller. At the end of the crystal-growth experiments, GaPO$_4$ crystals were separated from the solidified mixture by dissolving the flux in warm water. Then, the flux-grown crystals were carefully cleaned with the help of an ultrasonic cleaner and dried.

2.2. Solubility

The solubility was determined using the dissolution–extraction method by introducing large α-GaPO$_4$ crystals, grown by the hydrothermal method, in the X$_2$O:3MoO$_3$ fluxes (X = Li, K), at different controlled temperatures (from 600 to 950 °C). After saturation for 3 days, the Pt crucible was removed from the furnace and quenched into water. Then, the remaining undissolved GaPO$_4$ material was separated from the saturated solution and the mass change was determined. The weight loss at each temperature gives the corresponding solubility (Fig. 1).

2.3. Sample characterizations

The cell parameters were examined from X-ray single-crystal data collected with an Xcalibur (Oxford diffraction) CCD diffractometer using Mo-K$_\alpha$ radiation. Infrared transmission measurements were carried out at room temperature, using a BRUKER-IR microscope mounted on a Fourier transform BRUKER IFS 133V spectrometer, with a spectral resolution of $\pm 2\,\text{cm}^{-1}$. DSC measurements were conducted using a SETARAM-LABSYS system in an inert (nitrogen) atmosphere. Temperatures were changed between room temperature and 1200 °C at heating and cooling rates of 10 °C min^{-1}.
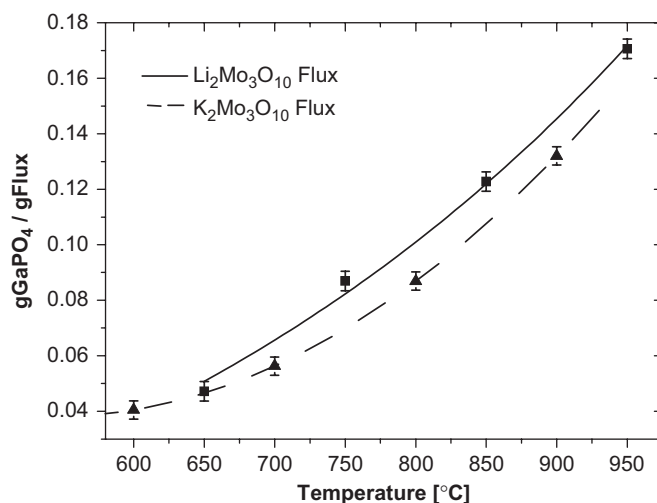

Fig. 1. Solubility curves of α-GaPO$_4$ single crystals in X$_2$O–3MoO$_3$ fluxes with X = Li, K.

2.4. Brillouin scattering measurements

A high-resolution Brillouin spectrometer (HRBS) using the backscattering geometry was used to determine the elastic constants of our flux-grown α-GaPO$_4$ single crystals. The sample was placed on a goniometer and received an incident wavelength λ, equal to 514.5 nm. The scattered light was collected and analyzed by the spectrometer. This spectrophotometer is equipped with a microscope, which permits experiments on small-size samples with an improved spatial, lateral and depth resolution. The high-resolution setup of the spectrometer enables to detect very small sound velocity or elastic constant variations.

Concerning GaPO$_4$ with the α-quartz structure, both the ordinary and the extraordinary refractive indexes, n_o and n_e, at room temperature were taken from Ref. [7] and were, respectively, equal to 1.6147 and 1.6332. The position (in GHz), amplitude and width of the measured modes (the Brillouin lines) were obtained by least-squares fits to the scattering spectra.

3. Results and discussion

3.1. Growth experiments

For the flux choice, one important parameter was the melting temperature of the selected compound, which should be well below 950 °C (transition temperature of α-GaPO$_4$). The melting temperature of both the K$_2$O:3MoO$_3$ and the Li$_2$O:3MoO$_3$ fluxes are close to 565 °C [6]. The direct solubility of GaPO$_4$ is little bit higher in Li$_2$O:3MoO$_3$ than in K$_2$O:3MoO$_3$ as can be seen in Fig. 1.

