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Dielectric properties of hydrothermally grown gallium orthophosphate single crystals

SHINICHI HIRANO, PAN CHAE KIM, HIROSHI ORIHARA*, HIROSHI UMEDA*, YOSHIHIRO ISHIBASHI*
*Department of Applied Chemistry, and *Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan*

$GaPO_4$ single crystals of the low-temperature form were hydrothermally grown in 4 M H_3PO_4 solution at 180° C. Single crystals $5.0 \times 5.2 \times 3.7\,mm^3$ in size could be grown in a silica glass vessel of 10 mm inner diameter. The dielectric properties of grown crystals were measured with the electric field parallel ($E \parallel c$) and perpendicular ($E \perp c$) to the c-axis. The values of dielectric constant (ε') of $E \parallel c$ and $E \perp c$ are about 10.3 and 7.8, respectively, at frequencies from 10 kHz to 1 MHz, and these are nearly independent of frequency at room temperature. However, these values increase with temperature in the temperature range about 310 to 500 K and in the frequency region below 1 MHz. Dielectric loss (ε'') increases with increasing temperature at around 300 K ($E \parallel c$) and 310 K ($E \perp c$). From the log σ (conductivity) against $1/T$ plot in the intrinsic region at higher temperatures, the values of activation energy (E) for conduction are calculated to be about 0.17 and 0.33 eV, for $E \parallel c$ and $E \perp c$, respectively.

1. Introduction

The low-temperature form of $GaPO_4$ has an isomorphous structure derived from α-quartz by replacing Si^{4+} ions with Ga^{3+} and P^{5+} ions, which results in a doubling of the unit cell along the c-axis. In the present work, many efforts have been performed for various techniques to grow large $GaPO_4$ single crystals needed for piezoelectric characterization. Single crystals could have been successfully synthesized by the horizontal temperature gradient method with seed crystals in the low-temperature region [1, 2]. $GaPO_4$ single crystals, which have a similar structure to $AlPO_4$ single crystals, have been expected to exhibit superior electrical properties to α-quartz. However, compared with the extensive studies on α-quartz and $AlPO_4$ single crystals for dielectric properties [3–9], there were very few reports on $GaPO_4$ single crystals. This paper describes the features of hydrothermal growth of relatively large $GaPO_4$ single crystals and dielectric properties of grown single crystals.

2. Experimental procedure

The starting particles of $GaPO_4$ for the crystal growth were prepared by the solid state reaction using Ga_2O_3 and $NH_4H_2PO_4$ mixture and the subsequent hydrothermal treatment in H_3PO_4 solution. Typical capsules made of silica, pyrex glass or teflon were used for hydrothermal treatments and the growth runs of $GaPO_4$ single crystals. These experiments were carried out by the horizontal temperature gradient method. The hydrothermal treatment and growth conditions in 4 M H_3PO_4 solution were at temperatures between 150 and 180° C. Morphologies of the grown crystals were observed by optical microscopy. The direction of the c-axis (optical axis) of these crystals was determined using a polarizing microscope on ground and polished crystals. The analyses of prepared raw materials of $GaPO_4$ particles and grown single crystals were carried out by X-ray diffraction (XRD) and X-ray fluorescence (XRF). The quantitative analysis of impurities was carried out by inductively coupled plasma spectrometry (ICP). The water content of grown single crystals used for measurement of dielectric properties was investigated by Fourier transform–infrared spectroscopy (FT–IR).

The electrodes were made by sputtering gold onto both sides of the single crystal specimen and attaching platinum leads with silver paste. The dielectric constants were measured in the frequency region 120 Hz to 1 GHz and in the temperature range 100 to 500 K, with a Hewlett Packard HP 4262 A in the range 120 to 10 kHz, HP 4275 A in the range 10 kHz to 10 MHz and HP 4191 A in the range 1 MHz to 1 GHz.

