Influence of growth conditions on the optical, electrical resistivity and piezoelectric properties of \( \text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14} \) single crystals

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Piezoelectric \( \text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14} \) (CTGS) single crystals are grown by the Czochralski technique and investigated in detail for high temperature sensor applications. The influence of the oxygen partial pressure during the growth on material properties is investigated by the use of Ir crucibles, as well as Pt ones. Colorless crystals are obtained, indicating that the typical yellowish coloration of CTGS crystals is related with the use of Ir-crucibles. Colored crystals present three absorption bands at 340, 450 and 1790 nm, however, related crystal defects do not affect the electrical properties of grown crystals. Dielectric and piezoelectric properties do not vary significantly with the growth conditions. Instead, it is found that the electrical resistivity depends on the oxygen partial pressure and it is higher for CTGS crystals grown under oxygen-less atmosphere.

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1. Introduction

High temperature (HT) piezoelectric sensors, such as piezoelectric combustion pressure sensors and gas injectors, are highly desired for a broad range of applications in industry and science due to their fast response, high sensitivity and compactness. Well-known piezoelectric materials, however, have different drawbacks for HT applications, like phase transition, pyroelectricity, instability under oxidizing or reducing atmospheres, and difficult single-crystal growth. For example, a phase transition takes place in Perovskite PZT and \( \alpha \)-quartz, while oxyborate crystals (ReCOB) and \( \text{GaPO}_4 \) present pyroelectricity and a difficult growth, respectively. On the other hand, AIN is limited by a poor oxidation resistance at HT. As an alternative for HT applications, the piezoelectric langasite family is attracting much attention. These crystals do not present any phase transition up to their melting point (1300–1500°C), exhibit good piezoelectric properties, are non-pyroelectric, and can be grown by the Czochralski (Cz) technique. For example, at room temperature (RT), the piezoelectric coefficient \( d_{11} \) of langasite single crystals ranges between 4–7 pC/N, which is larger than that of \( \alpha \)-quartz, namely 2.31 pC/N.

Langasite crystals crystallize in the trigonal space group P321 with the formula \( \text{A}_2\text{BC}_3\text{D}_2\text{O}_{14} \), where \( \text{A} \) represents the dodecahedral site, \( \text{B} \) the octahedral one, and \( \text{C} \) and \( \text{D} \) are two different tetrahedral sites. The langasite family is generally classified into two types depending on the ionic distribution. In ordered langasites each cationic site is occupied by a different element, while in disordered ones, the same element enters in more than one site. This is the case of e.g. \( \text{La}_3\text{Ga}_5\text{Si}_3\text{O}_{14} \) (LGS), in which \( \text{Ga}^{3+} \) ions occupy the \( \text{B} \) and \( \text{C} \) sites, plus half of the \( \text{D} \) site in a random way. In comparison with disordered crystals, ordered ones possess a higher acoustic velocity, a better thermal stability of piezoelectric properties at HT, and a resistivity one or even two orders of magnitude higher. Generally, a high resistivity is requested to reduce the electrical losses and to improve the signal/noise ratio of the sensors. In addition, the bandwidth of these can be extended by a large time constant \( RC \), where \( R \) and \( C \) are the electrical resistance and the capacitance, respectively.

Among the ordered langasite crystals, \( \text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14} \) (CTGS) is of particular interest since it possesses a high resistivity, with a value over \( 10^9 \Omega \cdot \text{cm} \) at 500°C. Also, its \( RC \) has been reported to be as high as 2.36 ms at 500°C (approximately two orders of magnitude higher than that of LGS), which reinforces its potential for high temperature and low frequency sensing applications. Further, it exhibits a higher thermal stability of dielectric and piezoelectric properties compared to the other three promising ordered langasites.

Reported CTGS single crystals, grown so far with Ir crucibles, present a yellowish coloration, although according to their bandgap and constituents they should be colorless. Ir contamination is considered to be the origin of the coloration in langasite crystals. Therefore, the use of a different crucible for growth is needed in order to elucidate if Ir traces affect the intrinsic properties of CTGS crystals. Furthermore, the influence of oxygen partial pressure during growth on the properties of CTGS has not been investigated so far, mainly due to the use of Ir crucibles, which critically limit the maximum concentration of oxygen to a few percent.