From spontaneous crystallization with the slow cooling method, colorless and transparent as-grown α-GaPO$_4$ crystals of millimeter size have been obtained [6]. The biggest one, Figs. 2(1) and (2), was 8 mm long to 3 mm wide and presented a morphology with two major faces. This
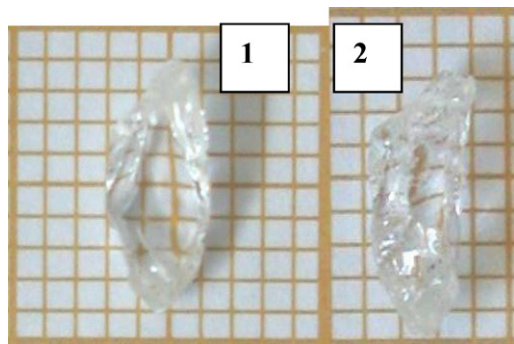
Fig. 2. Optical photographs of an as-grown GaPO$_4$ single crystal (1 = face, 2 = thickness).
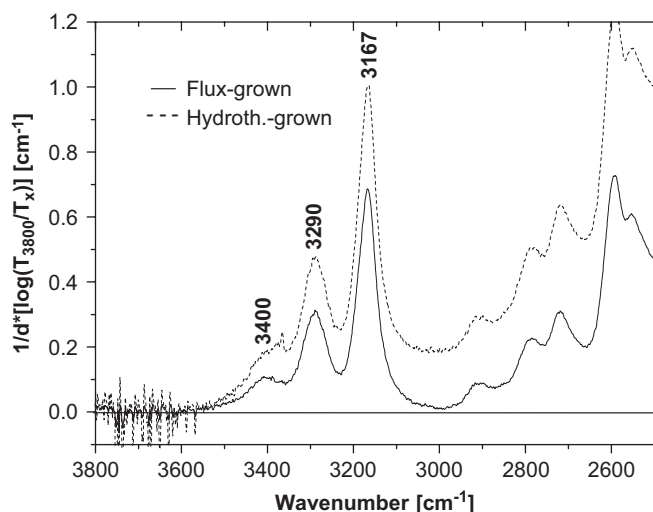

Fig. 3. Comparison of infrared absorbance spectra of α-GaPO$_4$ single crystals grown by the flux and the hydrothermal methods.

crystal was obtained in Li$_2$O:3MoO$_3$ flux with a slow cooling rate of 0.1 °C from 950 to 750 °C, followed by a cooling rate of 2 °C from 750 to 600 °C.

X-ray powder diffraction measurements of the synthesized single crystals revealed that only GaPO$_4$ with the hexagonal space group was formed. The experimental lattice parameters registered at room temperature were consistent with those determined on hydrothermally grown GaPO$_4$ with the α-quartz structure [6].

3.2. Infrared transmission study

It is well demonstrated that hydrothermally grown GaPO$_4$ crystals with the hexagonal structure present non-negligible hydroxyl contamination, which would enter the crystalline lattice during the crystallization via the growth medium [4,5]. An absorbance infrared (IR) spectrum, registered at room temperature, of an α-GaPO$_4$ single crystal grown by the hydrothermal method in our laboratory is presented in Fig. 3. The experimental growth conditions of this hydrothermally grown α-GaPO$_4$ crystal are given in Ref. [8]. Its IR spectrum presents a large band between 3700 and 3000 cm^{-1} (O–H infrared region) super-

imposed to 3 well-separated peaks centered at 3167, 3290 and 3400 cm^{-1}. From the literature [6], the wide band is related to the presence of OH groups in the crystal and the peaks at 3167 and 3290 cm^{-1} to third order lattice vibrations. The amplitude of the peak centered around 3400 cm^{-1} is attributed one part to the absorption by the GaPO$_4$ lattice, and another part to O–H stretching vibrations [9,10]. This is why, some authors [9,10] have proposed an OH estimation into α-GaPO$_4$ crystals, to calculate the extinction coefficient, α, at 3400 cm^{-1} from the expression $a = 1/d[\log(T_{3800}/T_{3400})] - \alpha^*_{3400}$, where d represents the sample thickness in cm, T the % IR transmission at, respectively, 3800 and 3400 cm^{-1} and α^*_{3400} the absorption coefficient due to intrinsic lattice vibrations ($\alpha^*_{3400} = 0.078$ cm^{-1}).

