Physical Characterizations of α-$GaPO_4$ 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 $X_2Mo_3O_{10}$ fluxes with X=Li, K. Infrared transmission measurements have revealed samples without significant hydroxyl groups and thermal analyses have pointed out the total reversibility state of the phase transition α-quartz $GaPO_4$ ↔ β-cristobalite $GaPO_4$. The first measurement of several elastic constants made on α-$GaPO_4$ material grown with the flux technique, using plates of simple orientations, was undertaken. The values found for these constants were slightly higher to those measured on hydro-thermally grown $GaPO_4$ crystals.**

I. INTRODUCTION

$GaPO_4$ is a very promising material to build piezoelectric devices because it exhibits both a higher coupling coefficient and a higher thermal stability as compared to α-quartz. Our α-$GaPO_4$ crystals have been growing using hydrothermal method since the early 90's in our laboratory. However, for this material, it is quite difficult to obtain high quality crystals with this growth technique due to quite high level hydroxyl group incorporation via the growth medium. In order to avoid the OH contamination, a new and very promising single-crystal growth method for this piezoelectric material has been studied; the high temperature flux growth technique.

Using $X_2Mo_3O_{10}$ fluxes (X=Li, K), clear and transparent $GaPO_4$ single crystals with the α-quartz structure were synthesized. This work will present an overview of the main results obtained from several physical characterizations undertaken on these piezoelectric materials of the MXO_4 family (M= Al, Ga, Fe and X=As, P). Differential Scanning Calorimetric (DSC) data and infrared transmission spectra will be discussed in some details in the view of observations made on hydrothermally-grown crystals of the quartz family.

First measurements of several elastic constants made on α-$GaPO_4$ material grown with the flux technique, using plates of simple orientation, will also be reported.

II. EXPERIMENTAL CONSIDERATIONS

A. Crystal Growth Experiments

Different amount (wt %) of the $X_2Mo_3O_{10}$ flux (X=Li, K) were mixed with the α-$GaPO_4$ powder and homogenized in an agate mortar. The α-$GaPO_4$-flux mixture was put in Pt crucible covered with a lid, heated from room temperature to 950°C and held at this temperature during several hours for homogenization. The melted charge (α-$GaPO_4$-flux) was then slowly cooled down. $GaPO_4$ single crystals were grown in a direct solubility range between 950°C and 600°C. From various solute-flux weight ratios, it was found that 85 wt% of the flux for 15 wt% of α-$GaPO_4$ gave crystals of better quality.

The as-grown single crystals were separated from the growth solution by dissolving the residual $X_2Mo_3O_{10}$ flux (X=Li, K) in warm water (30-45°C). The crystals were carefully cleaned with the help of an ultrasonic cleaner and dried.

B. Physical Characterizations

The lattice parameters were examined with an Xcalibur CCD X-ray diffractometer using the Mo-K_α 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 $\pm 2 cm^{-1}$. Differential Scanning Calorimetry data collection was conducted using a SETARAM-LABSYS in an inert (nitrogen) atmosphere. Temperatures were changed between room temperature and 1200°C at heating and cooling rates of $2°C min^{-1}$. Powder samples, with an average grain size of 20 μm, with masses of 42.4±0.1mg were placed in Pt crucibles. Phase transformation temperatures were determined from the onset of the differential signal.

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C. *Elastic Constant Measurements*

The values of the elastic constants, at room temperature, of the piezoelectric material were derived from the resonance behaviour (registered with a network analyser Agilent HP4294A) of suitably shaped specimens subjected to a sinusoidally varying electric field. We have measured the frequencies thanks to the air-gap method. The piezoelectric plate was sandwiched in two electrodes, but the upper electrode was not in contact with the plate. Indeed the upper electrode of lower diameter than the plate dimensions was placed near the sample by using a micrometric screw. This system allows to access at the simple mode of vibration without disturbing electric signals due to some coupling effects because they are trapped under the electrode and have a negligible amplitude in plate side.

