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Crystal growth and characterizations of a quartz-like material: GaPO₄

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ABSTRACT : This paper concerns the GaPO₄ crystal growth process which consists of an alternation of the vertical reverse temperature gradient (VTG) in sulfuric acid medium and the slow heating method (SHT) in phosphoric acid. Since this process is not usable at an industrial scale, we have investigated the crystal growth in phosphoric acid medium by VTG in order to find a direct way to synthesize GaPO₄ crystals. The as-grown crystals have been characterized by IR and NIR spectroscopies : the -OH content seems to decrease continuously without any plateau being observed at the last step of crystal growth as it was observed in berlinite. Moreover, both dielectric constants (ϵ'^T) and dielectric loss (ϵ'') have been studied in terms of temperature, frequency and -OH content. ϵ'^T_{11} and ϵ'^T_{33} have been found equal respectively to 6.2 and 6.6 at 20°C and 50kHz.

1- INTRODUCTION

The α gallium orthophosphate (GaPO₄), as berlinite (AlPO₄), belongs to the crystal family MXO₄ with a structure similar to quartz. Following our previous works devoted to the growth and physical characterizations of berlinite crystals, we have undertaken the study of this new material, GaPO₄.

Indeed, it was shown that it presents very interesting piezoelectric characteristics better than those of quartz (table 1).

In particular, for the same AT cut, it exhibits a larger coupling coefficient in comparison with quartz [1-3]. This makes it a promising material in the field of wide band filters. Furthermore, there is no α - β transition, thus, it can be used in a very wide range of temperatures for filters and sensor devices.

| | Quartz | AlPO ₄ | GaPO ₄ | LiTaO ₃ |
|---|-------------------|-------------------|--------------------|--------------------|
| coupling coeff.*k % | 8.5 | 11.0 | >16.0 | 45 |
| surtension coeff.* Q | 3.10 ⁶ | 10 ⁶ | >5.10 ⁴ | 10 ³ |
| Transition $\alpha \leftrightarrow \beta$ °C | 573 | 586 | non | non |

* AT cut

Table 1: comparison of some physical properties

We present here the GaPO₄ crystal growth process and the results of characterizations :

- on one hand the determination of OH content by IR and NIR spectrometries, and the control of crystalline quality by X-ray topography.
- on the other hand, the studies of the physical properties of GaPO₄ : piezoelectric and particularly dielectric properties.

2 - CRYSTAL GROWTH STUDIES

2.1 - GaPO₄ crystal growth process

At present, the best method to obtain GaPO₄ crystals of good crystalline quality needs successive growths in sulfuric and in phosphoric acid media [4].

Table 2 summarizes the different stages of the GaPO₄ crystal growth.

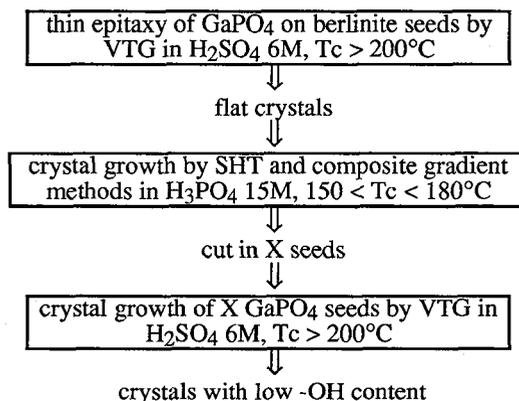


Table 2 : Schematic representation of GaPO₄ crystal growth process.

The first stage of GaPO₄ crystal growth process is the epitaxy of GaPO₄ on berlinite seeds. This is possible since the cell volume of both materials is very close ($Al_{1-x}Ga_xPO_4$, $V = 231 \pm 1 \text{ \AA}^3$ for $0 \leq x \leq 1$ [5]). Such an epitaxy allows to obtain directly large seeds of gallium phosphate since it is possible to start from berlinite seeds of 5 to 8 cm long. The GaPO₄ epitaxy on Z berlinite seeds is realised in sulfuric acid medium 6 M at a growth temperature T_c greater than 200°C, by the vertical reverse temperature gradient (VTG). The resulted crystals are "flat" since the crystal growth rates V_Z and V_Y are very weak in sulfuric acid medium.

The second stage consists of growing these flat crystals to give rise to two dimensions crystals (X and Z). The growth is realised in phosphoric acid medium 15 M, at T_c ranging from 150 to 180°C in a glass vessel, following the three methods mentioned below [4-7] :

- the slow heating method (SHT).
- the horizontal gradient method (HTG), with nutrient in the coldest side of the glass vessel.
- the composite method : (SHT + HTG).