The collected IR spectrum of an as-grown α-GaPO$_4$ crystal obtained in Li$_2$Mo$_3$O$_{10}$ flux is also given in Fig. 3. Compared with the spectrum of the hydrothermally grown GaPO$_4$, it does not present the characteristic large absorption band from 3700 to 3000 cm^{-1} due to OH contamination of the sample. Only the three peaks at 3167, 3290 and 3400 cm^{-1} were registered in the O–H IR domain. The value of the extinction coefficient at 3400 cm^{-1} is close to 0.03 cm^{-1} for flux-grown GaPO$_4$ and close to 0.15 cm^{-1} for hydrothermally grown material (see Fig. 3).

As already mentioned, the flux-grown α-GaPO$_4$ crystals were obtained by slow cooling, from 950 to 600 °C. Considering this temperature range and the nature of the flux, the incorporation of O–H groups during the crystallization is rather improbable. In this context, the presence of the 3400 cm^{-1} vibration peak could not be attributed to the O–H stretching vibrations but only to the intrinsic lattice vibrations occurring in this wave-number region as for the 3167 and the 3290 cm^{-1} bands.

3.3. Thermal behavior

Figs. 4a and b show the DSC plots of, respectively, hydrothermally grown and flux-grown α-GaPO$_4$ single crystals from our laboratory [6,8]. On heating runs, an endothermic peak appears at the onset temperatures of 1105 °C in Fig. 4a and 950 °C in Fig. 4b. This feature is caused by the well-known transition from the thermodynamically stable α-quartz GaPO$_4$ phase to the β-cristobalite modification [11–13]. No other feature was observed up to our maximum DSC experimental temperature, i.e. 1200 °C. Both the shape and the temperature position of the DSC peaks between the two samples present some differences, which can be attributed to the samples themselves and/or to the experimental conditions.

Concerning the hydrothermally grown GaPO$_4$ material, the succeeding cooling curve in Fig. 4a, from 1200 °C back to room temperature, shows two main exothermic peaks. The first one with an onset temperature of 910 °C corresponds to a partial transformation of the β-cristobalite GaPO$_4$ phase to the α-quartz phase. The exothermic peak at lower temperature, close to 578 °C, is attributed to
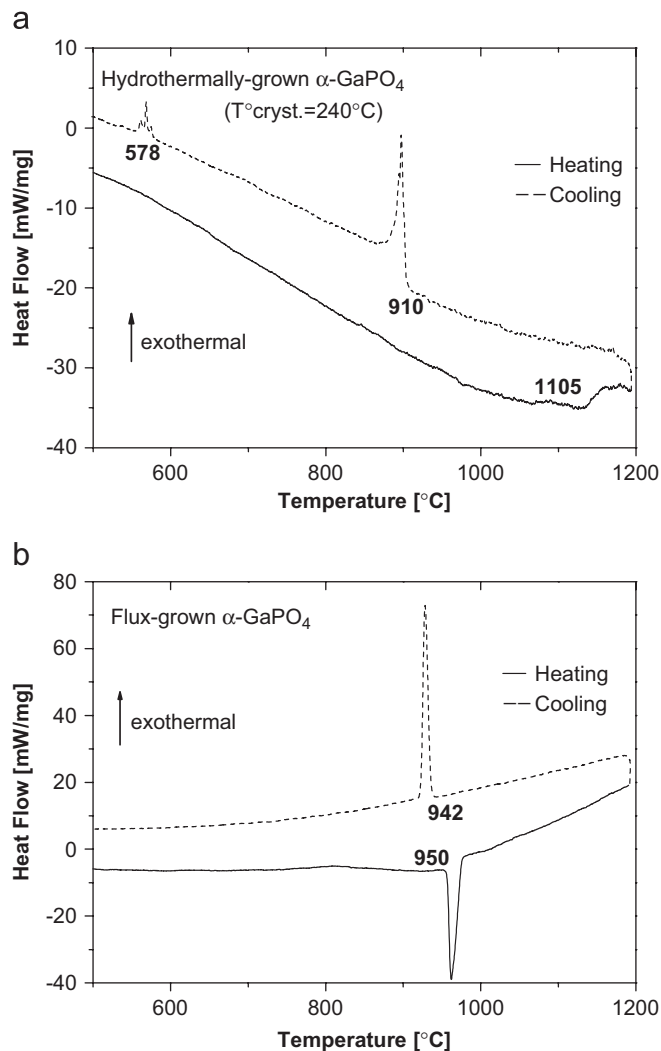
a