III. RESULTS

Colorless and transparent $GaPO_4$ single crystals of millimeter-size were grown by spontaneous nucleation using the slow cooling method. Photographs in Fig. 1 show inclusion-free crystals with a two-face morphology grown in $Li_2Mo_3O_{10}$ or $K_2Mo_3O_{10}$ flux. The registered cell parameters at room temperature of the flux-grown $GaPO_4$ single crystals are given in Table I. They crystallize in the hexagonal space group and their lattice parameters are in perfect agreement with those already published on hydrothermally-grown α-$GaPO_4$ material [1].

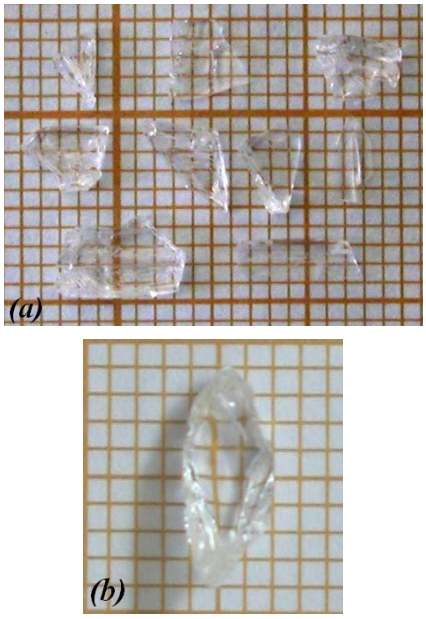

Figure 1. $GaPO_4$ single crystals obtained from (a) $K_2Mo_3O_{10}$ and (b) $Li_2Mo_3O_{10}$ flux. The small grid division is 1 mm.

TABLE I. LATTICE PARAMETERS OF FLUX-GROWN α-$GaPO_4$

Flux	Cell parameters (Å)		Cell volume (Å^3)
	a	*c*	
$K_2Mo_3O_{10}$	4.892(1)	11.041 (1)	228.86
$Li_2Mo_3O_{10}$	4.895(1)	11.034 (1)	229.14

A. *Thermal Behaviour*

Figs. 2a and 2b show the DSC plots of flux-grown α-$GaPO_4$ single crystals. Temperatures were changed at heating and cooling rate of 2°Cmin^{-1}.

On heating runs, an endothermic peak appears at onset temperatures around 952 - 964±1°C. This sharp feature is caused by the well-known transition from the thermodynamically stable α-quartz $GaPO_4$ phase into the β-cristobalite modification stable above 960 -980°C [2, 7, 8]. No other feature is observed up to our maximum experimental temperature i.e. 1200°C.

The succeeding cooling (-2°C/min) curves, from 1200°C back to room temperature, show only one exothermic peak. For $GaPO_4$ crystals spontaneously grown in $Li_2Mo_3O_{10}$ flux, Fig. 2a, the registered exothermic peak is strong and sharp with the onset at 936±1°C. For crystals grown in $K_2Mo_3O_{10}$ flux, Fig. 2b, the onset temperature of the weak and broad feature is 908±1°C. These exothermic peaks correspond to a total transformation of the high-cristobalite $GaPO_4$ phase into the low-quartz phase as confirmed by the X-ray powder patterns of the end products of the DSC analyses.

This is in our knowledge, the first time that $GaPO_4$ is found, after an DSC cycle, exclusively in the low-quartz modification after cooling from the high-cristobalite phase without annealing periods.

B. *O-H Streching Bond Characterization*

The 2500-4000 cm^{-1} middle infrared absorption region of flux-grown α-$GaPO_4$ single crystals grown in $Li_2Mo_3O_{10}$ flux and $K_2Mo_3O_{10}$ flux are shown in Figs. 3a and 3b respectively.

The presented infrared absorption in Fig. 3, given in cm^{-1}, is equal to $1/d*[\log T_{3800} / T_x]$ with T_x, the IR transmission in % and T_{3800}, the IR transmission in % registered at 3800 cm^{-1}. d represents the average thickness of the sample in cm [4]. In our case, the collection of the infrared data was done on as-grown samples i.e. without polishing the surfaces. In these conditions, only qualitative information on the OH-group content can be obtained from the infrared spectra of Fig. 3.