Only these three methods in phosphoric acid medium allow to obtain a sufficient growth rate along the Z axis. Therefore, the Z thickness of these crystals is adequate sized to cut them in X seeds.

In a third stage, these so obtained X seeds are grown again in sulfuric acid through the VTG method at high temperature ($T_c > 200^\circ\text{C}$). GaPO₄ crystals of low -OH content are thus obtained.

Unfortunately, the alternation of the VTG method in sulfuric acid and the SHT or the composite methods in phosphoric acid is not convenient and cannot be realized at an industrial scale.

Thus, we currently search a direct way to synthetize crystals with sufficient growth rates V_X and V_Z and with a good crystal quality. This requires the use of the VTG method. Since good results are obtained by using phosphoric acid medium with the SHT method, we have decided to investigate this medium to obtain good crystal growth conditions, but, in this case, with the VTG method.

2.2 - Crystal growth in phosphoric acid medium by VTG

Before studying the crystal growth for different phosphoric acid concentrations (7.5, 9 and 15 M), it was essential to define the solubility of GaPO₄ in these acid solutions. Experimental measurements of these solubilities have been undertaken by well known methods described elsewhere [8], (fig. 1).

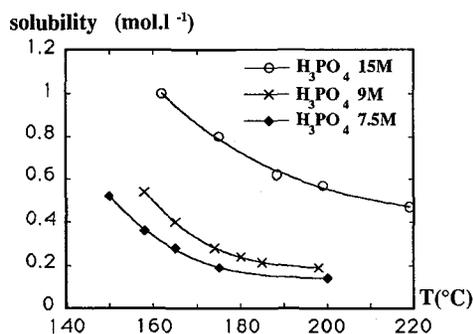


Fig 1- Solubility of GaPO₄ in H₃PO₄

| | |
|----------------------------|---|
| growth solutions | H ₃ PO ₄ saturated in GaPO ₄ at the crystal growth temperature. concentrations : 7.5M, 9M, 15M |
| crystal growth temperature | 150, 180, 210°C |
| filling of autoclave | 80% |
| boring ratio of baffle | 8.2% |
| seeds | X, Z GaPO ₄ seeds |
| ΔT(°C) | 2.9 < ΔT < 7.2 |
| nutrient | 2-4 mm |

Table 3-Fixed growth parameters used for the crystal growth of GaPO₄.

The crystal growth has been carried out through the reverse temperature gradient method (VTG). A systematic study has been undertaken in terms of temperature gradient (ΔT°C), crystal growth temperature (Tc) and acid concentration. All parameters are summarized in table 3. All the results about the growth rates are shown in the figure 2 and the table 4.

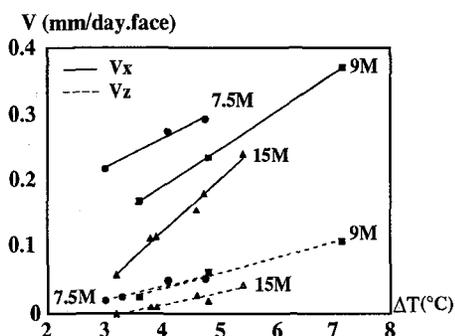


Fig 2- Growth rates Vx and Vz for Tc = 150°C in H₃PO₄ media.

In table 4, the results about the evolution of growth rates as a function of the crystal growth temperature Tc are noted for the phosphoric acid medium 7.5 M.

| Tc | ΔT | 4.6°C | 7.8°C |
|-------|-----------|-----------|-----------|
| 150°C | Vx = 0.29 | Vx > 0.5 | Vz = 0.13 |
| 210°C | Vx = 0.11 | Vz = 0.04 | Vz = 0.06 |

Table 4-Evolution of growth rates (mm/day.face) as function of Tc, in H₃PO₄ 7.5M. At 150°C, for ΔT=7.8°C, the Vx and Vz values are extrapolated from curves of fig 2.

When Tc increases, the growth rates Vx and Vz seem to decrease. This result can be explained by the decrease of supersaturation when temperature is raised [9].

Further investigations are necessary to confirm these results. In all cases, relatively good results are obtained for crystal growth experiments : the growth restart is of good quality and particularly at 150°C. At this step, the first characterizations of these crystals have been undertaken.

