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# Structure-piezoelectric property relationships in α-quartz isotypes : design and characterization of high performance piezoelectric materials

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*Abstract*- **Structure-property relationships established for α-quartz isotypes indicate that the materials with the most distorted structures exhibit both the highest piezoelectric coupling coefficients and the highest thermal stability. It is found that thermal disorder results in a loss of piezoelectric properties, most noticeably a significant reduction in the Q-factor, particularly in the case of the least distorted materials such as a-quartz itself and this at temperatures well below the α–β phase transition. The most promising materials are predicted to be $GeO_2$ and $GaAsO_4$. These predictions are confirmed by piezoelectric measurements on Y-cut plates of GaAsO4, which yield a piezoelectric coupling constant of about 20 %, which is more than twice that of α-quartz.**

## I. INTRODUCTION

α-Quartz is the most used piezoelectric material at the present time. However, its performances are too limited for certain technological applications in microelectronic components such as frequency filters and resonators requiring high frequencies and consequently miniaturization. This has spurred research into finding analogous materials with better intrinsic properties. Structure-property relationships have been developed for a series of α-quartz and ternary $ABO_4$ ($A$ = B, Al, Ga, Fe; $B$ = P, As) α-berlinite ($AlPO_4$) isotypes [1-5] relating their thermodynamic, dielectric and piezoelectric properties to the degree of distortion present in their crystal structures. Based on the three materials quartz, berlinite and gallium orthophosphate, the piezoelectric coupling coefficient was found to increase linearly as a function of structural distortion with respect to the β-quartz structure type [2]. This distortion can be described in terms of the intertetrahedral $A$-O-$B$ bridging angle θ or the tilt angle δ with respect to the β-quartz structure type. The most distorted structures found among α-quartz homeotypes are those of $GeO_2$ and $GaAsO_4$. Based on structure-property relationships, these compounds should exhibit the highest piezoelectric coupling coefficients for α-quartz-type materials.

An important property of a piezoelectric material from the point of view of potential applications is its thermal stability. The temperature domain of application of α-quartz, for example, is limited by the α-β phase transition at 573°C and the consequent loss of piezoelectric properties. The stability of the structures of the most promising materials, $GaAsO_4$ and $GeO_2$, were studied at high temperature by neutron diffraction.

It is also essential to correlate the piezoelectric properties (Q and k factors) of α-quartz homeotypes at high temperature to the disorder present in their crystal structures, as up to now, no detailed studies have been performed in spite of the importance of such results for understanding the origin of the observed high-temperature behavior of these materials. Results obtained by total neutron scattering and piezoelectric measurements on resonators as a function of temperature on quartz will be presented along with preliminary results on gallium orthophosphate.

All the results of these studies will enable electrical engineers to select new materials for future applications.

## II. EXPERIMENTAL

### A. Crystal Growth

A PTFE-lined autoclave was used for crystal growth experiments on $GaAsO_4$. The solution is prepared from galline, GaOOH dissolved in arsenic acid $H_3AsO_4$. The temperature is slowly increased until 230°C (reverse solubility) to grow $GaAsO_4$ crystals [11].

### B. Structural Studies

Single crystal x-ray data on $GaAsO_4$ as a function of temperature were collected on a Nonius KappaCCD diffractometer.

Time-of-flight (TOF) neutron diffraction data as a function of temperature were obtained on the LAD (α-quartz) [6,7], GEM ($GaPO_4$), Polaris ($GeO_2$, $FePO_4$) [5,8] powder diffractometers at the ISIS spallation source of the Rutherford Appleton Laboratory and on SEPD ($GeO_2$) at the IPNS spallation source at the Argonne National Laboratory. In the cases of α-quartz and $GaPO_4$, total neutron scattering data were obtained. These data were corrected in the usual way [9]. Three-dimensional structural models were refined using reverse Monte Carlo (RMC) modeling [10]. These models are essentially a 'snapshot' of the disordered structure, and are consistent with the Rietveld refined average structure, the



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measured pair correlation functions and the local network topology. The distributions of δ and the intertetrahedral O-O-O angles were extracted directly from these models.