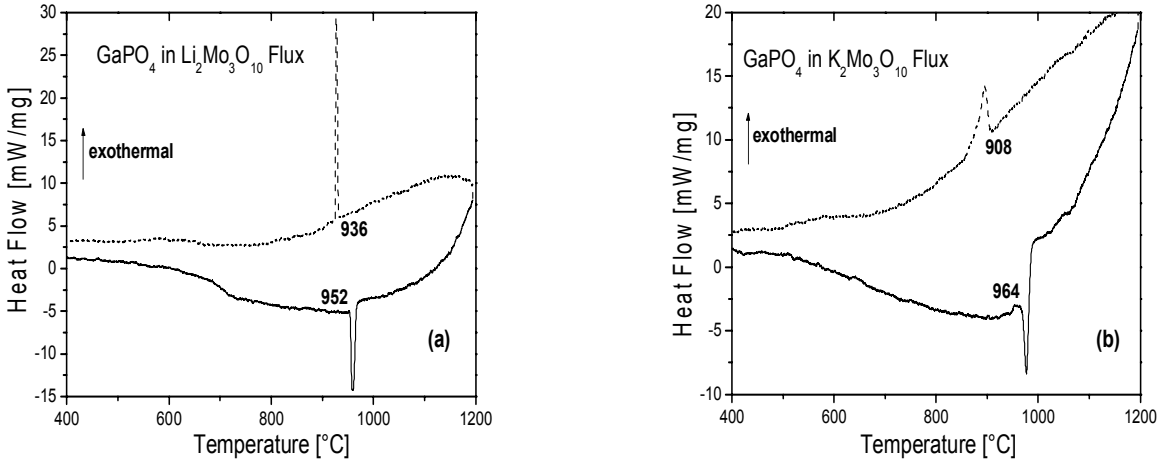

Figure 2. DSC plots of as-grown α-$GaPO_4$ single crystals obtained in $Li_2Mo_3O_{10}$ (a) and $K_2Mo_3O_{10}$ (b) flux (solid curves-heating, dashed curves-cooling).

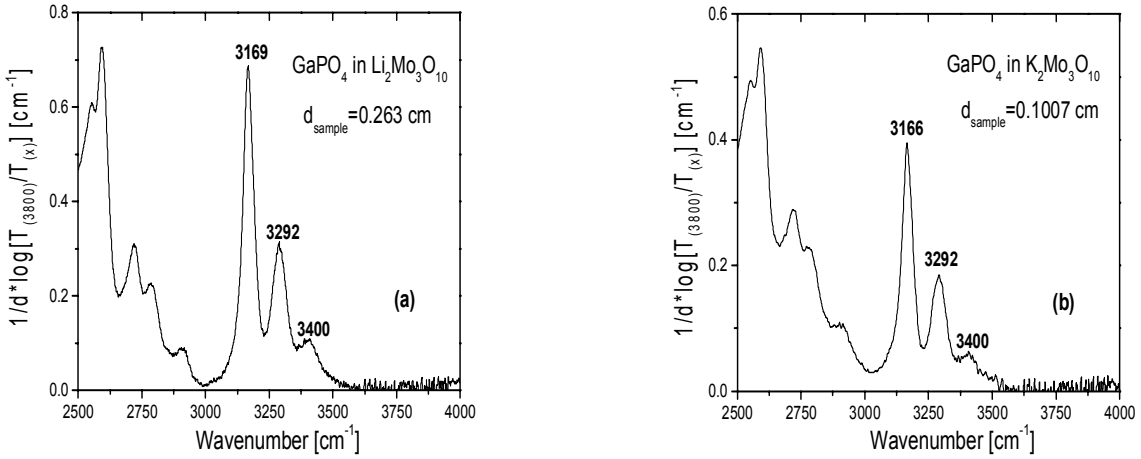

Figure 3. Infrared absorption spectra of α-$GaPO_4$ single crystals obtained in $Li_2Mo_3O_{10}$ (a) and $K_2Mo_3O_{10}$ (b) flux.