3. Results and discussion

3.1. Growth of $GaPO_4$ single crystals

The starting particles of $GaPO_4$ were prepared by the solid state reaction with Ga_2O_3 and $NH_4H_2PO_4$ twice at 1000° C for 24 h and subsequently hydrothermally treated at 150° C for 30 h in 4 M H_3PO_4 solution. The synthesized particles were confirmed to consist only of the low-temperature type of $GaPO_4$ formed as a single phase. These single-phase $GaPO_4$ particles were used as a nutrient for the single-crystal growth. The nutrient was set at the low-temperature zone (i.e. dissolution region), while seed crystals were placed in the high-temperature zone (i.e. growth region), because the solubility of $GaPO_4$ was found to be of negative

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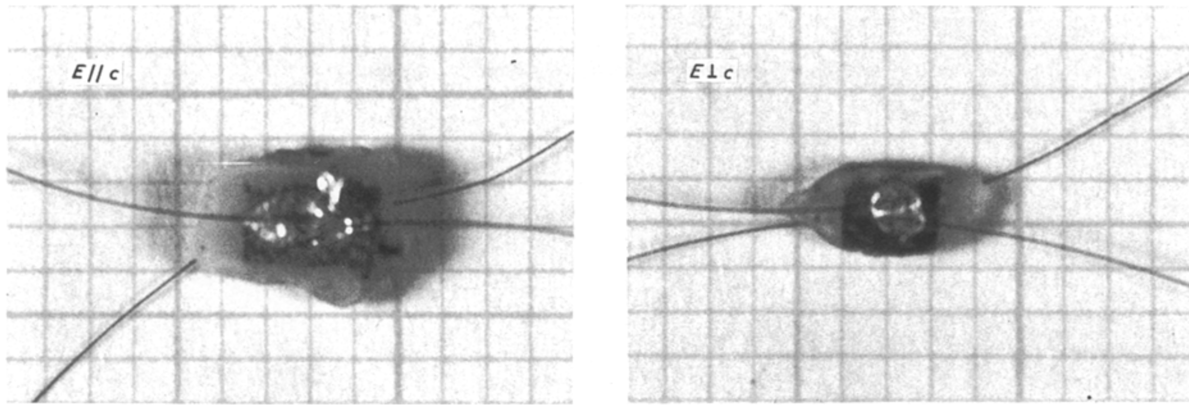

Figure 1 Photographs of ground and polished $GaPO_4$ single crystals used in dielectric constant measurements.

temperature coefficient type in 4 M H_3PO_4 solution [2]. With this arrangement it was expected that the dissolved nutrient would be used to grow the crystal on the seed without the occurrence of spontaneous nucleation on the capsule wall.

Growth runs were carried out under hydrothermal conditions at 180° C for 7 days in 4 M H_3PO_4 solution. Single crystals with rough surfaces and the irregular morphology were grown by the spontaneous nucleation over the two zones at the large temperature difference of 60° C. This result indicated that the supersaturation and the growth rate were too high. It was found that an adequate supersaturation at a horizontal temperature difference of 40° C and a large size of Pyrex or silica glass capsule of 10 mm inner diameter, gave the expected growth results. Large single crystals, about $5.0 \times 5.2 \times 3.7\,mm^3$ in size, with euhedral morphology could be grown with seed crystals.