b

Fig. 4. DSC curves of as-grown α-GaPO₄ single crystals obtained by the hydrothermal (a) and the flux (b) methods.

the partial β-cristobalite → α-cristobalite GaPO₄ transition [11–13].

For GaPO₄ crystals spontaneously grown in $Li_2Mo_3O_{10}$ flux, the registered exothermic peak is strong and sharp with the onset at 942 °C. It corresponds to a total transformation of the high-cristobalite GaPO₄ phase into the α-quartz GaPO₄ phase as confirmed by the X-ray powder pattern of the end product of the DSC experiment.

This is in our knowledge, the first time that GaPO₄ is found exclusively in the α-quartz modification after cooling from the high-cristobalite phase without annealing periods as reported in Refs. [11,13].

3.4. Elastic constants

The average small size of the flux-grown GaPO₄ single crystals, 4–6 mm in length, did not allow us to get rotated orientations, which could be useful for the measurements of the whole elastic constant set. In this context, only 5 out of 6 independent elastic constants could be obtained from

our plates of $X(1\,0\,0)$, $Z(0\,0\,1)$ and $Y(0\,1\,0)$ simple orientations.

The Brillouin shift is approximately given by the relation

$$\Delta v_B = \frac{2nV}{\lambda} \sin\left(\frac{\theta}{2}\right), \tag{1}$$

where n is the optical index of the sample, V the sound velocity and θ the scattering angle. In the backscattering geometry, the expression of the sound velocity is given by

$$V(\text{m s}^{-1} =) \frac{v_B \lambda}{2n}. \tag{2}$$

The expressions of the elastic constants, $\overline{C} = \rho V^2$ for the D_{3h} class are shown in Table 1. The propagation directions to be measured first were those for which the relationship between the elastic constant C_{ij} and both the density, ρ, and the sound velocity, V, was the simplest. It was in the form $C_{ij} = \rho V^2$ for C_{33} and C_{44}, cf. Table 1, or when the piezoelectric effect had to be taken into account, the relationship was in the form $C_{ij} = \rho V^2 - \xi$ as for C_{11} and C_{66}. In second, we measured the propagation directions for which the sound velocity is no more a function of only one constant but of a combination of several elastic constants (see Table 1). The extraction of the desired constant is obtained by the differentiation of the other constants for which we have already determined the values. It is then of great importance to determine in the most accurate way the elastic constants obtained from the simple expression of the sound velocity.

The value of the room temperature density was taken from Ref. [7] as $3570\,\text{kg m}^{-3}$ and the value of the piezoelectric effect was given as $e_{11}^2/\varepsilon_{11} = 0.85 \times 10^9\,\text{N m}^{-2}$ at room temperature [7]. The elastic constants from Brillouin shifts at any temperature were computed with the use of the room temperature values of the density, the refractive indices, n_o and n_e, and the piezoelectric effect.