The presence of OH-groups, which decrease the Q-factor of the resonators, is largely reported in the literature concerning the crystal growth of α-$GaPO_4$ by the hydrothermal method [1, 2, 4-6]. In a typical infrared spectrum of a $GaPO_4$ material containing significant OH-groups, a broad band between 2500 and 3600 cm^{-1} is observed. This broad band is superimposed upon a sharp absorption band at 3508 cm^{-1} related to an isolated OH-group stretching band [4-6]. The 3169 cm^{-1}, 3292 cm^{-1} and 3400 cm^{-1} bands are assigned to third overtone vibrations with an absorption respectively equal to 0.697 cm^{-1}, 0.285 cm^{-1} and 0.078 cm^{-1} [4].

In Figs. 3a and 3b, the broad band and the sharp band at 3508 cm^{-1} characterizing significant OH-groups contamination in α-$GaPO_4$ samples are not detected. These registered infrared absorption spectra of α-$GaPO_4$ synthesized by the flux techniques provide a proof that the presence of OH group is not observed by infrared spectroscopy [4]. The flux method appears to be a powerful way to synthesize OH-free materials.

C. Elastic Constants Determination

A Y-oriented parallel plate (surface ⊥ to the OY axe (in the Cartesian axes), which is not a symmetry axe of the crystal) with an average thickness of 1.220 mm was obtained from the crystal in Fig. 1b. A second crystal of 4 mm long and 2.5 mm large was used to realize an X-oriented plate (surface ⊥ to the 2-order symmetry OX axe) with an average thickness of 0.617 mm.

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 one dimensional model of an infinite plate with massless electrodes and solving the Christoffel equation are given in [9, 10]. From the determination of these velocities, the elastic constants, C_{ij}^{E}, at constant electric field E, can be deduced.

To determine the whole tensorial characteristics of a piezoelectric crystal, several plates with different orientations are necessary in order to reach exact vibration modes and then to access to the elastic, dielectric and electro-mechanic

parameters. However, only two plates of simple orientation (X and Y-cuts) have been shaped from our spontaneously crystallized materials. In this context, only 4 out of 6 independent elastic constants could be derived from these two plates of respectively X (2-10) and Y (010) orientation. Moreover, we made the assumptions that these two plates have infinite laterally dimensions compared with their thickness for use the one dimensional model.

In Table II are presented the 4 resulting elastic constants C_{11}, C_{14}, C_{44} and C_{66} at room temperature, compared to published results obtained on hydrothermally-grown α-$GaPO_4$ cuts by Brillouin scattering [11] and pulsed-echo technique [12]. For the calculation of these constants, the dielectric permittivity at constant strain ε^S_{11}, was measured at high frequency and at room temperature. Its value, 5.83, is very close to the one reported in [13]. The value of the piezoelectric coefficient e_{11}, 0.21 C/m^2, was taken from [14]. The density, at 20°C, is calculated from X-ray diffraction measurement (Table I) and is equal to 3571.4 kg/m^3 in perfect agreement with [15].

Compared to these published values, the experimental elastic constants obtained for our samples present some slight differences, as it can be seen in Table II. The values of the elastic constants C_{14}, C_{66} and also C_{44} are higher than the ones registered for hydrothermally-grown α-$GaPO_4$ material. On the opposite, the value of the longitudinal constant C_{11} appears to be lower.

IV. DISCUSSION

The flux growth of α-$GaPO_4$ is a new growth method of this material. The thermal analysis shows that the transition β-cristobalite $\leftrightarrow$ α-quartz is totally reversible for the first time. This different behavior would be related to the growth method of the $GaPO_4$ crystals (direct solubility, process temperature, morphology, OH-groups free crystals and flux impurities).