In this work, CTGS single crystals were grown by Cz method under various oxygen partial pressures with both Ir and Pt crucibles. By the use of Pt crucibles for the first time, we aimed at the growth of CTGS crystals free from Ir traces, on the one hand,
and at the application of higher oxygen partial pressures during the growth, on the other hand. Grown crystals were characterized in terms of compositional analysis, transmittance, powder X-ray diffraction (XRD), electrical resistivity, and piezoelectricity. The latter two properties were measured as a function of temperature to evaluate the actual potential of CTGS for HT sensor applications.

2. Experimental

CTGS single crystals were grown by the Cz method with a 30 kW RF generator. High purity raw materials (≥99.99%) of commercially available CaCO₃, Ta₂O₅, Ga₂O₃ and SiO₂ were weighed stoichiometrically according to Ca₃TaGa₃Si₂O₁₄ and subsequently mixed. Then powders were pressed at around 30 MPa, and afterwards, sintered at 1200°C for 20 h. The reacted polycrystalline CTGS ingots were loaded into the crucibles. Single crystals were pulled with a-axis CTGS seeds. The rotation and pulling speeds were fixed at 12 rpm and 0.5 mm/h, respectively. Table 1 lists the growth conditions in terms of crucible type and growth atmosphere.

The chemical composition of grown single crystals was determined by the induced coupled plasma optical emission spectroscopy (ICP-OES), using a SPS3520UV-DD model from SII nano technology Inc. Data collection of powder XRD was carried out using a Rigaku SmartLab 9 kW diffractometer equipped with a CuKα radiation. The lattice parameters of CTGS were calculated from XRD data using the software FullProf. The lattice constants are fitted by following equations:

\[ a = 8.121663(1) \text{Å}, \quad b = 4.980483(4) \text{Å}, \quad c = 5.026565(4) \text{Å} \]

The necessary sample cuts to determine the coefficients of the various materials properties (dielectricity, piezoelectricity and elasticity) are given in detail in reference.5)

3. Results and discussion

CTGS single crystals were successfully grown by the Cz method under different oxygen partial pressures. Crystals grown with Ir crucibles present a yellow coloration. Instead, those obtained with Pt crucibles are colorless, suggesting the suppression of crystal defects that cause the yellow coloration. As examples, Figs. 1(a) and 1(b) show the photographs of CTGS single crystals grown with an Ir crucible under N₂+1%O₂ and a Pt crucible under air, respectively. As can be seen, grown crystals are free of cracks and inclusions, always exhibiting a strong faceting character. Using a Back-Reflection Laue apparatus, the wide crystal facets were identified to be γ-planes, while the perpendicular narrow ones correspond to c-planes.

The chemical composition of as-grown CTGS single crystals was analyzed by the ICP-OES technique, and the results are shown in Table 2. Neither Ir nor Pt were detected in the crystals within the detection limit of the ICP-OES technique. As it can be seen, there is no any clear compositional shift with the growth conditions, and rather all samples present a stoichiometric composition within the experimental error of the detection technique.

Temperature dependent XRD of powdered CTGS crystals was measured from RT to 1200°C. All obtained diffraction patterns present the same reflections. As an example, Fig. 2 shows the XRD pattern measured at 1200°C together with the simulated one, from single-crystal structure analysis, using the software Mercury. It can be seen that they are in very good agreement with each other, indicating the absence of secondary phases and of a crystallographic phase transition.

The lattice parameters of CTGS were calculated from XRD data using the software FullProf. The lattice constants are given as a = 8.121663(1) Å and c = 4.980483(4) Å at RT, and both increase with temperature, reaching the value of a = 8.200913(1) Å and c = 5.026565(4) Å at 1200°C. Thermal expansion ratio of CTGS crystal versus temperature is shown in Fig. 3. The experimental data are fitted by the following equations:

\[ \alpha = (1-\varepsilon)^{-1} \]

\[ \gamma = \frac{1}{\alpha} \]

Table 1. Growth conditions of CTGS single crystals

| Run No. | Crucible | Growth atmosphere |
|---------|----------|--------------------|
| 1       | Ir       | N₂                |
| 2       |          | N₂+1%O₂           |
| 3       |          | N₂                |
| 4       | Pt       | N₂+1%O₂           |
| 5       |          | Air               |