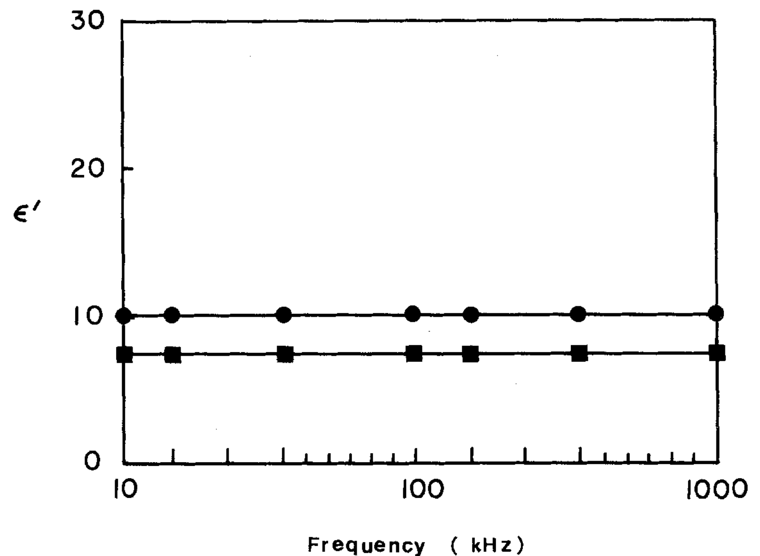

Figure 2 Dielectric constant as a function of frequency for $GaPO_4$ single crystals along (●) $E \parallel c$ and (■) $E \perp c$ at room temperature.

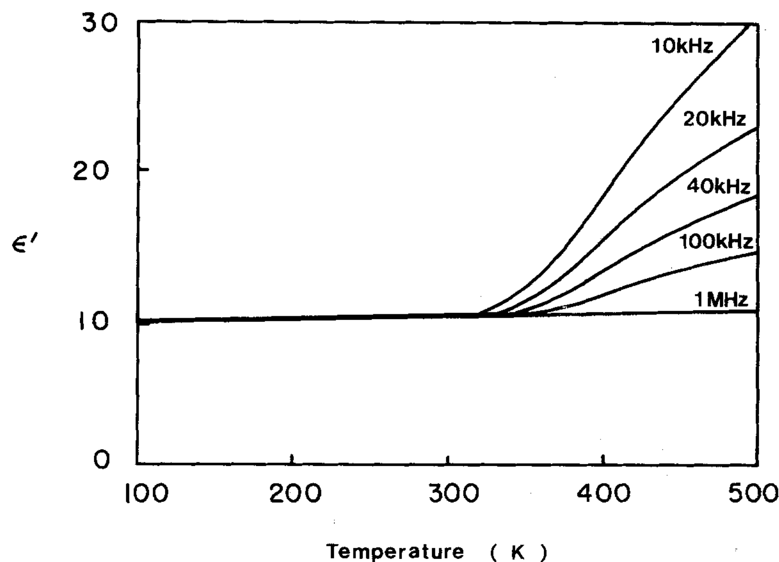

Figure 3 Dielectric constant as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \parallel c$.

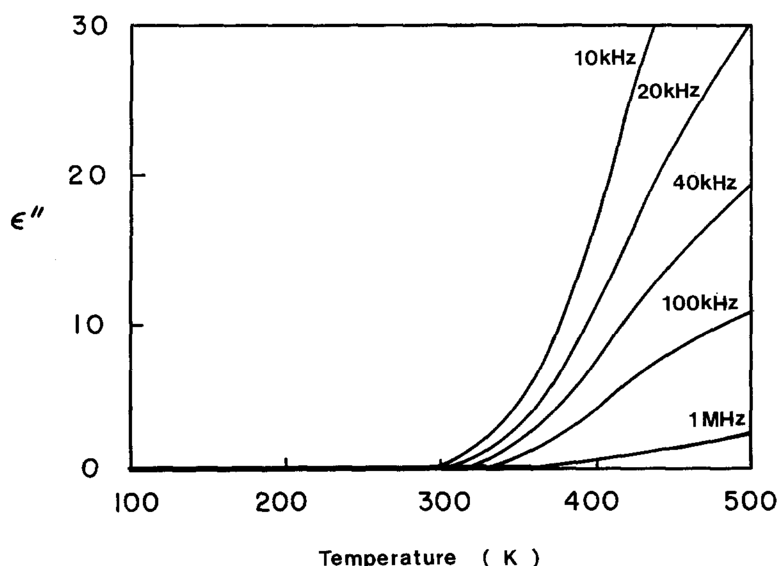

Figure 4 Dielectric loss as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \parallel c$.

