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Lanthanum-Gallium Tantalate Crystals and their Electrophysical Characterization

A.P. Kozlova*, N.S. Kozlova, I.M. Anfimov, D.A. Kiselev, A.S. Bykov

National University of Science and Technology "MISiS", 4, Leninskiy Pr., 119049 Moscow, Russia

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Lanthanum-gallium tantalate single crystal ($La_3Ta_{0.5}Ga_{5.5}O_{14}$, langatate, LGT) is a perspective piezoelectric material as an active component of pressure sensors. An investigation of the growth conditions influence (the growth atmosphere) on the electrophysical characterization of LGT, obtained in different atmospheres (Ar, Ar + O_2) was carried out. The frequency dependences of the relative dielectric constant ($\varepsilon_{11}/\varepsilon_0$) and of the admittance depend on the growth atmosphere. The langatate electrophysical characterization in alternating electric fields were analyzed by means of the impedance spectroscopy method. The behavior of short circuit currents in specimens of polar cuts of LGT single crystals with the same material electrodes without preliminary polarization is described.

Keywords: Langatate, Polar dielectric crystal, Impedance, Short circuit current.

PACS numbers: 82.45.Fk, 82.45.Gj, 82.45.Un

1. INTRODUCTION

Lanthanum-gallium tantalate single crystals $La_3Ta_{0.5}Ga_{5.5}O_{14}$ are of interest as piezoelectric material. A first characterization of $La_3Ga_{5,5}Ta_{0,5}O_{14}$ is dated 1982 [1]. These crystals are widely used in the design of sensors based on the direct piezoelectric effect. The main requirements for pressure sensors are small size of the element and time stability of basic characteristics. Particular requirements of materials for such pressure sensors are [2]:

– absence of phase transitions up to ~ 1200 °C;
– absence of the pyroelectric effect;
– absence of physical properties hysteresis;
– high sensitivity, caused by high values of piezoelectric coefficients;
– high value of specific resistance.

Lanthanum-gallium tantalate single crystal has all these necessary properties [2].

The single crystals were grown by the Czochralski method in Ar or Ar + O_2 atmospheres, but generally, the growth technology in argon-oxygen atmosphere is more frequently used. Some amount of oxygen in the growth chamber is necessary to prevent evaporation of gallium oxide and lack of gallium in the melt, which leads to the crystal non-stoichiometry.

Polar cuts of langatate single crystals are used as pressure sensors active component in high temperature devices. The technology of high temperature sensors based on langatate single crystals includes the coating of their polar cuts surfaces with a thin conducting layer. One of the problems of such sensors is the surface aging and surface degradation during the sensor use especially at high temperatures.

A peculiarity of langatate is the structural complexity of the unit cell and a tendency to form a disordered distribution of its matrix ions within the crystal lattice [2, 3]. Inhomogeneity of thus obtained crystals leads to heterogeneity of physical properties.

The nature of the nonequilibrium crystals state, and consequently, the possibility of occurrence of processes leading to crystals state changes may be caused by the crystal properties itself, by its post-growth treatment and by service conditions. It is well known that there are deviations from the equilibrium caused by external effects, for example, crystalline elements degradation under the effect of electric fields. Less evident are processes and their consequences determining the variation of crystals in the absence of external effects. This process includes the short circuit current (SCC) detected in polar crystals. This phenomenon was detected in lithium iodate [4].

Thus, identifying the causes and nature of changes in the crystal state, which manifests itself in the anomalous behavior of some LGT properties and the SCC occurrence, is not only of practical interest, but is also important for a number of polar crystals fundamental studies.

2. EXPERIMENTAL PROCEDURE

In this study, langatate crystals produced by the "Fomos-Materials" company were used. The crystals were grown in iridium crucibles in an Ar atmosphere and in a mixture of argon and oxygen (Ar + (2 %)O_2). The samples represent plates of polar cut polished on both sides. The samples represent plates of polar cut polished on both sides with DC-magnetron sputtered electrodes (gold with a titanium sublayer, pure gold and pure iridium).