Table 2 presents the room temperature elastic constants of our flux-grown α-GaPO₄ single crystals compared to those previously published concerning hydrothermally grown α-GaPO₄ crystals. The values of the elastic stiffness

Table 1
Expressions of the elastic constants C_{ij} for α-GaPO₄

Plate's orientation	Mode	Expression of ρV^2
X	L^a	$C_{11} + e_{11}^2/\varepsilon_{11}$
X	FT^a	$(C_{66} + C_{44})/2 + [(C_{66} - C_{44})^2 + 4C_{14}^2]^{1/2}/2$
X	ST^a	$(C_{66} + C_{44})/2 - [(C_{66} - C_{44})^2 + 4C_{14}^2]^{1/2}/2$
Y	PL^a	$(C_{44} + C_{11})/2 + [(C_{44} - C_{11})^2 + 4C_{14}^2]^{1/2}/2$
Y	PT^a	$(C_{44} + C_{11})/2 - [(C_{44} - C_{11})^2 + 4C_{14}^2]^{1/2}/2$
Y	T^a	$C_{66} + e_{11}^2/\varepsilon_{11}$
Z	L^a	C_{33}
Z	T^a	C_{44}

[a]L = longitudinal,   PL = pseudo-longitudinal,   T = transverse, PT = pseudo-transverse, ST = slow transverse, FT = fast transverse.

Table 2
Elastic constants obtained at room temperature on both flux-grown and hydrothermally grown α-GaPO$_4$ single crystals

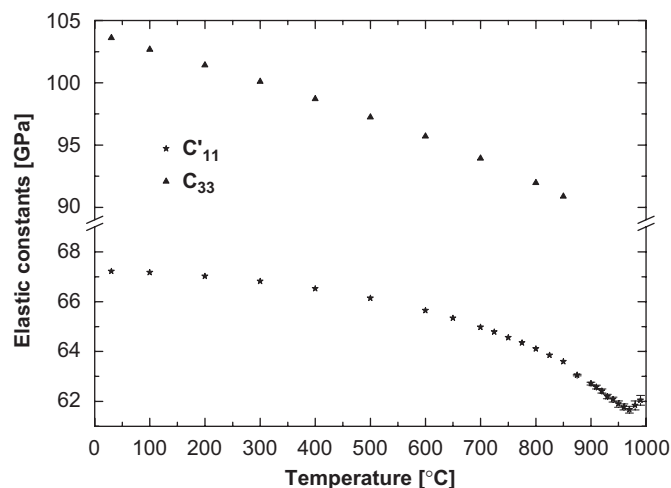| Elastic constant (10^9 N m^{-2})	This work	[14]	[7]
C_{11}	66.37 ± 0.03	66.35 ± 0.02	66.58 ± 0.37
C_{14}	4.93 ± 0.27	4.20 ± 0.08	3.91 ± 0.33
C_{33}	103.29 ± 0.04	101.31 ± 0.04	102.13 ± 0.55
C_{44}	37.85 ± 0.14	37.80 ± 0.01	37.66 ± 0.27
C_{66}	22.46 ± 0.06	22.35 ± 0.01	22.38 ± 0.32

Fig. 5. Evolution with temperature of the longitudinal elastic constants C'_{11} and C_{33} registered from flux-grown α-GaPO$_4$ plates.

constants found by these authors were in good agreement in most constants as seen in Table 2.

The evolution with temperature of the two longitudinal elastic constants $C'_{11}(= C_{11} + e_{11}^2/\varepsilon_{11})$ and C_{33} of the flux-grown GaPO$_4$ material is presented in Fig. 5. This is the first and preliminary investigation of the elastic constant evolution with temperature for flux-grown α-GaPO$_4$ single crystals. Since for the Brillouin scattering spectroscopy, the samples are not to be coated with metal layers (electrodes), measurements at high temperatures are not disturbed by problems with the electrical signal transmission. Furthermore, C_{11} and C_{33} elastic constants present the advantage to be directly obtained from the velocities of longitudinal waves, cf. Table 1, and to give intense Brillouin lines.

C_{11} was measured from room temperature up to 1000 °C to follow the phase transition α-quartz/β-cristobalite already mentioned in the thermal behavior part. From DSC or Brillouin scattering measurements, the maximum temperature of the unique phase transition on heating was well reproducible and close to 970 °C.