Highly pure (99.99%) Ga_2O_3 was used as a starting raw material which contained trace of nickel as found by qualitative analysis with XRF. However, the purification could be performed by the hydrothermal crystal growth of $GaPO_4$ which was contaminated by nickel of below 1 p.p.m. detected with ICP. This impurity level of nickel in grown single crystals does not seem to influence seriously the dielectric properties. The impurity level is lower than that in synthetic quartz single crystals. The grown single crystals of $GaPO_4$ did not exhibit the presence of any OH bonds using FT–IR.

In order to measure the dielectric constants, hydrothermally grown single crystals of $GaPO_4$ were ground and polished as shown in Fig. 1. The final dimensions of the specimens with electrodes were $5.0 \times 1.0 \times 3.7\,mm^3$ ($E \parallel c$) and $2.3 \times 5.3 \times 0.6\,mm^3$ ($E \perp c$), respectively.

3.2. Dielectric properties of grown single crystals

It is well known that the specimen dimensions, flaws and water content of the grown single crystals significantly influence the measurement of dielectric property. Fig. 2 shows the dielectric constant as a function of frequency for $GaPO_4$ single crystals along $E \parallel c$ and $E \perp c$ at room temperature. The values of ε' for $E \parallel c$ and $E \perp c$ are about 10.3 and 7.8, respectively, and are independent of frequencies. The loss factor, ε'', was also measured on these single crystals. The data of ε' and ε'' are shown in Figs 3 to 6. The values of ε' are independent of frequency below 1 MHz at room temperature (Fig. 2) and increase with increasing temperature above around 300 K, as shown in Fig. 3. The values of ε'' are very small up to 300 K, while the values increase steeply above 300 K, as shown in Fig. 4. The changes of ε' and ε'' for orientation $E \perp c$ are quite similar to those for orientation $E \parallel c$, as shown in Figs 5 and 6.

The magnitude of ε' depends on the degree of polarization of charge displacement in the crystals. The dielectric constant of materials consists of a combination of electronic, ionic, dipolar, space charge polarizations, of which the contributions depend on frequencies. At low frequencies all four contributions may be active. The frequency independence of ε' at room temperature in this crystal indicates that mainly electronic and ionic polarizations contribute to the dielectric constant of $GaPO_4$. These two polarizations always exist below 10^{13} Hz. The present result indicates

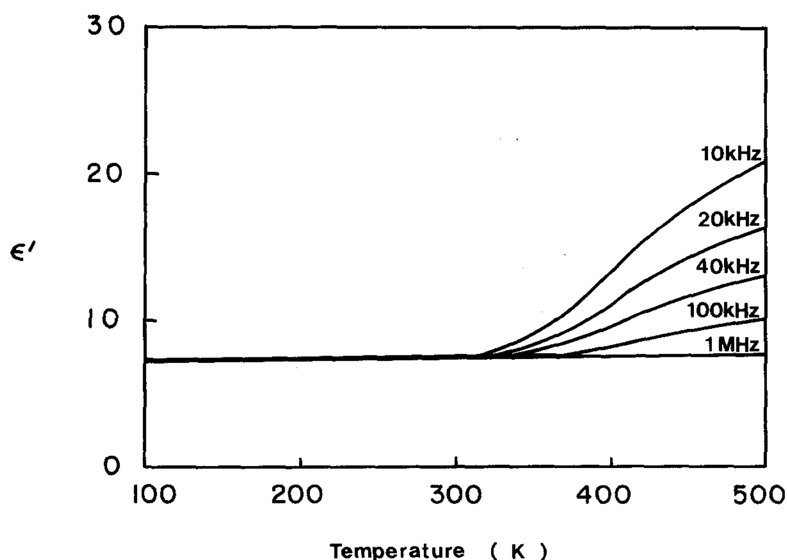

Figure 5 Dielectric constant as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \perp c$.

