Material Parameters of $Ca_3TaGa_3Si_2O_{14}$ (CTGS) Piezoelectric Single Crystal at Extreme Temperatures

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***Abstract*—The complete set of material parameters including elastic, dielectric and piezoelectric constants as well as thermal expansion were measured by different methods for the promising piezoelectric single crystal CTGS at extreme temperatures (4.2 – 1170 K).**

Keywords—CTGS; material parameters; extreme temperatures.

I. INTODUCTION

Single crystals of the langasite family are promising piezoelectric materials for various applications as ultrasonic transducers, bulk- and surface acoustic wave filters, resonators, actuators, and different kinds of sensors. Langasites have a trigonal structure (space group P321) as α-quartz but compared with piezoquartz they exhibit higher electromechanical coupling and absence of any phase transition below their melting point (1300…1500 °C). Specific features of the structure give the opportunity to synthesize more than hundred compounds with the structural formula $A_3BC_3D_2O_{14}$. Most crystals of the family (LGS, LGT, LGN) have a disordered structure resulting in increased dielectric and acoustic loss. Unlike crystals mentioned above, CTGS has an ordered structure resulting in better properties at elevated temperatures. In spite of many publications devoted to CTGS material parameters, its properties are still contradictory even at room temperature not to mention the elevated temperatures [1-6]. As for the cryogenic temperature range, there are no published data for now. To our best knowledge, data on the thermal expansion of CTGS are not available as well.

In this contribution, the full characterization of dielectric, piezoelectric and elastic constants as well as thermal expansion of CTGS single crystal is presented for a wide temperature range including cryogenic temperatures.

II. SAMPLES AND METHODS

CTGS single crystals used in this study were grown by the well-developed Czochralski technique by JSC Fomos-Materials (Moscow, Russia), and by Leibniz Institute for Crystal Growth, IKZ (Berlin, Germany). A set of rods and plates of different crystallographic orientations with the dimensions of 2x0.5x10 mm^3 and 10x10x0.5 mm^3, respectively, was prepared for electromechanical resonant method and dielectric spectroscopy. Crystal cubes of about 7x7x7 mm^3 size of the appropriate orientations were prepared for both ultrasonic pulse-echo and thermal expansion measurements. The resonant measurements were carried out with a network analyzer (Agilent E5100A). Sound velocity measurements were performed by a RITEC Advanced Ultrasonic Measurement System RAM-5000. Thermal expansion was determined using inductive Netzsch DIL-402C dilatometer and a homemade capacitive device. Additionally, piezoelectric coefficients were derived using laser Doppler vibrometry (Polytec OFV-505).

III. THERMAL EXPANSION

The thermal expansion coefficients were measured in the 2 K to 1200 K temperature range. The measurements were carried out on a cube sample with Y- and Z-cut faces (100 K – 1200 K) and on thin plates along Y- and Z directions (2 K – 100 K). Note that for the 32 class crystals, the X- and Y directions are equivalent from the point of view of the thermal expansion properties. The results obtained are shown in Figs. 1-2.

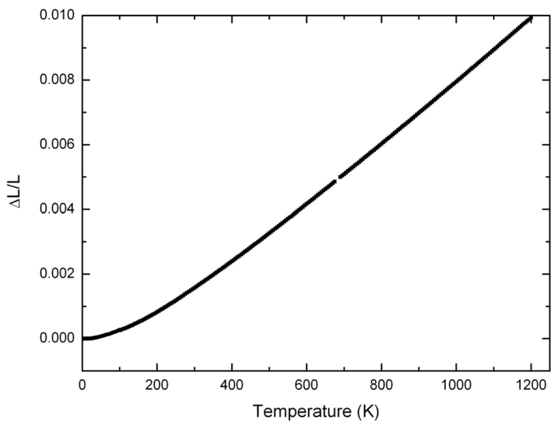

Figure 1. Relative length change versus temperature for the Y direction of CTGS single crystal.

