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Langasite-Type Resonant Sensors for Harsh Environmentsⁱ

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ABSTRACT

Operation of single crystalline $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ (CTGS) and $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) bulk acoustic wave resonators is demonstrated up to 1270 °C and 1470 °C, respectively. The mass sensitivity of such devices is about 35 cm² Hz/μg at 800 °C. Therefore, they are sensitive transducers suited to monitoring, for example, mass deposition processes at high temperatures. The electromechanical loss in CTGS is found to be significantly lower than that in LGS. Platinum coated CTGS samples show a remarkable long-term stability at 1000 °C in air. After an initial period of 300 h, the conductivity is found to remain nearly constant for at least 2400 h. Measurements of resonance frequency of CTGS for 1000 h show a qualitatively similar sequence, with an initial systematic increase followed by nearly constant values. In contrast, measurements on platinum-coated LGS plates show a conductivity decreasing by 15 % over a period of 5000 h.

INTRODUCTION

Piezoelectric single crystals of the langasite family enable novel sensing mechanisms in harsh environments. In particular, they do not exhibit phase transformations up to temperatures of about 1400 °C [1]. The frequencies of bulk-acoustic-wave (BAW) resonators fabricated from these crystals reflect mechanical and electrical properties even of nanometer-scale films deposited on the transducer. Applications of such resonators include nanogram-resolution mass balances, gas sensors and characterization of phase transformations of thin films. The high quality factors (Q) of BAW resonators enable robust and precise sensor-data acquisition, which is facilitated by data acquisition units of reasonable cost in the low megahertz range [2].

The stability of these crystals is a precondition for their application, and this needs to be determined through high-temperature measurements in relevant gaseous environments. This paper explores fundamental properties such as electrical conductivity, resonance frequency, loss and thermal conductivity as a function of temperature and time. Changes in properties at elevated temperatures over long time periods are a particular focus.

EXPERIMENT

Circular bulk acoustic wave (BAW) resonators and rectangular plates were prepared from Czochralski-grown $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ (CTGS) and $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) crystals. The crystal orientations, dimensions, fundamental frequency, and manufacturers of the resonators are listed in Table 1 along with the types of measurement methods that were employed.

The high-temperature measurements on all samples except LGS-II were performed in air at atmospheric pressure. For these samples, about 3 μm thick keyhole-shaped platinum elec-

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trodes were deposited by screen printing (print ink: Ferro Corporationⁱⁱ, No. 6412 0410). Subsequently, the resonators were annealed at 1000 °C for about 30 min. The platinum-electroded samples were mounted in an alumina holder inside a tube furnace. Unless otherwise stated, the samples were heated at a rate of 1 K/min starting at room temperature. The maximum temperature is defined individually for each resonator material and type of experiment. The long-term measurements were performed at 1000 °C with an accuracy in temperature control of ± 5 K (confidence interval of 95 %).

Measurements on LGS-II were performed in a vacuum of 1×10^{-4} Pa with no electrodes on the crystal surface. The crystal holder, noncontacting electrodes, electronic system, and methods employed in these measurements are described elsewhere [3].

Table. 1: Crystal cut, dimensions, fundamental frequency, manufacturer, and measurement methods for samples in this study.

sample name	cut	dimension	frequency	manufacturer	method
CTGS-I	Y	diam. 13 mm	5 MHz	a	α , β
CTGS-II		diam. 10 mm	3 MHz	b	α , β
CTGS-III			5 MHz	c	α , β
LGS-I			2 MHz	d	γ
LGS-II			1.5 MHz	b	α , β
LGS-III					
CTGS- ϵ_Z	Z	$7\times7\times0.5\text{ mm}^3$	-	a	α
CTGS- ϵ_X	X		-		
CTGS- λ_1	Y	diam. 10 mm, thick. 1.0 mm	-	b	δ
CTGS- λ_2		diam. 10 mm, thick. 1.2 mm	-	b	δ
LGS- λ_1		diam. 10 mm, thick. 0.6 mm	-	c	δ
LGS- λ_2		diam. 10 mm, thick. 0.9 mm	-	c	δ
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^a impedance spectroscopy; ^b acoustic measurements on samples with Pt electrodes; ^c acoustic measurements with contactless excitation; ^d thermal conductivity measurements.					