### C. *Dielectric and Piezoelectric measurements*

$GaAsO_4$ (space group $P3_121$ or $P3_221$) has only two independent dielectric constants $\varepsilon_{11}$ and $\varepsilon_{33}$ and thus only X-cut and Z-cut crystals were investigated [11]. Dielectric measurements at frequencies between 1kHz and 100kHz were performed using a 1693 RLC Digibridge Genrad analyzer. The piezoelectric response of AT (athermal, i.e. –35.15° Y-rotated cut) cut, α-quartz resonators (C-MAC Frequency Products) was measured with a Hewlett-Packard 8753A network analyzer using the third harmonic signals at close to 10 MHz. Similar measurements were performed at close to 5 MHz on an AT cut (-15,9°) $GAPO_4$ resonator (AVL GmbH). High-temperature experiments up to 450°C for α-quartz [7] and 750°C for $GaPO_4$ were performed in a controlled temperature furnace (±0.5°C) and the temperature measured with a thermocouple.

## III. RESULTS AND DISCUSSION

### *Structure-property relationships*

It is apparent, based on three materials [2,3], quartz, berlinite ($AlPO_4$) and $GaPO_4$, that the piezoelectric coupling constant increases linearly with decreasing values of the intertetrahedral *A*-O-*B* bridging angle θ (figure 1) and increasing values of the tilt angle δ (tetrahedral tilt angle with respect to the β-quartz structure, figure 2).

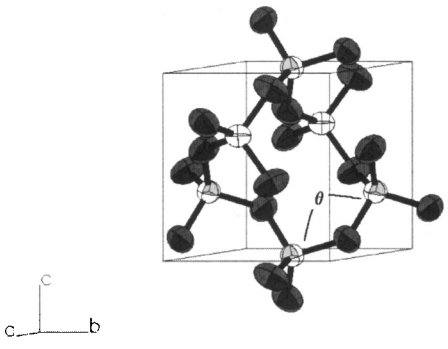


Fig.1. Intertetrahedral *A*-O-*B* bridging angle θ

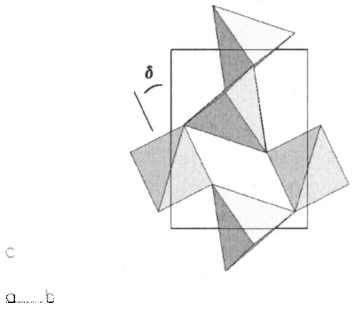


Fig.2. Tetrahedral tilt angle δ with respect to the β-quartz structure

In fact, the most distorted structures would be expected to exhibit the highest piezoelectric coupling constants. The present study indicates that the two materials with the most distorted structures, $GeO_2$ (θ= 130.0°, δ= 25.7°) and $GaAsO_4$ (θ= 129.6°, δ= 26.9°), should exhibit coupling coefficients of about 22%, which is three time higher than that of α-quartz (8.5%).

### *Temperature stability*

In respect to their thermal stability, it has been shown that the α–β transition is absent for highly distorted materials i.e when θ angle is less than 136° and δ greater than 22° [1]. Piezoelectric properties of α-quartz are in principle limited by the α–β phase transition at 573°C, however the Q factor begins to decrease well below this temperature [7]. This decrease in of the Q factor for high temperature above 300°C (figure 3) can be explained by a statistical disorder in the instantaneous structure found by total neutron scattering. Parallel to the dramatic decrease in the Q factor above 300°C, the distribution in the intertetrahedral bridging angle θ becomes very broad. In addition, the local disorder characterized by the intertetrahedral O-O-O bridging angles becomes similar to that observed for β-quartz, disordered high-temperature β-cristobalite and silica glass. Such disorder leads to a dissipation of induced dipoles and the loss of piezoelectric properties.