Financial support from the German Research Foundation (DFG grants SO 1085/2-1 and FR 1301/21-1) as well as support from German BMBF (InnoProfile-Transfer 03IPT610Y) are gratefully acknowledged. Yu.S. and H.F. acknowledge the support of the Energie-Forschungszentrum Niedersachsen, Goslar, Germany

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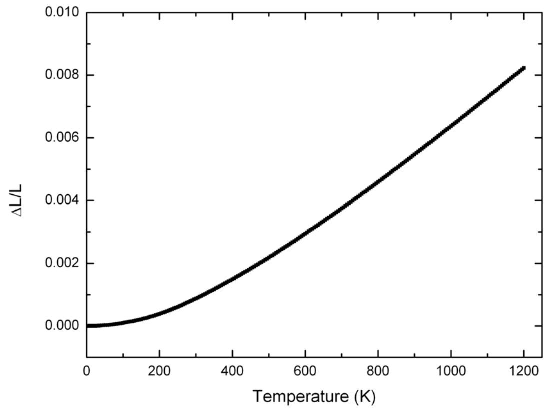

Figure 2. Relative length change versus temperature for the Z direction of CTGS single crystal

It is seen that at elevated and high temperatures ΔL/L for both Y- and Z directions vary almost lineary while at T ~ 200 K the slope changes and a plot saturates at cryogenic temperatures. Such behavior is qualitatively similar to that found in α-quartz crystal [7]. Thermal expansion data were used for the correct determination of the materials parameters at extreme temperatures.

IV. DIELECTRIC CONSTANTS

The relative dielectric constants ε_{11} and ε_{33} were measured at a frequency of 10 kHz which is far below frequency position of any electromechanical resonance. Temperature dependences of the dielectric constants at temperatures between 4.2 and 300 K are depicted in Figs. 3, 4.

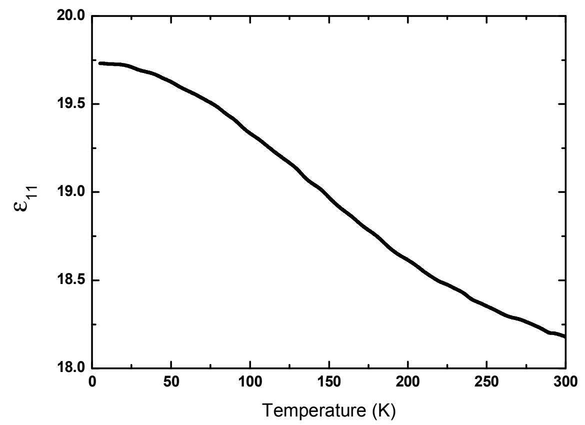

Figure 3. Relative dielectric constant ε_{11} versus temperature for CTGS single crystal

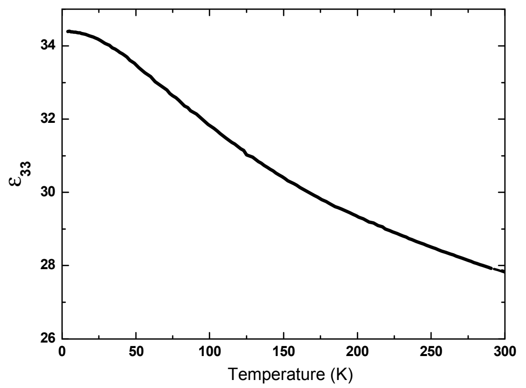

Figure 4. Relative dielectric constant ε_{33} versus temperature for CTGS single crystal

High temperature tails of the dielectric constants are presented in Ref. [6]. As is seen from Figs. 3, 4, both ε_{11} and ε_{33} increase with temperature decreasing followed by a saturation at low temperatures. Notice that this behavior is typical of so called incipient ferroelectrics and usually explained by quantum effects at cryogenic temperatures.