The electrical parameters measurement was performed on a "Keithley" 6517A electrometer. The investigations of electrical parameters frequency dependencies were performed in the frequency range from 5 to 500 000 Hz on a "Tesla" BM 507 impedance meter. Impedance measurement was carried out in the temperature range 20-450 °C and SCC in the range 20-600 °C. Specific admittance σ_z and relative dielectric constant ε were calculated on the basis of measured impedance Z values and phase angle φ according to equations (1) and (2)

* anna_kozlova_2009@mail.ru

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$$\sigma_Z = \frac{d}{l \cdot h} \cdot \frac{1}{Z}, \quad (1)$$

where σ_z = specific admittance, $\mathrm{Ohm}^{-1} \cdot \mathrm{m}^{-1}$, d = sample thickness, m; l = electrode length, m; h = electrode width, m; Z = impedance, Ohm;

$$\varepsilon = \frac{1}{2 \cdot \pi \cdot \varepsilon_0} \cdot \frac{d}{l \cdot h} \cdot \frac{\sin \phi}{f \cdot Z}, \quad (2)$$

where ε = relative dielectric constant, f = frequency, Hz; ε_0 = permittivity of vacuum ($8{,}86 \cdot 10^{-12}$ F/m).

The temperature-frequency dependences of admittance and relative dielectric constant were investigated. According to these results the near-electrode processes contribution to electrophysical properties was determined. The measurements in the frequency range up to 500 kHz showed the admittance value increases on three orders for all investigated samples.

The temperature dependence is absent up to 400 °C for the crystals grown in the Ar atmosphere, change of admittance starts only at 450 °C, while in crystals grown in the Ar + O_2 atmosphere the temperature influence is absent up to 450 °C.

The relative dielectric constant temperature-frequency dependences of crystals obtained in different atmosphere with identical iridium electrodes and obtained in identical atmosphere with different electrodes were investigated (Table 1). It allowed revealing the influence of the growth atmosphere and the conducting coating material on the relative dielectric constant value. Data with an uncertainty limit are shown in Table 1.

Table 1– The values ($\varepsilon_{11}/\varepsilon_0$) of dielectric constant of langatate samples at different temperatures in the frequency range 5 Hz-500 kHz

Relative dielectric constant / Atmosphere, Electrode material	($\varepsilon_{11}/\varepsilon_0$) at T = 20-400 °C	($\varepsilon_{11}/\varepsilon_0$) at T = 450 °C
Ar, electrode - Ir	34 ± 2	43 ± 3
Ar + (2 %)O_2, electrode – Ir	43 ± 3	49 ± 3
Ar + (2 %)O_2, electrode – Au+Ti	35 ± 2	39 ± 3

The classical solid electrolyte is connected in parallel resistor and capacitor. We suppose that the near-electrode processes on polar cuts of LGT have an electrochemical nature.

To analyze the results of measurements of the specific impedance the impedance hodographs were constructed. The shape of the hodograph can be seen in the equivalent circuit of the investigated process, and thus about the process. Several equivalent circuits for the pattern "electrode-solid electrolyte-electrode" were analyzed: the equivalent circuit of Ershler-Randles (Fig. 1a), and Frumkin-Melik-Gaykazyan (Fig. 1b). According to the Ershler-Randles circuit the impedance of such a reaction can be represented as the impedance of the circuit consisting of series-connected resistors R_F, characterizing the charge transfer, and the Warburg impedance Zw, which characterizes the diffusion process. The resistor Re is the resistance of the electrolyte, Cd is part of the double layer capacity due to indifferent ions. Equivalent Frumkin-Melik-Gaykazyan circuit describes the electrochemical processes taking place into account of the electrochemical reactions products adsorption in "electrode-solid electrolyte-electrode" systems. R' characterizes own speed elementary act of adsorption-desorption and capacity C' – additional double layer capacity associated with adsorption of surface – active particles. Based on the experimental results of impedance spectroscopy for all samples of LGT crystals complex impedance Z components for both equivalent circuits have been identified by analytical method. For both circuits of LGT sample grown in Ar + O_2 mixture with Au/Ti electrodes [5] impedance components demonstrate that the main contribution to the value of the electrical resistance is the resistance of near-electrode processes. The near-electrode processes are of electrochemical nature.

