# The temperature-stable piezoelectric material $GaPO_4$ and its sensor applications

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**SUMMARY**

Gallium (ortho) phosphate ($GaPO_4$) has a similar structure as quartz, but the high thermal stability up to 970 °C and the high sensitivity make it a very attractive choice for a wide range of uncooled high temperature applications. Furthermore it shows no pyroelectricity, no outgassing and a high electric resistance to guarantee high precision piezoelectric measurements. $GaPO_4$ offers good temperature compensation for a new generation of crystal microbalances operating at temperatures up to at least 700 °C as shown in thermogravimetric and film thickness measurements. It also allows the production of SAW sensors with a very high thermal stability.

**Keywords:** Gallium (ortho) phosphate, sensor material, high temperature

## Introduction

In recent times there is an increasing demand for miniaturised sensors with a higher precision at highest temperatures and high pressures. But these requirements often cause problems to the sensor material. The sensitivity decreases significantly, temperature changes cause interference to the sensor signal and the crystal material may show unwanted effects like outgassing due to structural changes. Gallium phosphate ($GaPO_4$) is a piezoelectric crystal which has been developed for the production of pressure transducers allowing miniaturisation and high thermal stability without cooling, while maintaining high sensitivity and accuracy. It belongs to the same point group as quartz, therefore the lack of pyroelectricity guarantees that temperature changes do not cause interference to the sensor signal. Moreover there exists no quartz-like α-β phase transition, so it does not change its high piezoelectric sensitivity under high stress. The crystal lattice is stable and the piezoelectric coefficient remains at a high level up to a reconstructive phase transition at 970 °C [1].

$GaPO_4$ has been used for the production of pressure transducers for seven years now and the manufacturing experiences together with today's crystal growth facilities helped to make it available for a lot of different applications.

## Direct piezoelectric effect applications

The most remarkable feature for applications using the direct piezoelectric effect is the temperature stability of the piezoelectric coefficient $d_{11}$. It does not deviate significantly from its room temperature value of 4.5 pC/N, about twice the value of quartz, up to 500 °C and stays within few percent of that up to 700 °C. Above this temperature, no reliable data exist, but a slow decrease until the phase transition temperature is assumed (Fig.1 and Table 1).

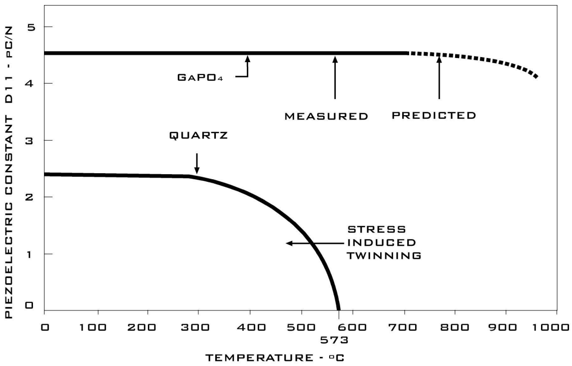


***Fig.1:*** *Temperature dependence of the longitudinal piezoelectric effect $d_{11}$ of quartz and $GaPO_4$*

***Table 1:*** *Piezoelectric constants of $GaPO_4$*

| pC/N | 20 °C | 500 °C | 700 °C | 950 °C |
|---|---|---|---|---|
| $d_{11}$ | 4.5 | 4.5 | 4.5 | 4.1 * |
| $d_{14}$ | 1.9 | 1.6 | 1.4 * | 1.0 * |

