Lanthanum – Gallium Tantalate Crystals: Surface processes and their effect on electrophysical properties

N S Kozlova¹, O A Buzanov², A P Kozlova¹, and I M Anfimov¹

¹ National University of Science and Technology "MISIS", Moscow, Russia
² Company Fomos-Materials, Moscow, Russia

E-mail: anna_kozlova_2009@mail.ru

Abstract. The behaviour of short - circuit currents in specimens of the polar cuts of lanthanum-gallium tantalate crystals with identical deposited electrodes before and after preliminary polarization is investigated. The temperature dependences of short - circuit currents in the temperature range 200-600 °C were measured. These currents are caused by the electrochemical processes on opposite polar cuts surfaces taking place at the crystal /electrode boundary.

1. Introduction

Currently, the investigation and application of lanthanum-gallium tantalate crystals (La₃Ga₅,Tₐ₀.₅O₁₄, langitate, LGT) is an intensively developing direction of the research in piezoelectronics (in particular, in the production of high-temperature devices based on the direct piezoelectric effect [1, 2, 3]).

One of the most important requirements for crystals used in piezoelectronics is their physical properties stability determined by the nonequilibrium state of the crystal and the kinetics of the process of charge transfer.

The nature of the nonequilibrium state of crystals and, consequently, the possibility of occurrence of processes leading to changes of their state may be caused by the properties of the crystal itself, by its production history and operation conditions. It is well known that there are deviations from the equilibrium caused by external effects, for example, degradation of crystalline elements 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 langitate [3, 4].

The technology of high-temperature devices based on langitate crystals includes the coating of the surfaces of their polar cuts with a thin layer of a conducting material. It is known [4] that the deposition of metal electrodes on the surface of the polar cuts of crystals leads to their aging and degradation due to the occurrence of electrochemical processes. In this context, one of the most important demands in designing high-temperature sensors based on lanthanum–gallium tantalate is the proper choice of the optimum material of the conducting coating.

2. Experiment results

We have shown that the short - circuit currents in LGT grown in the atmospheres of argon and argon with oxygen on level of 10⁻¹⁴÷10⁻⁸ A are detected always even if symmetric (identical) electrodes are placed on the polar cuts of the crystal. The short - circuit currents were observed on all specimens without preliminary polarization with symmetric electrodes from different materials (gold, gold with a titanium sublayer, iridium, silver with a chromium sublayer) [3, 5].

¹ Author to whom any correspondence should be addressed
Short-circuit currents can be induced in solid insulators using the following techniques:

- symmetric (identical) electrodes are deposited on the crystal surface, and the samples are preliminarily stimulated using thermo-, photo-, electric, X-ray, or piezoelectric effects or polarization at high temperatures.

- asymmetric electrodes ($E_1$, $E_2$) are deposited on the insulator (I) surface according to the scheme $E_1/\text{I}/E_2$. In this case, the short-circuit currents are observed without preliminary polarization. This is due to the difference in the electrochemical processes occurring during the contact of the insulator surface with different metal electrodes, as well as due to the different activity of the electrode coatings.

If the crystal between two electrodes is examined as a galvanic cell, then for a cell with the solid electrode of the type $E/E_1/\text{I}/E_2/E$, where $I$ is a solid electrolyte, $E$ is the material conducting leads, the value of electromotive force (emf) is written in the form:

$$\mathcal{E} = \phi_g^{(E_1)} - \phi_g^{(E_2)} + \phi_g^{(E)}$$

where $\phi_g$ is the Galvani potential at the electrode/electrolyte phase boundary, $\mathcal{E}$ is the electrode potential at the i-th electrode.

On the basis of the experimental investigation of near-electrode surface of a polar crystals, e.g. $\alpha$-LiIO$_3$ [6] and LGT [3, 5], it was determined that the origin of the short-circuit currents observed in the polar cuts without application of an external electric field or any other preliminary polarization was due to generation of an intrinsic emf (0.02–0.04 V) as a result of the electrochemical processes on the sample surface coming in contact with the electrodes.

The object examined in this work can be represented as an electrochemical cell with symmetric electrodes $E/E_1/pr_1/I/pr_2/E_1/E$, where $I$ is a solid electrolyte, $E$ is the material conducting leads, $E_1$ is the material of the electrode coatings, $pr_1$ and $pr_2$ are the products of electrochemical reactions. A standard electrochemical cell with solid electrolytes and symmetric electrodes should have zero emf. However, when polar cuts of the polar crystals are used as a solid electrolyte, an emf is generated due to the different electrochemical processes on the opposite surfaces of the polar cuts as a result of their different activity.