C_{33} presents a monotonous decrease with temperature up to 850 °C, while C'_{11} presents a slight variation over the temperature range 20 °C–500 °C followed by a stronger variation when approaching the phase transition temperature, see Fig. 5. C'_{11} is assumed to be the sum of two terms according to $C'_{11} = C_{11} + e_{11}^2/\varepsilon_{11}$. C_{11} arises from the

mechanical properties of the crystalline network while $e_{11}^2/\varepsilon_{11}$ is the contribution of the piezoelectric effect which may be considered as a constant up to around 500 °C [15]. For higher temperature, the value of ε_{11} increases rapidly [15] and, as a consequence, the C'_{11} curve's slope becomes larger.

4. Conclusions

Using the spontaneous crystallization in X$_2$O:3MoO$_3$ fluxes (X = Li, K) from the slow cooling method, millimeter-size α-GaPO$_4$ single crystals have been successfully synthesized. An IR study has pointed out that these as-grown crystals were free from OH groups. Another important result concerns the thermal behavior of these flux-grown α-GaPO$_4$ crystals compared with the hydrothermally grown ones. The DSC experiments have pointed out a total reversible α-quartz ↔ β-cristobalite transition with only the low-quartz GaPO$_4$ phase as the end product of the DSC cycle for our sample. This result is an indication of the high thermal stability of the flux-grown α-GaPO$_4$ single crystals, which is confirmed by the monotonous evolution of the elastic constants C_{ij} with temperatures.

The physical characterization results on these flux-grown α-GaPO$_4$ single crystals are very encouraging for developing the top-seeded solution growth technique (TSSG) to obtain centimeter-size samples. Indeed, the production of larger-size plates will enable us to make a resonator to determine the piezoelectric constants and, above all, to measure the mechanical quality factor Q.

References

[1] J.-C. Jumas, A. Goiffon, B. Capelle, A. Zarka, J.-C. Doukhan, J. Schwartzel, J. Détaint, E. Philippot, J. Crystal Growth 80 (1987) 133.
[2] O. Cambon, P. Yot, D. Balitsky, A. Goiffon, E. Philippot, B. Capelle, J. Détaint, Ann. Chim. Sci. Mater. 26 (2001) 79.
[3] E. Philippot, A. Goiffon, A. Ibanez, M. Pintard, J. Solid State Chem. 110 (1994) 356.
[4] P. Yot, O. Cambon, D. Balitsky, A. Goiffon, E. Philippot, B. Capelle, J. Détaint, J. Crystal Growth 224 (2001) 294.
[5] E. Marinho, D. Palmier, A. Goiffon, E. Philippot, J. Mater. Sci. 33 (1998) 2825.
[6] M. Beaurain, P. Armand, P. Papet, J. Crystal Growth 294 (2006) 396.
[7] W. Wallnöfer, P.W. Krempl, A. Asenbaum, Phys. Rev. B 49 (15) (1994) 10075.
[8] D.V. Balitsky, E. Philippot, Ph. Papet, V.S. Balitsky, F. Pey, J. Crystal Growth 275 (2005) 887.
[9] P. W. Krempl, F. Krispel, W. Wallnofer, G. Leuprecht, in: Proceedings of the Ninth European Frequency and Time Forum, 1991, p. 143.
[10] F. Krispel, P. W. Krempl, P. Knoll, W. Wallnofer, in: Proceedings of the 11th European Frequency and Time Forum, March 1997, p. 233.
[11] K. Jacobs, P. Hofmann, D. Klimn, J. Reichow, M. Schneider, J. Solid State Chem. 149 (2000) 180.
[12] A. Perloff, J. Am. Ceram. Soc. 39 (3) (1956) 83.
[13] R.-U. Barz, J. Schneider, P. Gille, Z. Kristallogr. 214 (1999) 845.
[14] D. Palmier, Ph.D. Thesis, Université Montpellier II, France, 1996.
[15] I.A. Dan'kov, O.V. Zvereva, V.I. Ivannikov, E.F. Tokarev, F. Sh. Khatamov, Sov. Phys. Krystallogr. 36 (1991) 277.