The electrical conductivity σ is determined by impedance spectroscopy in the frequency range from 1 Hz to 1 MHz using an impedance/gain-phase analyzer (Solartron 1260). An electrical equivalent-circuit model consisting of a constant phase element connected in parallel with the bulk resistance R_B is fitted to data. The bulk conductivity σ is then calculated through the relation $\sigma = t(AR_B)^{-1}$, where t and A are the thickness of the sample and the electrode area, respectively. The dielectric constants are determined using the same Solartron 1260 analyzer at a frequency of 10 kHz, which is far below the resonance frequency. The resonant properties are characterized with a high-speed network analyzer (Agilent E5100A). Thereby, the electrical impedance is acquired in the vicinity of the resonance frequency. From those data the resonance frequency and the Q -factor are extracted. This procedure is described in more detail in [4].

The thermal conductivity is determined by a Laser Flash Analytical (LFA) instrument (NETZSCH LFA 427) equipped with a Nd-YAG laser. Measurements are carried out in a flowing nitrogen atmosphere (purity 99.999 %). Details of the method are described in [5]. The mass densities ρ used here are 4.63 g/cm^3 for CTGS [6] and 5.743 g/cm^3 for LGS [7].

ⁱⁱ Identification of commercial products is provided here for technical completeness and does not reflect an endorsement by NIST.

RESULTS

Material properties

The temperature-dependent electrical conductivities of the samples CTGS-I, CTGS-II, CTGS-III and LGS-I are shown in the Arrhenius plot, Fig. 1. As it can be seen from the figure, the CTGS electrical conductivity is lower by more than two orders of magnitude than that of LGS. Moreover, CTGS samples from different manufacturers exhibit different conductivity values in the measured temperature range. The difference in conductivities of the samples CTGS-II and CTGS-III may be caused by the varying properties within a crystal boule. The data for CTGS-I are linear in this presentation below 500 °C, indicating that a single thermally-activated process determines the conductivity. Above about 560 °C, the slope changes (see marks in Fig. 1), which means that a different process prevails. At temperatures below 700 °C, electronic conduction governs the conductivity in LGS [8], and this leads to an Arrhenius relation of the form $\sigma = \sigma_0 \exp[-E_A/(kT)]$ where σ_0 , k and T are a constant pre-exponential coefficient, the Boltzmann constant and the absolute temperature, respectively. At higher temperatures, ionic conduction dominates, and the corresponding Arrhenius expression has a pre-exponential factor that is inversely proportional to T . Activation energies obtained by fitting the data to these expressions and the temperature ranges for fitting are summarized in Table 2. Potentially, the samples are far from the equilibrium state during these short-term measurements. Nevertheless, the activation energies for the electrical conductivity of the samples LGS-I and CTGS-I are determined.

Table 2. Activation energies for σ and σT at different temperatures.

CTGS-I	$T = 420\text{ °C} - 500\text{ °C}$	$E_{A,\sigma} = 0.75 \pm 0.03\text{ eV}$	$T = 560\text{ °C} - 880\text{ °C}$	$E_{A,\sigma T} = 1.16 \pm 0.03\text{ eV}$
LGS-I	$T = 400\text{ °C} - 700\text{ °C}$	$E_{A,\sigma} = 0.82 \pm 0.05\text{ eV}$	$T = 700\text{ °C} - 1000\text{ °C}$	$E_{A,\sigma T} = 1.15 \pm 0.05\text{ eV}$

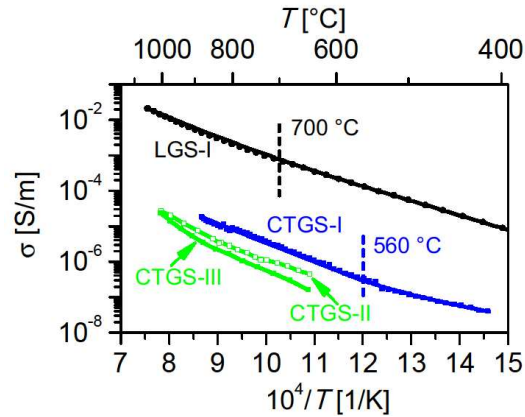


Fig. 1: Temperature dependent electrical conductivity of CTGS and LGS.