V. ELASTIC AND PIEZOELECTRIC CONSTANTS AT EXTREME TEMPERATURES

Piezoelectric response of CTGS was found to be strong in the whole measured temperature range including both very low (cryogenic) and very high temperatures confirming the successful operation of this crystal. As for acoustic attenuation, it was found to be very low at cryogenic temperatures while still reasonable at very high temperature. Figs. 5, 6 show ultrasonic pulse-echo patterns for Y-cut CTGS samples at

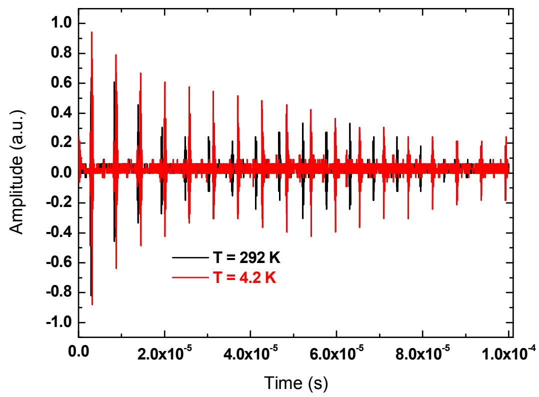

Figure 5. Pulse-echo pattern for the Y-cut CTGS single crystal at 292 K (black line) and 4.2 K (red line).

room temperature and at 4.2 K and 1125 K, respectively. Sound excitation and receiving were realized using the internal piezoelectric effect of the crystal.

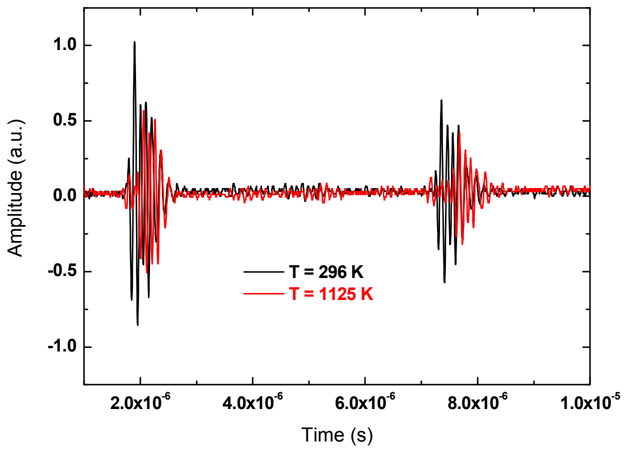

Figure 6. Pulse-echo pattern for the Y-cut CTGS single crystal at 296 K (black line) and 1125 K (red line).

The common feature of the temperature behavior of the elastic constants in CTGS is an increase with temperature decreasing followed by a saturation at cryogenic temperatures (the only exclusions are C_{44} and C_{66}). Figs. 7 and 8 show as examples temperature dependences of C_{11} and C_{44} elastic constants, respectively in the temperature range from 4.2 K to 1170 K.

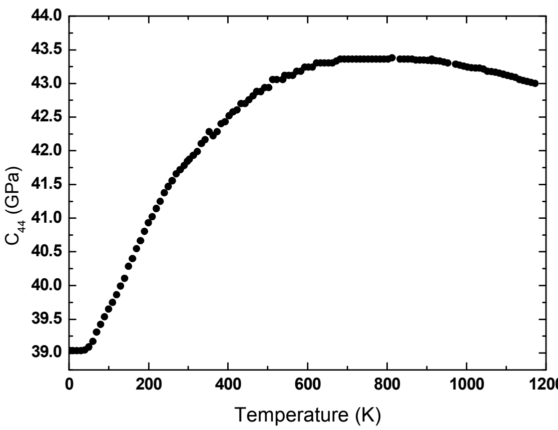

Figure 7. Temperature dependence of the elastic constant C_{44} for CTGS single crystal.

As examples, Figs. 9 and 10 represent temperature dependence of the elastic constants C_{33} and C_{12} in the low temperature range.