Table 2. ICP-OES results of grown CTGS single crystals

| Crucible | Atmosphere | Ca (±0.08) | Ta (±0.02) | Ga (±0.06) | Si (±0.08) |
|----------|------------|------------|------------|------------|------------|
| Ir       | N₂        | 2.99       | 1.00       | 3.00       | 2.02       |
|          | N₂+1%O₂   | 3.02       | 0.97       | 3.07       | 1.94       |
| Pt       | N₂        | 2.97       | 1.01       | 3.01       | 2.01       |
|          | N₂+1%O₂   | 2.98       | 1.01       | 2.99       | 2.02       |
|          | air       | 3.03       | 0.97       | 3.07       | 1.94       |

Fig. 1. Photographs of CTGS single crystals grown with (a) an Ir crucible under N₂+1%O₂ and (b) a Pt crucible under air.
where $\Delta a/a_0$ and $\Delta c/c_0$ are the increase of lattice parameters respect to RT, $a_0$ and $c_0$ are the lattice parameters at RT, and $T$ is the temperature in Celsius. On the other hand, the average thermal expansion coefficients obtained by linear fits are $\alpha_a = 8.49 \times 10^{-6}$ and $\alpha_c = 8.17 \times 10^{-6} \text{K}^{-1}$. These two values are quite close, indicating that CTGS single crystal exhibits a weak anisotropic thermal expansion, what is beneficial to prevent cracking in HT applications.

The RT density of CTGS measured by the Archimedes method is $4.616 \pm 0.007 \text{g/cm}^3$, which is in good agreement with the calculated value of $4.62 \text{g/cm}^3$ using the lattice parameters.

The transmittance spectra of two representative CTGS crystals are shown in Fig. 4. From 190 to 2500 nm, crystals grown with the Ir crucible exhibited three absorption bands centered at 340, 450 and 1790 nm. On the contrary, no absorption peaks were observed for crystals grown with the Pt crucible. These were colorless and highly transparent. Therefore these results are a further sign that the yellowish coloration can be related with the use of Ir crucibles. The bandgap of CTGS, estimated by the standard method in the inset of Fig. 4, is as large as 4.96 eV, corresponding to a short cutoff at 250 nm. On the other hand, both crystals grown with Ir and Pt crucibles show a similar transmittance in the wavelength range 2500-8000 nm, with the long cutoff at 7300 nm.

The dependence on temperature of the resistivity $\rho$ of grown CTGS crystals is shown in Fig. 5. For the sake of comparison, the reported resistivities of CTGS crystals, as well as that of $\text{La}_3\text{Ta}_0.5\text{Ga}_5.1\text{Al}_{0.4}\text{O}_{14}$ (LTGA), the another typically considered candidate, are also plotted together. In accordance with previous reports, the resistivity decreases exponentially with the temperature increase, as seen in the linear fits of the Arrhenius plots. As a general trend, it is seen that the resistivity is higher the lower the oxygen partial pressure in the growth atmosphere. These results suggest that oxygen vacancies do not play a role in the conductivity of CTGS crystals, since their concentration is expected to diminish with the increase of the oxygen partial pressure. Resistivity values over $10^{10} \Omega\text{cm}$ at 400°C for oxygen-less ($\leq 1\%$) atmosphere are achieved, i.e. two orders of magnitude higher than the reported for LTGA$^{1)}$ and similar to the best report for CTGS.$^{3)}$ On the other hand, the defects related with the yellow coloration seem not to be electrically active, so that the resistivities of colored and colorless crystals are comparable. Independently of the oxygen partial pressure, the calculated activation energies are about 1.30 eV, in good agreement with the reported value of 1.26 eV$^{3)},6)$ and larger than that of LTGA with the value 0.82 eV$^1).$

The dielectric and piezoelectric properties of as-grown CTGS single crystals were also studied as a function of temperature. All crystals exhibited a similar piezoelectric behavior regardless of the growth conditions. As an example, the results of the CTGS single crystal grown with the Pt crucible under N$_2$ atmosphere are
discussed in the following.

In the case of the langasite crystal structure, the total number of independent material constants is 10, including two independent dielectric constants \( \varepsilon_{ij} \), two independent piezoelectric coefficients \( d_{ij} \) and six independent elastic compliances \( s_{ij} \). Table 3 lists the measured dielectric, piezoelectric and elastic constants of CTGS at RT in comparison with those reported for CTGS and \( \alpha \)-quartz. As can be seen, both \( \varepsilon_{11}/\varepsilon_0 \) and \( \varepsilon_{33}/\varepsilon_0 \) are slightly smaller than the reported ones, while they are around 4 times and 5 times larger than those of \( \alpha \)-quartz, respectively.\(^2\) The measured \( d_{11} \), with a value of 4.0 pC/N, is equal to one of the reported values\(^3\) and a bit smaller than another one of 4.58 pC/N.\(^7\) Also, the \( d_{14} \) of this work is comparable to the reported one. On the other hand, the \( d_{11} \) and \( d_{14} \) of CTGS are about 1.7 and 14 times larger than the ones reported for \( \alpha \)-quartz.\(^5\) The calculated electromechanical coupling factor \( k_{12} \) is 10.9%, in good agreement with the reported value (11%).\(^3\) Further, the obtained elastic constants are comparable to the ones reported.