In order to quantify the OH incorporation in the material, we have proceeded at infrared absorption measurements. Indeed it has been assured that the absorption coefficient caused by the presence of OH groups can be determined with sufficient accuracy from the expression : α (cm^{-1}) = $1/d*[\log T_{3800}/T_{3400}] - \alpha_0$ with T, the IR transmission in % at 3800 and 3400 cm^{-1} respectively and d, the thickness of the sample in cm [4]. α_0 is the absorption of the intrinsic lattice vibrations of $GaPO_4$ at 3400 cm^{-1} and is close to 0.078 cm^{-1} [4]. If we calculate the α value of our material, we find 0.002 cm^{-1} and 0.032 cm^{-1} for $GaPO_4$ obtained in, respectively, $K_2Mo_3O_{10}$ and $Li_2Mo_3O_{10}$ flux. These results confirm that there is no OH contamination in α-$GaPO_4$ synthesized by flux. Moreover the value of α* suggested by F. Krispel for single crystal hydrothermally grown [4] corresponds to the absorption of the significant intrinsic bands at 3400 cm-1 and the quantification of the OH in the MXO4 [16, 17] is perhaps overestimated. A part of the absorption can be applied to the framework and not to the OH groups.

As to the determination of the elastic constants, the first results presented in this paper indicate a rise of the elastic constants, excepted the C_{11}. The synthesis of α-$GaPO_4$ single crystal by flux method requires high temperature and the solid state diffusion of impurities in the crystal network has to be considered. These impurities, associated with crystalline defects like dislocations, can justify the values of elastic constants found for this material. Except for C_{11}, the higher values of the other constants could be explained by a network rigidity of the material obtained by the flux method. It is well known that hydrothermally-grown $GaPO_4$ crystals with the hexagonal structure present non-negligible hydroxyls contamination. These OH groups, sometimes even present as water molecules, would act as impurities into the framework and then, would reduce their piezoelectric properties [5]. A similar augmentation of the elastic constants was already observed with berlinite $AlPO_4$ when the OH concentration was reduced by modification of the hydrothermal growth conditions [18].

V. CONCLUSION

Transparent α-$GaPO_4$ single crystals were grown by spontaneous crystallization with the slow cooling method from high temperature $X_2Mo_3O_{10}$ fluxes (X= Li, K).

An infrared study has pointed out that this crystal are free from OH groups. Thereby the feasibility of growing OH-free α-$GaPO_4$ single crystals by the flux method was established.

Another important result concerns the thermal behaviours of these as-grown α-$GaPO_4$ single crystals. The DSC experiments have pointed out a total reversible α-quartz$\leftrightarrow$ β-cristobalite transition with only the low-quartz $GaPO_4$ phase as the end product of the DSC cycles.

Finally, according to the elastic constants determination from the resonance behaviour of X- and Y-plates, it seems that the lack of OH contamination into these materials would induce a more rigid network. However, these results should be regarded as preliminary. Indeed, the opposite tendency of the C_{11} elastic constant and the fact that we were not in the best experimental conditions to use the one dimensional model lead us to conclude that extra elastic constant measurements are necessary to confirm this first promising dynamical behaviour of flux-grown α-$GaPO_4$ crystals.

All measurements indicate that ours crystals are free from OH and that these OH groups decline the piezoelectric but also the thermal behavior of gallium orthophosphate crystals. These findings confirm the interest of α-$GaPO_4$ flux growth.

TABLE II. ELASTIC CONSTANTS OF FLUX-GROWN α-$GaPO_4$

Elastic constants (10^9 N/m^2)	This work	[11]	[12]
C_{11}	64.01 $\pm$ 1.92	66.58 $\pm$ 0.37	66.35 $\pm$ 0.02
C_{14}	5.52 $\pm$ 0.17	3.91 $\pm$ 0.33	4.20 $\pm$ 0.08
C_{44}	39.39 $\pm$ 1.17	37.66 $\pm$ 0.27	37.80 $\pm$ 0.01
C_{66}	25.25 $\pm$ 0.75	22.38 $\pm$ 0.32	22.35 $\pm$ 0.01

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