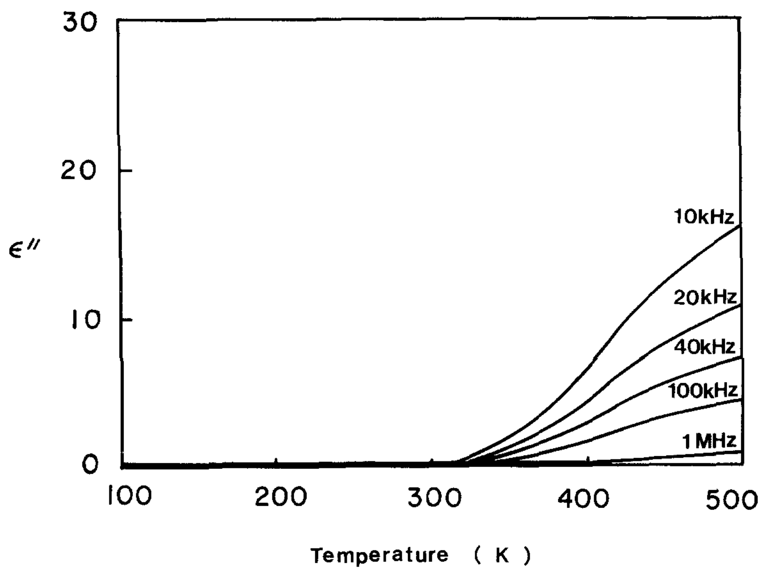

Figure 6 Dielectric loss as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \perp c$.

that the values of ε' on $E \parallel c$ are comparatively larger than those on $E \perp c$. The magnitude of ε' is a measure of the order of the electrostatic binding strength between ions in that direction. The larger values of ε' can be attributed to the lower electrostatic binding strength.

By the fact that the values of ε'' around room temperature are very small, the space charge polarization caused by impurities or crystal defects seems to be small at low temperature. In the lower frequency region, ε'' shows the larger values due to the loss associated with ionic mobility.

The dielectric conductivity (σ) is defined by the equation of $\sigma = \omega \, \varepsilon' \varepsilon_0 \tan \delta$, where $\omega = 2\pi f$. ω is the angular frequency and ε_0 is the dielectric constant in vacuum, $8.85 \times 10^{-12} \, \mathrm{F\,m^{-1}}$, and then f is the measuring frequency. The value of $\tan \delta$ is given by the ratio $\varepsilon''/\varepsilon'$. The temperature dependence of σ reflects the activation energy of conduction which is given by the Arrhenius equation. Conductivities as a function of temperature at various frequencies are plotted in Figs 7 and 8. From the slopes of Figs 7 and 8, the values of activation energy, E, in the intrinsic region at higher temperatures were calculated to be about 0.17 and 0.33 eV, for $E \parallel c$ and $E \perp c$, respectively. In the intrinsic region at higher temperatures, the ionic conductivities are determined by the concentration of thermally induced defects. Therefore, the slightly larger values of activation energy for conduction suggest that it is connected with the movement of lattice defects like vacancies.

4. Conclusions

The starting particles of $GaPO_4$ were prepared as a single phase by the solid state reaction of a