* expected value

This means that exceptional temperature stability can be achieved for piezoelectric sensors of longitudinal compression type ($d_{11}$), transverse compression type ($d_{12} = -d_{11}$) and shear type ($d_{26} = -2\ d_{11}$).
The bending strength was measured on x-bars by the 3 point method. It is above 100 $Nmm^{-2}$ and thus similar to quartz.
Due to the high homogeneity of hydrothermally grown crystals compared to crystals grown from the melt and the strong chemical bond of the oxygen atoms to the phosphorus atoms in the $PO_4$ tetrahedron, which is much stronger than the bond between e.g. the relatively large Nb atoms and O in lithiumniobate, no outgassing has been observed.
Since also the insulation resistance is similar to that of quartz (actual measurements showed values $>10^{15}$ Ohm*cm at room temperature and values $>10^{11}$ Ohm*cm at 500 °C), this allows precise measurements with uncooled pressure transducers for combustion engines, gas turbines and injection molding machines, as well as accelerometers and force sensors.
The high thermal stability of $GaPO_4$ also enables to extend the operating range of ultrasonic transducers up to very high temperatures [2].

## Bulk acoustic wave applications (BAW)

For the new generation of crystal microbalances [3] and other sensors based on thickness shear resonators such as viscosimeters, biosensors (liquid cells) and gas sensors, a good temperature compensation is necessary. $GaPO_4$ meets these requirements, since for any operating temperature in the stability range a temperature-compensated cut can be given including an orientation with very flat cubic characteristic in the range 350 °C - 650 °C (Fig. 2). These cuts have a higher coupling than quartz [4],as well as a higher sensitivity due to the lower damping in fluids.

In Table 2 an overview of the elastic constants and their temperature coefficients is given [5].

***Table 2:** Elastic constants of $GaPO_4$*

| | **at 25 °C [GPa]** | **TC (1) [$10^{-6}$ $K^{-1}$]** | **TC (2) [$10^{-9}$ $K^{-2}$]** | **TC (3) [$10^{-12}$ $K^{-3}$]** |
|---|---|---|---|---|
| $c_{11}^E$ | 66.58 | -44.1 | -28.5 | -59.4 |
| $c_{12}^E$ | 21.81 | -226.7 | -70.8 | -205.7 |
| $c_{13}^E$ | 24.87 | -57.6 | 41.3 | -109.9 |
| $c_{14}^E$ | 3.91 | 507.2 | 280.6 | -99.9 |
| $c_{33}^E$ | 102.13 | -127.5 | -18.3 | -134.8 |
| $c_{44}^E$ | 37.66 | -0.4 | -43.8 | -37.1 |
| $c_{66}^E$ | 22.38 | 44.9 | -7.9 | 11.9 |

The initial sensitivity of a crystal microbalance is given by the resonant frequency of the “unloaded” resonator. The fundamental mode resonant frequency of most commercially available quartz resonators for QCM (quartz crystal microbalance) applications is in the range 6 MHz to 10 MHz.
The maximum resolution of a microbalance measuring system (e.g. film thickness resolution) is limited by the used oscillator circuit and the Q-value of the piezoelectric resonator. While the resolution of the oscillator circuit remains essentially constant, the resonator becomes more damped with increased mass loading. For that reason, the resolution of the microbalance system decreases during the mass loading process (e.g. film-thickness monitoring). This limits the measuring range of the microbalance system.