Previously in [3, 5] it was shown the SCC changes 4 to 6 orders of magnitude depending on electrode material. Therefore, in this study, we performed experiments with langatate crystals with the identical electrodes of Ta before and after preliminary polarization. This choice of electrode material is related to the fact that tantalum is part of the single crystal composition. The crystals were produced by the “Fomos-Materials” company and were grown in iridium crucibles in a mixture of argon and oxygen (Ar+(2%)O$_2$). The samples were made in form of plates of polar cut polished on both sides with magnetron sputtered electrodes. The thickness of the deposited electrodes was approximately 200 nm. The electrical parameters were measured on a “Keithley” 6517 A electrometer. SCC measurements were carried out in the range 20 – 600 °C, the heating rate was constant (2 °C/min). Charge state of each surface was determined by the piezoresponse technique. In the experiment, the samples were always installed in a crystal holder considering the surface charge sign.

SCC dependence of LGT samples with Ta electrodes is shown in Figure 1a. We observed a well-defined peak, which can be divided into two different. This fact shows good stability of the electrode-dielectric-electrode system and the absence of serious competing processes that could contribute in the short-circuit currents.

The preliminary polarization of specimens was carried out at a field of 50 V/mm while heating up to 500 °C, then the sample was kept for one hour at this temperature and rapidly cooled. The preliminary stage is necessary to detect the contribution in SCC of greater number of defects than without preliminary polarization. This effect is related to the fact that during the voltage supply and heating the following processes occur in the sample: processes of space-charge generation and their polarizations enhanced by heating and thermally stimulated conductivity. The short-circuit currents are recorded after preliminary polarization and this dependence is shown in Figure 1b.
After the preliminary polarization of the sample value of the current amplitude decreased by 2 orders of magnitude (10$^{-8}$ to 10$^{-10}$ A). The equilibrium conductivity near the electrodes leads to the accumulation of the volumetric charges of opposite sign under the application of an external electric field. These charges screen electric field generated in polar crystal.

![Figure 1. SCC dependence of LGT samples with Ta electrodes before (a) and after preliminary polarization (b).](image)

The method of mathematical processing of SCC experimental data – the method of initial rise – is described in [4]. This method is based on the results of theoretical investigation of thermo-stimulated currents. It was shown that the initial phase of thermally stimulated current is linearized in the coordinates of the Arrhenius $\ln I(1/kT)$ regardless of the mechanism and order of kinetics of non-isothermal relaxation of the charge of (figure 2).

The slope of a line, resulting in the construction of the initial phase of the peak thermo-stimulated current in the coordinates of the Arrhenius, allows calculation of the activation energy $W$ at $T \approx T_0$ [4]:

$$-W \approx d \ln I(T)/d(1/kT)$$

(1)
The advantage of the described method is its independence from the order of the kinetics of the relaxation process.

The values of activation energies show the dominance of one process over the other at a certain temperature. This allows separation of the contribution of the near-electrode processes in the release of electrically-active defects analyzing the temperature dependence of the SCC. The values of activation energy for the sample before and after the preliminary polarization are shown in table 1.

Table 1. Characteristics of the SCC peaks

| Temperature (°C) | Peak current (A) | Activation energy by the methods of initial rise (eV) |
|-----------------|-----------------|---------------------------------------------------|
|                 | Before preliminary polarization |                     |
| 575             | 1.5·10⁻⁸        | 1.0                                               |
|                 | After preliminary polarization |                   |
| 495             | 1.8·10⁻¹⁰       | 2.2                                               |

References

[1] Shimamura K, Takeda H, Kohno T 1996, J. Cryst. Growth 163 388
[2] Takeda H, Tanaka S, Izukawa J 2005 in Proc. 2005 Ultrasonic Symp. IEEE. 1 560.
[3] Buzanov O A, Zabelina E V, Kozlova N S, Sagalova T B 2008 Crystallography Reports 53 853–857
[4] Gorokhovatskiy Yu A and Bordovskiy G A 1991 Thermally Activational Current Spectroscopy of High-Resistance Semiconductors and Dielectrics (Nauka, Moscow) p 248 [in Russian]
[5] Kozlova N S, Kozlova A P, Anfimov I M, Kiselev D A, Bykov A S 2014 Lanthanum-gallium tantalate crystals and their electrophysical characterization Journal of Nano- and Electronic Physics 6 03034
[6] Blistanov A A, Kozlova N S and Geras’kin V V 1997 The Phenomenon of electrochemical self-decomposition in polar dielectrics Ferroelectrics 198 61-66