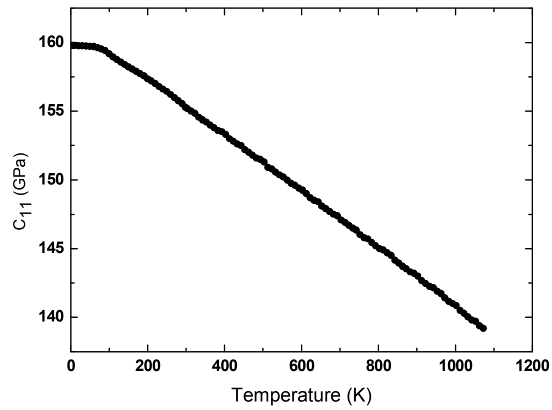

Figure 8. Temperature dependence of the elastic constant C_{11} for CTGS single crystal.

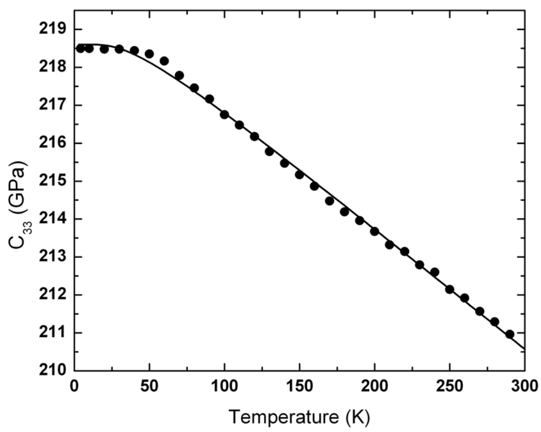

Figure 9. Temperature dependence of the elastic constant C_{33} for CTGS single crystal at temperatures between 4.2 and 300 K

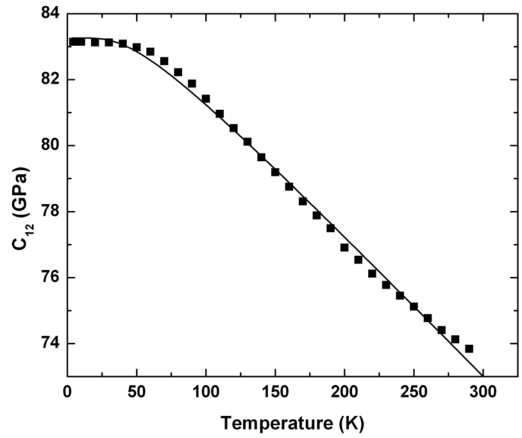

Figure 10. Temperature dependence of the elastic constant C_{12} for CTGS single crystal at temperatures between 4.2 and 300 K

The saturation of the elastic constants at cryogenic temperatures is connected with quantum effects; therefore C_{ij} versus T dependences can be fitted using the Varshni function developed on the base of Einstein oscillator model [8]:

$$C_{ij}(T) = C^0 - \frac{s}{\exp(t/T) - 1} \qquad (1)$$

where C^0 is the elastic constant at zero temperature, t relates to the Einstein temperature Θ_E, and s is the anharmonicity parameter of the lattice. The solid lines in Figs. 9 and 10 show least square fitting of the function (1) to the experimental points. The fitting parameters for different elastic constants are: C^0 =159.8 GPa, s = 4.08 GPa, t = 196 K for C_{11}; C^0 = 83.2 GPa, s = 5.9 GPa, t = 137 K for C_{12}; C^0 = 218.5 GPa, s = 3.28 GPa, t = 105.4 K for C_{33}. Finally, elastic, piezoelectric and dielectric constants of CTGS single crystal at extreme temperatures are presented in Table I. Notice that piezoelectric constant d_{11} at high temperatures was derived using different experimental techniques: pulse-echo method (PE), resonance method (R) and laser Doppler vibrometry (LDV).