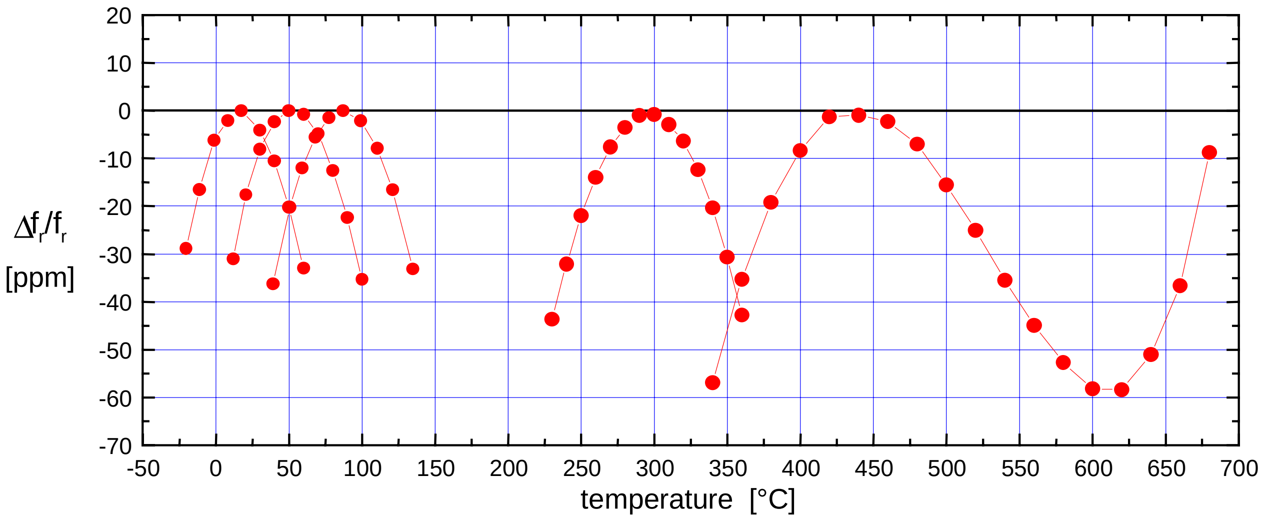


***Fig.2:** Frequency vs. temperature characteristic of singly rotated Y cuts with inversion temperatures between 20 °C and 600 °C*

A definition of the Q-value of a piezoelectric resonator can be given by:

$$Q = \frac{1}{2\pi f_R R_1 C_1}$$

$R_1$...motional resistance
$C_1$...dynamic capacity

Typical data for $GaPO_4$ resonators with a crystal diameter of 7.4 mm, an electrode diameter of 3.6 mm and a fundamental resonant frequency of about 6 MHz compared to a standard quartz resonator measured under the same conditions are given in Table 3.

***Table 3:*** *Typical resonator data*

| | $GaPO_4$ (Y-16.5 °)*) | Quartz AT-Cut |
|---|---|---|
| | At ambient pressure | |
| $R_1$ [Ω] | 5-10 | 7-50 |
| $C_1$ [fF] | 40-60 | 8-12 |
| $C_0$ [pF] | 2-3 | 1.6-2.6 |
| k [%] | 15-17 | 9 |
| Q | 100 000-200 000 | 10 000-100 000 |
| | in vacuum | |
| Q | 1200 000 | 900 000 |

The dynamic capacity $C_1$ is mainly determined by the properties of the used piezoelectric material, the thickness of the resonator plate and the diameter of the electrode. For that reason, $C_1$ remains essentially constant during thin film deposition onto the resonator surface.
The motional resistance $R_1$ represents the acoustic losses in the resonator. For that reason, $R_1$ increases with increasing mass loading. Figure 3 shows the measured values of $R_1$ of the GCM ($GaPO_4$ crystal microbalance) and the QCM during thin film deposition.
The motional resistances $R_1$ for the $GaPO_4$- and quartz resonators started at nearly the same value. But during the film deposition, the value of $R_1$ of the quartz resonator increased much more than that of the $GaPO_4$ resonator. This indicates clearly a larger possible measuring range for the $GaPO_4$ resonator for microbalance applications than it is possible with the AT-cut quartz resonator.
The physical reason for this very attractive behaviour is given by the higher coupling coefficient k of the $GaPO_4$ resonator which is twice as high as the coupling coefficient of the common used AT-cut quartz resonator (Table 2).