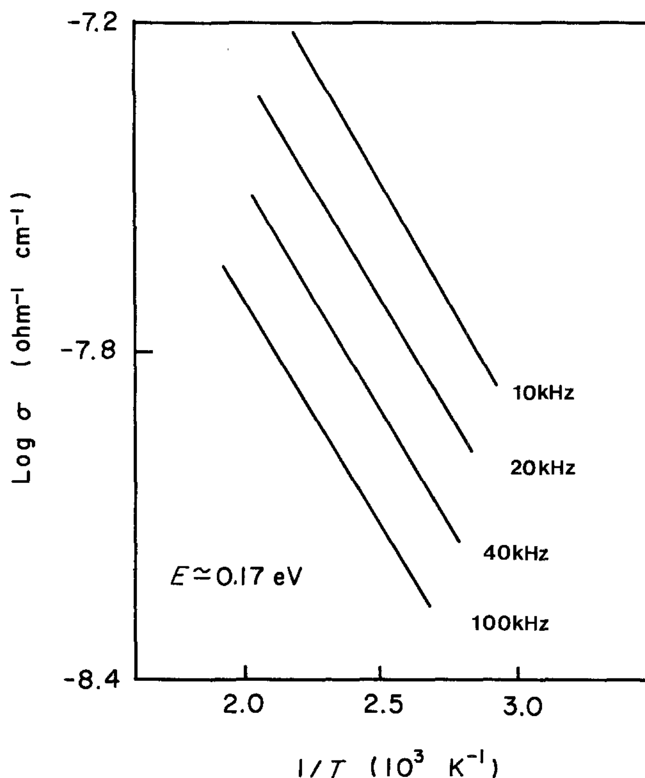

Figure 7 Log conductivity (log σ) as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \parallel c$.

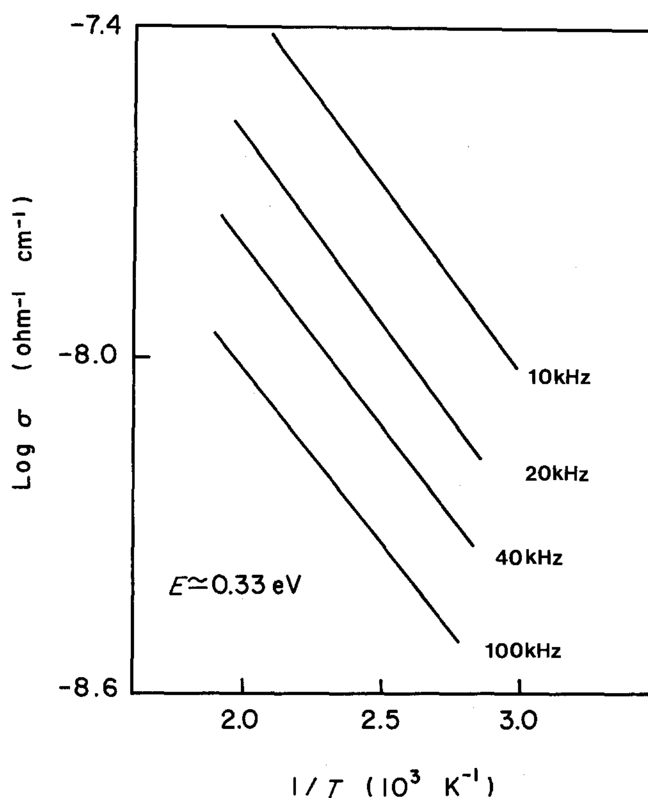

Figure 8 Log conductivity (log σ) as a function of temperature at various frequencies for $GaPO_4$ single crystal along $E \perp c$.

stoichiometric mixture of Ga_2O_3 and $NH_4H_2PO_4$ and subsequently by the hydrothermal treatment. Large single crystals of $GaPO_4$ with euhedral morphology could be grown at lower hydrothermal conditions; at 180° C for 7 days in 4 M H_3PO_4 solution and a horizontal temperature difference of 40° C. Single crystals $5.0 \times 5.2 \times 3.7\,mm^3$ in size were obtained in a silica glass vessel of 10 mm inner diameter. The dielectric properties of grown single crystals have been measured parallel and perpendicular to the *c*-axis. At room temperature, the values of ε' on $E \parallel c$ and $E \perp c$ are about 10.3 and 7.8, respectively, and are frequency independent, and the values of ε'' are very small. In the orientation $E \parallel c$, the values of ε' increase with increasing temperature above 300 K and are dependent on frequencies below 1 MHz. ε'' is quite small up to 300 K and increases with temperature. The values of ε' and ε'' changed in a similar way either for orientation $E \parallel c$ and $E \perp c$. The conductivities of $GaPO_4$ single crystals increase with increasing temperature, and the activation energies on $E \parallel c$ and $E \perp c$ were calculated to be about 0.17 and 0.33 eV, respectively.

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