TABLE I MATERIAL PARAMETERS OF CTGS SINGLE CRYSTAL AT EXTREME TEMPERATURES

Material constant	4.2 K	1073 K
C_{11} (GPa)	159.8	139.2
C_{12} (GPa)	83.15	60.1
C_{13} (GPa)	70.6	69.5
C_{14} (GPa)	1.2	0.57
C_{33} (GPa)	218.3	184.9
C_{44} (GPa)	39.02	43.1
C_{66} (GPa)	38.3	39.6
e_{11} (C/m^2)	-0.36	-0.43
e_{14} (C/m^2)	0.62	0.644
d_{11}(pm/V) (PE)	-4.81	-5.67
d_{11}(pm/V) (R)		-5.61
$\lvert d_{11} \rvert$ (pm/V) (LDV)		5.38
$\varepsilon_{11}/\varepsilon_0$	19.7	17.3
$\varepsilon_{33}/\varepsilon_0$	34.4	23.2

VI. HIGH TEMPERATURE STABILITY

The long-term properties of CTGS single crystals at high temperature (1000° C) were examined by measuring AC conductivity and resonance frequency of Y-cut shear thickness mode electromechanical resonators in air during 5250 hours. Fig. 11 shows electrical conductivity of two CTGS samples grown by JSC Fomos-Materials and IKZ, respectively. As it can be seen from the figure, the conductivity of both samples increases strongly within the first 500 hours of the thermal treatment and remains nearly stable during the next 1500 hours. Then, between 2000 – 5250 hours the conductivity of both samples decreases by about 20%. Fig. 12 represents the change of the resonance frequency of Y-cut resonator made from IKZ crystal. The change of the resonance frequency was about 0.25% during 5250 hours of the thermal treatment at 1000° C.

The Q-factor of the resonators at 1000° C was found to be about 3500.

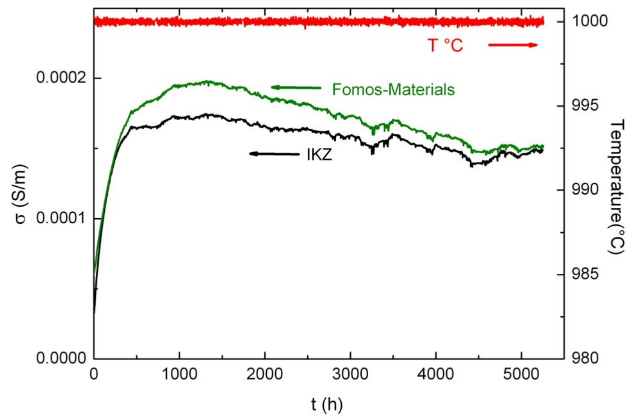

Figure 11. Electrical conductivity versus time for CTGS samples from two sources. Temperature is 1000°C.

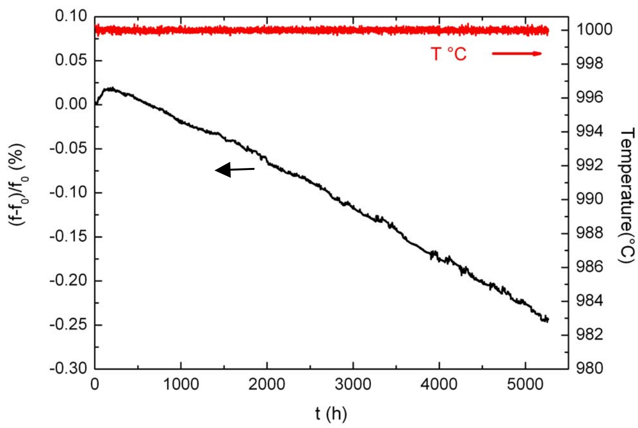

Figure 12. Relative change of the resonance frequency versus time for Y-cut CTGS resonator made from IKZ crystal. Temperature is 1000°C.

VII. CONCLUSIONS

The complete sets of material parameters were obtained for CTGS single crystals at extreme temperatures taking into account thermal expansion. Strong piezoelectric response as well as long-term stability at very high temperature predestine CTGS crystal as promising material for microacoustic and sensor applications for an extremely wide temperature range.

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