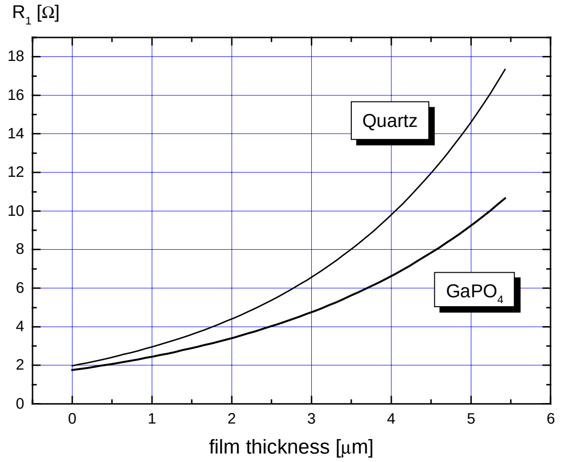


***Fig. 3:*** *Motional resistance of a $GaPO_4$- and a quartz thickness shear resonator during thin film deposition*

To show the high-temperature performance of the GCM, lubricating oil was applied to one side of the resonator surface and then the crystal was heated up to 720 °C.
For this measurement, a singly rotated Y-11°*) cut $GaPO_4$ resonator with 7.4 mm diameter and a resonant frequency near 6.2 MHz (fundamental mode) was used. The frequency vs. temperature behaviour of this resonator is very flat in the temperature range between 350 °C and 650 °C as reported in [6].
The behaviour of the resonant frequency during this experiment is shown in Figure 4.

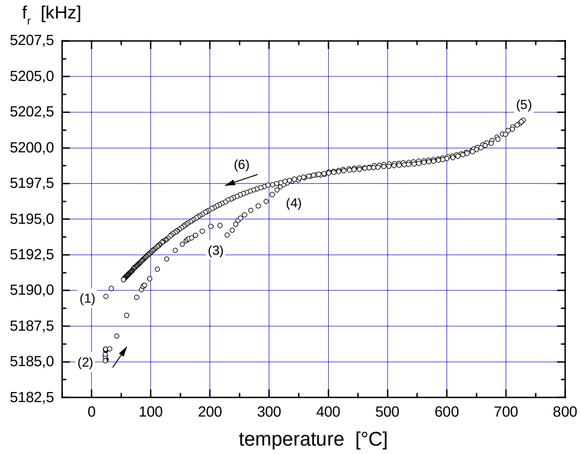


***Fig. 4:*** *Thermogravimetry and crystal cleaning by heating up to 720 °C. Steps (1) to (6) are explained in the following paragraphs*

*) Sign according to standard IEEE 176-1987

The lubricating oil was applied to the resonator surface. This caused a shift in the resonant frequency $\Delta f_R$ by 4.2 kHz from (1) to (2). Then the resonator was heated up and the resonant frequency increased rapidly because of the thermal influenced lowering of the viscosity and density of the liquid. Near 200 °C, the properties of the liquid film changed and became more elastic (3), which lowered the resonant frequency. With further increased temperatures, the liquid film evaporated from the resonator surface and near 350 °C the resonant frequency approached the „unloaded“ frequency-temperature behaviour of the resonator (4). During the following heating procedure, up to 720 °C (5), the resonant frequency approximated more and more the „unloaded“ behaviour. Finally the heater was switched off and the resonant frequency followed the well known cubic behaviour (6) which indicated a completely cleaned resonator surface.

## Surface acoustic wave applications (SAW)

For surface acoustic wave applications the high coupling and the very low temperature dependence of the resonant frequency or delay time, which make $GaPO_4$ attractive for filter applications [7] also allow the development of sensors with lower insertion loss and excellent temperature stability up to very high temperatures.

$GaPO_4$ has about twice the coupling but only half the temperature dependence of quartz. The lower SAW velocity allows the production of smaller devices. Up to 250 °C a good temperature compensation can be achieved by using singly rotated cuts and above that temperature multiply rotated temperature compensated orientations can be used.

This allows the application of SAW sensors even if the operating temperature is so high that other materials do not work reliably or stably. The possibility of passive sensor elements with wireless transmission allows precise measurements even in extreme environments or on moving parts.

An overview of typical $GaPO_4$-data for SAW applications is given in Table 4.

***Table 4:*** *Typical $GaPO_4$ data for SAW applications*

| | |
|---|---|
| $k^2$ | 0,3%...0,4% |
| $2^{nd}$ TCF | $-19*10^{-9}K^{-1}$... $-18*10^{-9}K^{-1}$ |
| v | 2300 m/s ... 2900 m/s |
| Temperature compensation up to 700 °C (up to 250 °C without beam steering) | |

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