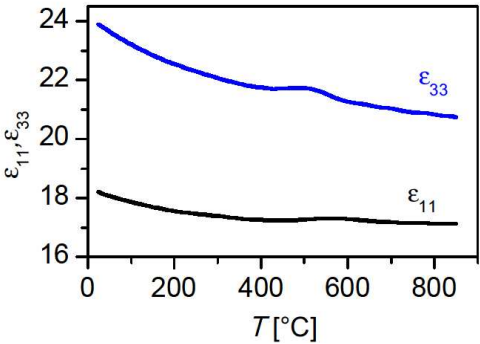


Fig. 2: Temperature dependent relative dielectric constants of CTGS measured at 10 kHz.

Fig. 2 shows the temperature dependence of the relative dielectric constants ϵ_{11} and ϵ_{33} of CTGS, which decrease with increasing temperature. Fig. 3 presents the thermal conductivity λ of Y-cut CTGS and LGS as a function of temperature.

Resonant properties

Fig. 4 presents the temperature dependent resonant frequency f of the fundamental mode of CTGS and LGS resonators relative to that at room temperature (RT). Resonance peaks are ob-

served even at 1270 °C and 1470 °C for CTGS and LGS, respectively. The resonance frequency of sample CTGS-I decreases approximately linearly with temperature over the entire measured range. In contrast, LGS resonators show a parabolic behavior which is the same (on the scale of Fig. 4) for resonators machined from the two LGS crystals from different manufacturers.

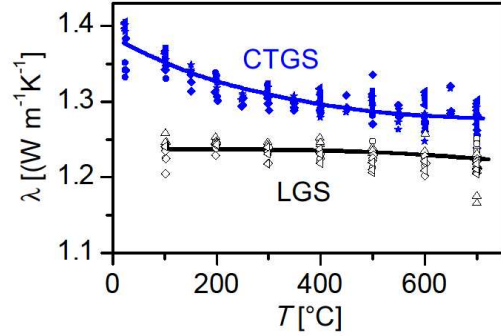


Fig. 3: Temperature-dependent thermal conductivity of CTGS and LGS.

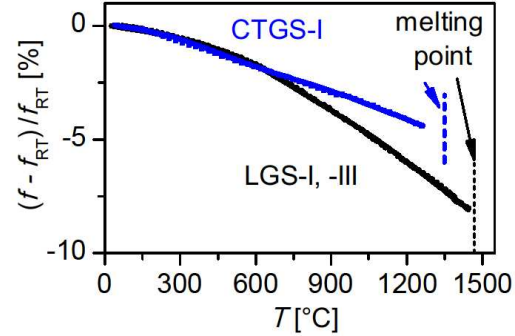


Fig. 4: Temperature-dependent relative change of the resonance frequency of CTGS and LGS.

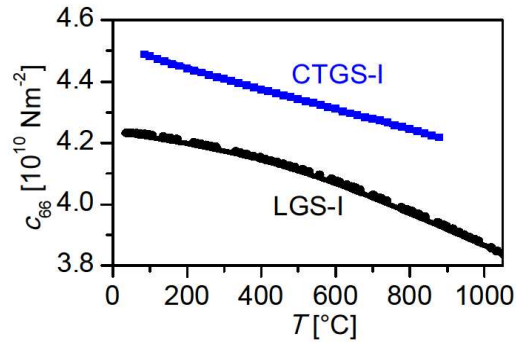


Fig. 5: Elastic constants c_{66} of samples CTGS-I and LGS-I as a function of temperature.