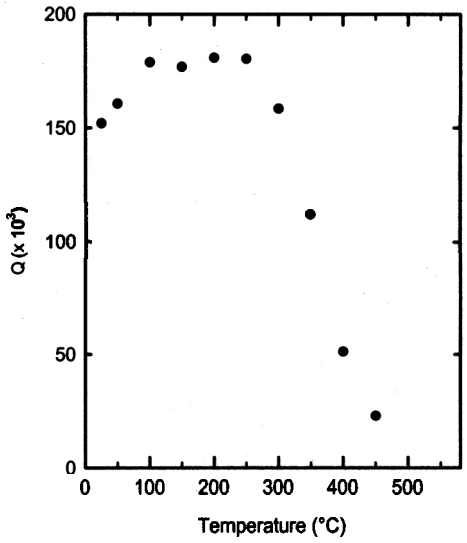


Fig.3. Q factor measurements of AT quartz resonators versus temperature.

Similar behavior is also observed with $GaPO_4$ material but at higher temperature. The Q factor decreases at temperatures above 750°C (figure 4). Recently, total neutron scattering data were collected on $GaPO_4$ powder. These data have not been completely analyzed, however, the diffraction data indicate that the α-quartz-type structure in $GaPO_4$ is stable up to 950°C. The

transition to the β-cristobalite form occurs above 950°C in agreement with the 970°C found in previous studies [12,13].

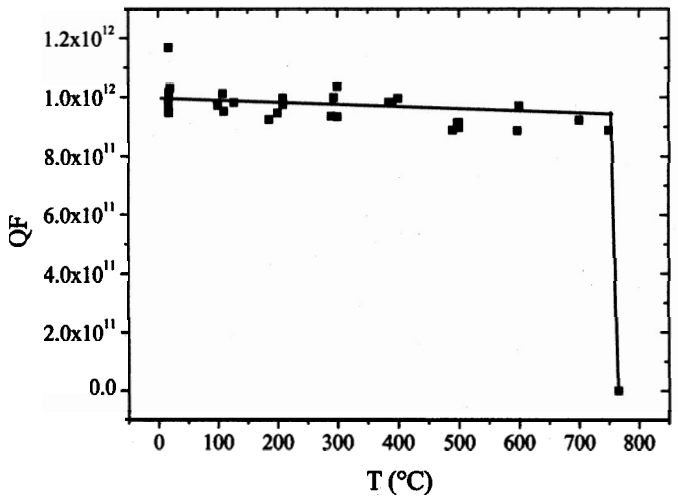


Fig.4. Qf factor measurements of AT $GaPO_4$ resonators in terms of temperature

Only structural data (Figure 5) are available at high temperature for the most distorted materials $GeO_2$ [5] and $GaAsO_4$ [3]. The α-quartz-type structure in $GeO_2$ remains highly distorted up to at least 1071°C, which is less than 50°C below the melting point. The tetrahedral tilt angle δ only decreases from 26.5° at ambient temperature to 23.7° at 1071°C. The α-quartz form of $GeO_2$ is thus stable at the highest temperature among this group of materials. There are phase stability problems at lower temperatures as below 1037°C, the rutile form is the stable phase and partial conversion to this form occurs. This presents problems for crystal growth of this material and eventual high temperature applications. Single crystals of $GaAsO_4$ have been studied by x-ray diffraction up to 800°C [3]. The results indicate that δ has the lowest temperature dependence of all α-quartz isotypes. $GaAsO_4$ has been reported to decompose into β-$Ga_2O_3$ and $As_2O_5$ at 1000°C [14].