The temperature dependence of the dielectric constant at 100 kHz is shown in Fig. 6. It decreases continuously from RT to the minimum at about 550°C, while the dielectric loss (tan \( \delta \)) remains more or less constant around zero (<1%) and then starts to increase rapidly, reaching ~4% at 700°C. According to the Clausius-Mosotti equation,\(^3\)

\[
TCE = \frac{(\varepsilon - 1)(\varepsilon + 2)}{\varepsilon} (A + B + C) + 0.05 \tan \delta, \quad (3)
\]

where TCE represents the temperature coefficient of the dielectric constant, \( (A + B) \) relates to the thermal expansion, and \( C \) takes into account the temperature dependence of the polarizability of the intrinsic ions and electrons with constant volume. For a material with \( \varepsilon > 10 \) and \( \tan \delta < 0.1 \%, \) the estimated TCE can be simplified as:\(^3\)

\[
TCE = \text{Constant} - \alpha \varepsilon, \quad (4)
\]

where \( \alpha \) is the thermal expansion coefficient. In the case of CTGS, tan \( \delta \) is less than 0.1% in the low temperature range, thus, the dielectric constant decreases with temperature according to Eq. (4). Afterwards, by a significant increase of tan \( \delta \) the TCE becomes positive. Further, the estimated \( RC \) at 500°C is 1.44 ms, which is in the same order of magnitude as the reported one (2.36 ms).\(^3\)

Figure 7 shows the variation of the resonance frequency \( \Delta f/f_0 \) and the calculated elastic compliance \( s_{11} \) as a function of temperature for CTGS.

| Parameters | CTGS | CTGS\(^1\) | \( \alpha \)-quartz\(^2\) |
|------------|------|------------|---------------------|
| \( \varepsilon_{11}/\varepsilon_0 \) | 16.93 | 18.15 | 4.51 |
| \( \varepsilon_{33}/\varepsilon_0 \) | 22.48 | 23.74 | 4.63 |
| \( d_{11} \) | 4.0 | -4.58 | 2.31 |
| \( d_{14} \) | -10.1 | 10.43 | 0.727 |
| \( s_{11} \) | 8.88 | 9.28 | 12.77 |
| \( s_{12} \) | -2.87 | -1.80 | -1.79 |
| \( s_{13} \) | -2.26 | -1.88 | -1.22 |
| \( s_{14} \) | -0.10 | -0.12 | 4.50 |
| \( s_{33} \) | 5.49 | 6.56 | 9.60 |
| \( s_{44} \) | 25.20 | 24.47 | 20.04 |

Fig. 7. Variation of the resonance frequency \( \Delta f/f_0 \) and the calculated elastic compliance \( s_{11} \) as a function of temperature for CTGS.

Fig. 8. Electromechanical coupling factor \( k_{12} \) and piezoelectric coefficient \( d_{11} \) versus temperature for CTGS.
4. Conclusion

High quality CTGS single crystals were successfully gown by the Cz method under various oxygen partial pressures with Ir crucibles, as well as Pt crucibles for the first time. By the growth with the Pt crucible colorless crystals could be obtained, eliminating therefore the defects related with the typical yellow coloration. These defects, however, do not seem to influence the electric properties of CTGS crystals. The measured thermal expansion coefficients along the $a$ and $c$ axes are quite close, what is beneficial to prevent cracking in HT applications. The dielectric and piezoelectric constants are independent of growth conditions and similar to those already reported for CTGS. Instead, the resistivity is found to depend on the oxygen partial pressure of the growth atmosphere, while its activation energy is approximately constant. The highest resistivities are found for crystals grown under oxygen-less ($\leq 1\%$) atmosphere, reaching values over $10^{10} \Omega \cdot \text{cm}$ at 400°C. This contrasts with the two orders of magnitude lower resistivity of the another candidate LTGA. Therefore, present results confirm that CTGS single crystals are promising for HT piezoelectric sensor applications.

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