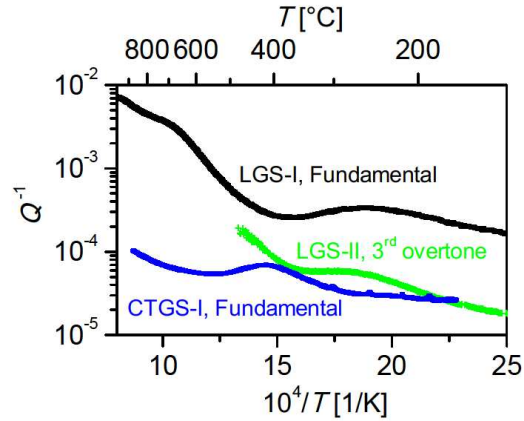


Fig. 6: Q^{-1} of fundamental modes of CTGS-I and LGS-I and the third overtone of LGS-III.

The temperature-dependent stiffness coefficients c_{66} of samples CTGS-I and LGS-I are shown in Fig. 5. The values are determined by applying the physical model and the fit procedure described in [4] and used to calculate the mass sensitivity $S = -A\Delta f/\Delta m = 2f^2/(\rho c_{66})^{1/2}$ [4] of 5 MHz CTGS and LGS resonators presented in Table 3. A , Δf and Δm represent the active electrode area, the frequency shift and the mass change, respectively. The mass sensitivities of CTGS and LGS resonators are lower than that of AT-cut quartz listed in Table 3 [9], but are still sufficiently high for sensitive transduction devices.

Table 3. Mass sensitivity of 5 MHz resonators at different temperatures [$\text{cm}^2 \text{ Hz}/\mu\text{g}$].

	cut	25 °C	400 °C	800 °C
α -quartz	AT	56.5	-	-
CTGS	Y	34.6	35.1	35.7
LGS	Y	32.1	32.4	33.1

Despite the fact that resonances can be detected in measurements of CTGS and LGS resonators even at temperatures close to the melting point of the crystals, some practical factors are

limiting their usage at high temperatures. In general, the applicability of high-temperature resonators is determined by their quality factor Q . Fig. 6 shows the loss-related parameter Q^{-1} as a function of temperature in the form of Arrhenius plots for the 5 MHz fundamental modes of resonators LGS-I and CTGS-I. The losses are governed by different mechanisms depending on the actual temperature [3]. Measurements of Q^{-1} for the 6 MHz third overtone of sample LGS-II are also shown in Fig. 6. The data from these samples show similar slopes near 500 °C. However, the loss in LGS-II below 300 °C is approximately one order of magnitude lower than that of LGS-I and comparable in magnitude to that of CTGS. This large difference between LGS-I and LGS-II cannot be attributed to the frequency dependence of internal loss mechanisms, which have dependences no stronger than $1/f$ at a given temperature [3]. It can be attributed to variability in the quality of crystals from different manufacturers and/or greater contributions to the loss from contacting excitation (with LGS-I) than from contactless excitation (with LGS-II).

Long-term behavior

In order to determine the stability of the resonators, the long-term properties of CTGS and LGS specimens, grown in an atmosphere of pure N₂ and a mixture of 98 % N₂ and 2 % O₂, respectively, are examined at 1000 °C in air. The time dependent electrical conductivities of samples CTGS-II, CTGS-III and LGS-III are shown in Fig. 7.

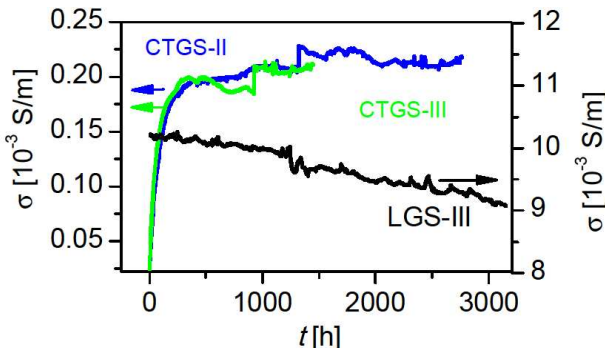


Fig. 7: Electrical conductivity of CTGS-II, CTGS-III and LGS-III samples at 1000 °C as a function of time.