3 - CHARACTERIZATIONS

3.1 - Infrared and near infrared spectroscopies

3.1.1 - Infrared spectroscopy

The infrared spectrometry in the range 4000 to 2600 cm^{-1} is the most appropriate method for the -OH content determination in quartz like materials. It is well known that -OH content influences both piezoelectric and dielectric properties [10-12].

Therefore, we have evaluated the -OH content of GaPO_4 crystals by calculating the absorption coefficient α from the following expression derived from that proposed by Steinberg et al. [13] :

$\alpha = 1/d_{\text{cm}} \log (T_{3800}/T_{3167})$ where d is the sample thickness in cm and where T_{3800} and T_{3167} are respectively the transmittance at 3800 and 3167 cm^{-1} (3167 cm^{-1} being the strongest absorption band probably due to Ga-OH).

The results obtained for crystal growth in phosphoric acid 9 M at 150°C, by VTG, are given in table 5.

| | | |
|-------------------------------|----------------------|----------------------|
| ΔT (°C) | 3.6 | 4.8 |
| $\alpha_{3167\text{cm}^{-1}}$ | $0.2 < \alpha < 0.4$ | $0.5 < \alpha < 1.7$ |

Table 5- Absorption coefficient α versus temperature gradient .

| | | |
|---|--------------------|----------------------|
| $[\text{H}_3\text{PO}_4]$ (mol.l ⁻¹) | 7.5 | 15 |
| $\alpha_{3167\text{cm}^{-1}}$ | $0.5 < \alpha < 1$ | $1.1 < \alpha < 2.4$ |

Table 6- Absorption coefficient α versus phosphoric acid concentration.

It can be noted that the α value increases with ΔT , i.e. with the growth rate acceleration for a given acid concentration.

The table 6 shows α variation versus acid concentration for $\Delta T=4.7^\circ\text{C}$. It is observed that the -OH content tends to increase with the acid concentration.

As previously observed for berlinite, infrared spectrometry is of high interest to evaluate the crystal quality, in particular at the growth restart point. In berlinite (fig.3) [14], for a successfull growth restart, the -OH content does not increase and remains constant after 1 or 2 mm of growth. Slightly different result is observed in GaPO_4 crystals, as shown in fig.4. In fact, the -OH content, in GaPO_4 , decreases until the end of the crystal growth whatever the crystal growth medium and temperature are. This result is of high interest for the crystal synthesis of GaPO_4 since it would be not necessary to work at temperatures higher than 200°C to get crystals of sufficient OH content for industrial applications.

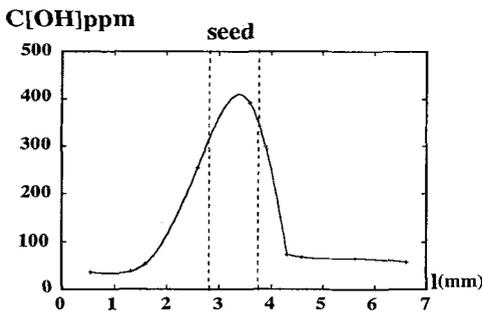


Fig.3- IR profile of a berlinite crystal.

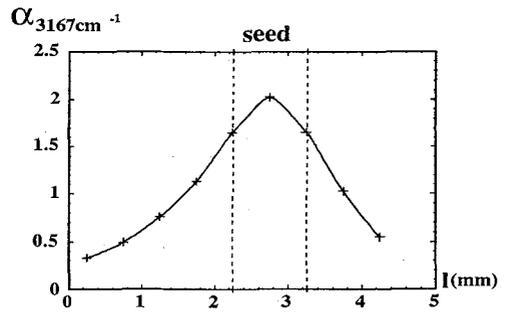


Fig.4- IR profile of a GaPO_4 crystal

3.1.2 - Near infrared spectroscopy

- In berlinite and quartz crystals, hydroxyl groups can occur under various forms [15]:
- isolated -OH point defects (interstitial or substitution).
 - molecular water under the form of very tiny fluid inclusions.

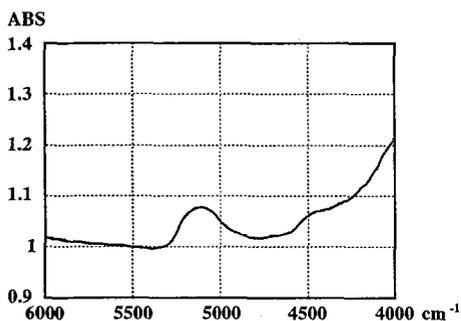


Fig 5- NIR spectrum of a GaPO₄ crystal.