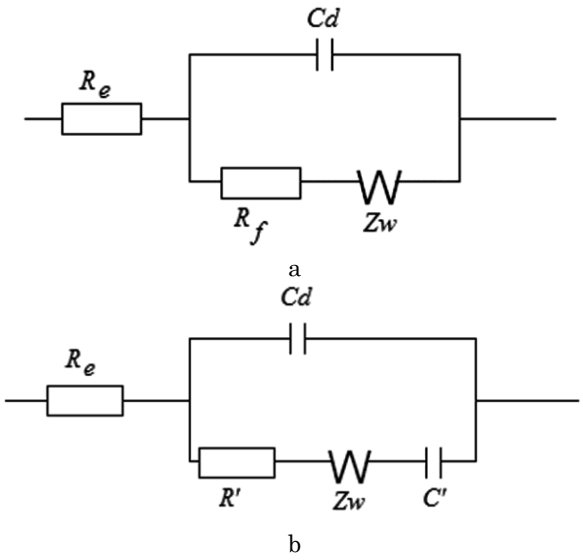

Fig. 1 – The equivalent circuit of Ershler-Randles (a), and Frumkin-Melik-Gaykazyan (b)

We have shown that the short circuit current in LGT is detected always even if the crystal is between symmetric (identical electrodes). The short circuit current is recorded without preliminary polarization of the specimen. The diagram of the experiment shows time dependences of the temperature and current (Fig. 2). SCC measurement process consists of three stages. The first stage t_1 is SCC measurement after shortening the circuit – the current decreases with time (t) in accordance with the law $I = I_0 \cdot (t/t_0)^{-a}$ to a stationary value which is retained for any period of time within about 1 hour. During the second stage t_2 the sample is kept for 30 minutes at room temperature after the current decay process. This step is necessary for accurate SCC measurements at the beginning of the heating process. After that, the linear heating with rate of 2 °C/min to the required temperature and the simultaneous registration of SCC parameters were carried out (stage t_3). The resulting dependence characterizes the near-electrode processes kinetics and activation of active defects in the bulk of the crystal. The duration of this stage is about 8 hours.

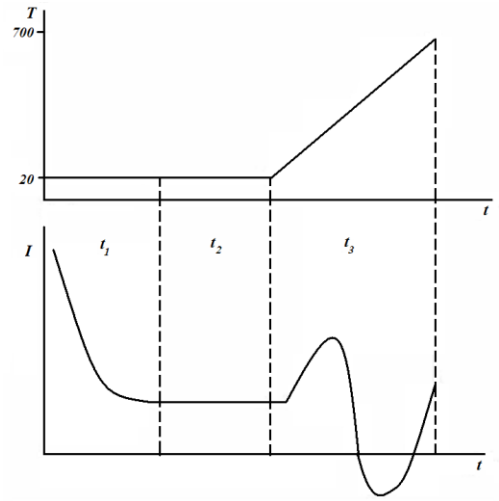

Fig. 2 – Scheme of the experiment: the plot of temperature and current change from time

Charge state of each surface was determined by the piezoresponse technique. In the experiment, the crystal is always placed with the same orientation due to surface charge sign with respect to the electrode holder. However, for testing, the sample was also placed on the opposite side with respect to the holder. The current direction changing is due to the processes within the sample. The behavior of the current schedule, depending on the setting of the sample shown in Figure 3.