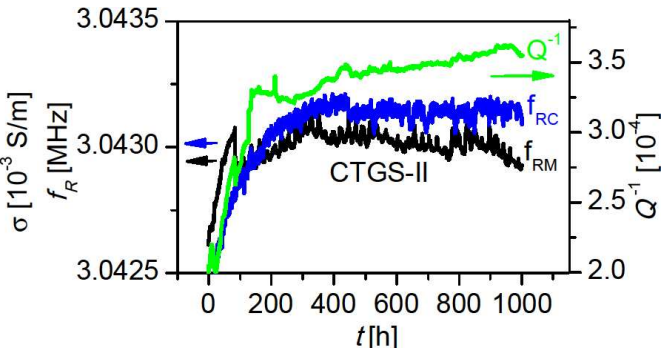


Fig. 8: Measured and temperature-compensated resonance frequency and $(Q)^{-1}$ of CTGS-II at 1000 °C as a function of time.

The initial conductivities of samples CTGS-II and CTGS-III are equal to $(2.6 \pm 0.2) \cdot 10^{-5}$ S/m and $(2.4 \pm 0.2) \cdot 10^{-5}$ S/m, respectively, as shown also in Fig. 1 for the short-term temperature dependent measurements. However, within approximately 300 hours of thermal treatment, the electrical conductivity of samples CTGS-II and CTGS-III increases by about of one order of magnitude. After this period of time the conductivity remains nearly stable with maximal fluctuation $\pm 2 \cdot 10^{-5}$ S/m. The latter is largely caused by the temperature fluctuations. The shift at about 1325 h for CTGS-II sample and at about 925 h for CTGS-III sample is related to an interruption of the experiment for about 150 h and 24 h, respectively. The origin of conductivity increase of the CTGS samples within the first 300 h is a subject of further investigations. The measured electrical conductivity of sample LGS-III decreases by about 15 % over a period of about 5000 h. Fig. 7 shows the period between 2000 h and 5000 h. This decrease is potentially caused by electrode degradation. However, this hypothesis also requires further investigation.

Fig. 8 shows the change of the fundamental resonant frequency of resonator CTGS-II as a function of time during annealing at 1000 °C. In order to exclude temperature effects from the resonance frequency measurements, a temperature compensation is applied: $f_{RC} = f_{RM} + c(T -$

1000 °C), where f_{RC} is the temperature compensated resonance frequency, f_{RM} is the measured resonance frequency, $c = \Delta f / \Delta T$ is the temperature coefficient at 1000 °C that reflects the change of resonance frequency with the temperature, and T is the measured temperature.

As can be seen from Fig. 8, a relatively large frequency shift of about 6 kHz is observed during the first 300 hours of investigation. The shift correlates with the time-dependent conductivity measurements (see Fig. 7). After 300 h, the temperature-compensated resonance frequency appears to be nearly constant with a short-term scatter ± 100 Hz, which can be associated with a variation of ± 0.5 °C in temperature. The inverse Q factor of CTGS-II resonator as a function of time is also shown in Fig. 8. Its behavior is similar to the electrical conductivity and resonance frequency with a relative rapid increase at the initial stage and much smaller changes after 300 h at 1000 °C.

CONCLUSIONS

In summary, high-temperature properties of CTGS and LGS crystals were studied. Measurements of the temperature dependent electrical conductivity show that values for CTGS are at least two orders of magnitude smaller than those of LGS. This great difference is of practical importance for sensors, since the conductivity can dominate the total loss at high temperatures [3]. Measurements of the temperature dependence of Q^{-1} show that losses in CTGS resonators are much less than those of LGS at temperatures above 500 °C, consistent with conduction-related loss being dominant in this range. Differences in the results from two LGS samples at lower temperatures indicate that variability of crystals and/or the degree of mechanical contact in acoustic measurements can substantially affect the loss in this range. The long-term behavior of CTGS shows that the conductivity and resonance frequency of CTGS exhibit essential drift during the initial 300 h. After this period of time, these properties remain nearly stable.

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