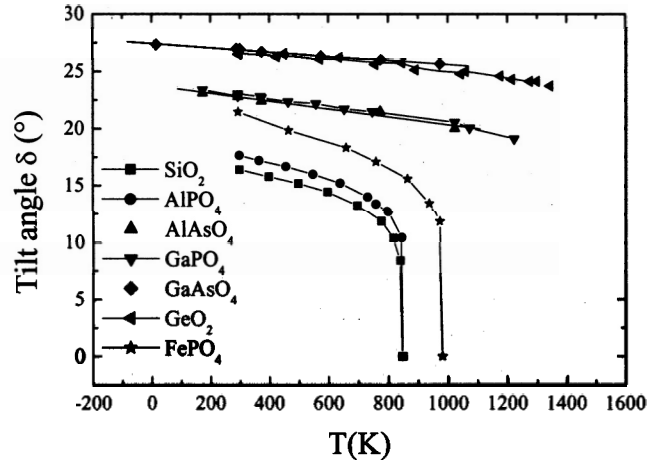


Fig. 5 Evolution of the tilt angle δ as a function of temperature for a series of α-quartz homeotypes. Data for $SiO_2$ [15], $GeO_2$ [5] $AlPO_4$ [16], $AlAsO_4$ [17-19], $FePO_4$ [8] $GaPO_4$ [17,18,20-22] and $GaAsO_4$ [3] are from the literature.

The combined results obtained for α-quartz isotypes indicate that from the point of view of high coupling coefficient and thermal stability, $GeO_2$ and $GaAsO_4$ should be the best potential piezoelectric materials of the α-quartz type. We have thus synthesized large $GaAsO_4$ single crystals by hydrothermal methods [11]. Infrared spectroscopy was used to quantify the chemical quality and particularly the OH-content (which tends to decrease the piezoelectric response by acoustic losses). The largest crystal (8 mm along the extended direction) was cut into X and Z plates in order to perform dielectric measurements. These values allow us to extend the structure-property relationships in α-quartz-type materials (figure 6).

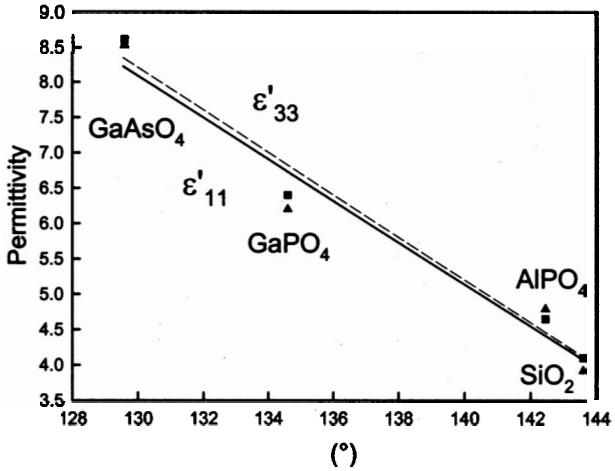


Fig.6. Permittivity in α-quartz materials as a function of structural distorsion.

The permittivity increases with the distortion and consequently with the coupling constant. In fact, it can be seen that the most distorted and most covalent material, $GaAsO_4$, exhibits the highest permittivity.

The piezoelectric performances of $GaAsO_4$ have been measured for the first time using the single crystals described above. The coupling coefficient obtained is close to 20% for a Y-cut, which confirms the established structure-property relationships. These studies indicate that it is possible to predict the performances of α-quartz type piezoelectric materials based only on a very precise neutron scattering study of powder samples (figure 7) and thus new higher performance materials can be proposed.

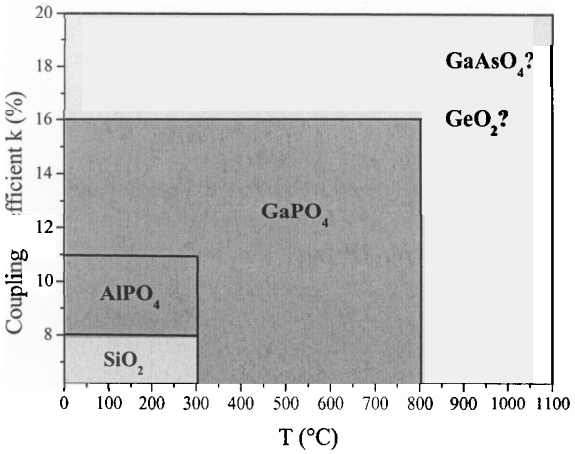


Fig. 8. Performances of α-quartz type materials

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