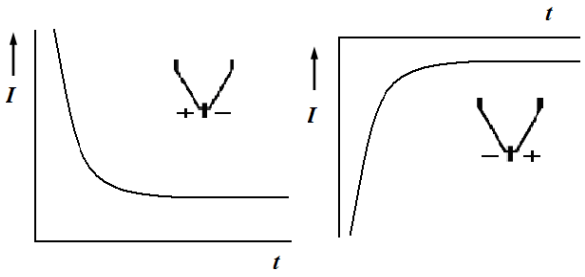

Fig. 3 – SCC behavior at different positions of the sample relative to the electrodes

SCC dependences of LGT samples with different electrodes (pure gold, gold with a titanium sublayer) are shown in Figure 4. A level of short circuit is $10^{-14} \div 10^{-6}$ A current in LGT with gold-on-titanium electrodes and $10^{-15} \div 10^{-9}$ A in LGT with gold electrodes.

As follows from these graphs, the temperature dependences of SCC are different for samples with different electrodes, however, there are main general patterns:

– nonmonotonic SCC dependences;
– SCC inversions;
– with a certain temperature current linearly increases by several orders.

Extrema are observed at 270 °C, 300 °C, 350 °C, 380÷430 °C, 480 °C, 530 °C, 580 °C for the sample with gold electrodes, at temperatures 160 °C, 260 °C, 300 °C, 360 °C, 460 °C, 520 °C for the sample with gold-on-titanium electrodes. Tendency to current increase is observed from 600 °C for both samples. Magnitude and direction of the stationary current value depend on the

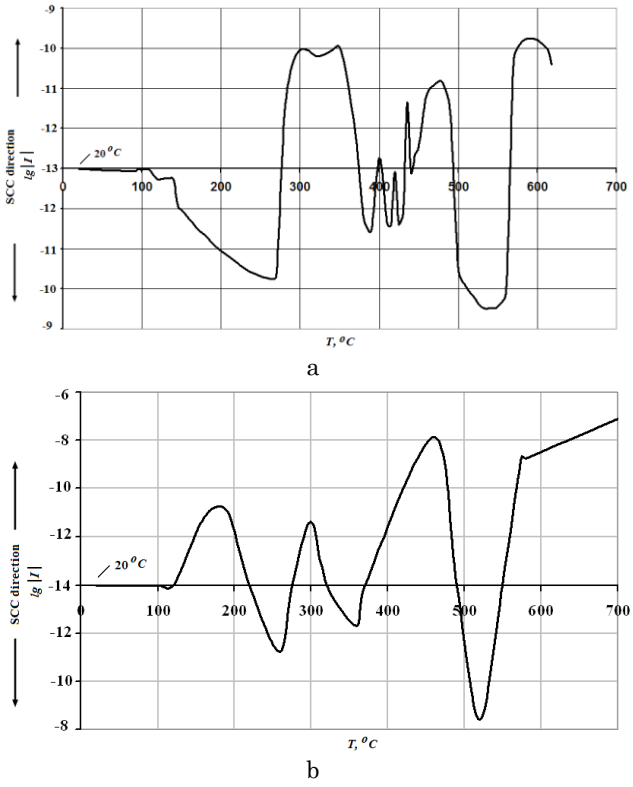

Fig. 4 – SCC dependences of LGT samples with gold electrodes (a) and with gold-on-titanium electrodes (b)

nature of the electrode. This shows that the detected short circuit current is determined by near-electrode processes.

The samples surfaces before and after short-circuit current temperature measurement were investigated by XRD on a "Bruker" D8 Discover diffractometer with Cu K α radiation. Analysis of results showed that both identical and different phases appeared on the opposite surfaces of samples after thermal testing. These results confirmed our assumption that short circuit currents have electrochemical nature.

3. CONCLUSION

The dependences of the LGT crystal electrical properties from its growth atmospheres and electrode material in alternating electric fields are investigated. Analysis of impedance spectroscopy results found that electrochemical processes on LGT crystal polar surfaces determinated the appearance of short circuit currents. Short circuit currents are recorded on LGT crystals polar cut with symmetrical electrodes without preliminary polarization of the specimen. The inversion of SCC taken place during heating, is associated with different phase changes on the polar surfaces of the crystal which are caused by the electrochemical processes.

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