Only near infrared (NIR) spectroscopy, in the range 6000 - 4000 cm⁻¹, allows both forms of incorporation to be distinguished [15-16]. Indeed, molecular water in fluid inclusions gives rise to a broad absorption band centered at about 5200 cm⁻¹ which is attributed to a combination of stretching and bending modes of the water molecules. On the other hand, the -OH groups absorb near to 4500 cm⁻¹.

The fig. 5 shows a NIR spectrum of a GaPO₄ crystal grown by VTG in H₃PO₄ 7.5 M at 150°C. The molecular water in this crystal is put into relief by the absorption band around 5200cm⁻¹.

3.2 - Characterizations of growth defects by X-ray topography

Several plates of GaPO₄ were studied by X Ray transmission topography using the white beam delivered by the DCI storage ring at LURE. This part is described in details elsewhere [17].

3.3 - Dielectric properties

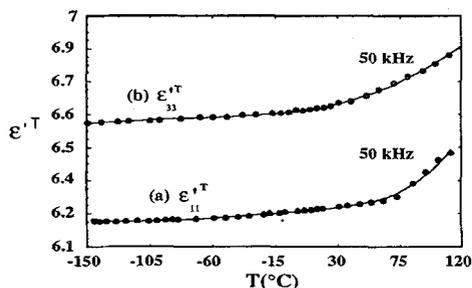


Fig.6- Dielectric behaviour of GaPO₄.

Both dielectric constants (ϵ'^T) and dielectric loss (ϵ'') have been studied. The ϵ'^T variations with temperature are presented in figure 6.

The two independent dielectric constants ϵ'^T_{11} (a) and ϵ'^T_{33} (b) behave identically versus temperature : ϵ'^T is nearly constant below room temperature, whereas an increase of ϵ'^T is observed above room temperature. This increase with temperature of the ϵ'^T value has been shown to be frequency dependent : the lower the frequency is, the higher the variations of ϵ'^T are [12].

Dielectric loss is associated with the ϵ'^T increase above room temperature indicating its origin from impurities. Dielectric loss is as well frequency dependent, being higher at low frequencies. The frequency dependence of both ϵ'^T and ϵ'' is explained by the fact that the space charge polarization is more prominent at low frequencies than at high frequencies.

As expected, the -OH content of GaPO₄ influences the variations of dielectric constants. For a given orientation, samples with a high OH content show the highest variations in ϵ'^T . Dielectric loss is as well proportional to the OH content of the samples.

Despite some small differences in the ϵ'^T value from sample to sample, values of ϵ'^T_{11} and ϵ'^T_{33} can be significantly calculated. Thus, we determine ϵ'^T_{11} and ϵ'^T_{33} to be equal respectively to 6.2 and 6.6 at 20°C and 50 kHz. The difference between ϵ'^T_{11} and ϵ'^T_{33} values appears to be a consequence of the anisotropy of the structural arrangement of GaPO₄.

3.4 - Piezoelectric characterizations

This study has been developed previously [4]. These first piezoelectric characterizations for resonators near the AT cut show GaPO₄ to be a very promising piezoelectric material with a large

coupling coefficient near 16%, a quartz-like thermal stability, a Q factor already nearly sufficient for the applications and the possibility to lead to devices with very low acoustic losses.

4- CONCLUSION

In this investigation, we have presented the GaPO₄ crystal growth process which requests the alternation of two solvents, H₃PO₄ and H₂SO₄. This process is not therefore usable at an industrial scale. So we have investigated a direct way to synthesize GaPO₄ crystals : in phosphoric acid medium by VTG. The obtained results are very encouraging : particularly at 150°C, the growth restart quality is very good. Moreover, the characterizations of these GaPO₄ crystals show that the OH content decreases until the end of crystal growth, whatever the crystal growth conditions are. This result is of high interest for the crystal synthesis of GaPO₄, since it would not be necessary to work at temperature higher than 200°C to get crystals of sufficient low OH content for industrial applications.

We have also specified the values of dielectric constants of GaPO₄ ($\epsilon^T_{11} = 6.2$ and $\epsilon^T_{33} = 6.6$ at 20°C and 50kHz) as well as the influence of temperature, frequency and impurities (hydroxyl groups). Permittivity is found nearly constant below room temperature, whereas it becomes temperature-frequency-impurities dependent above room temperature.

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