

# Dielectric properties of sodium nitrite particles embedded into porous alumina

**N O Alexeeva**

Pskov State University, Lenin square, 2, 180000 Pskov, Russia

E-mail: nataliaal@yandex.ru

**Abstract.** Porous anodic alumina templates were fabricated using a two-step anodization in oxalic and phosphoric acid solutions. Dielectric studies were carried out for ferroelectric sodium nitrite embedded into porous alumina. Phase transition temperature in sodium nitrite within porous alumina is shifted compared to the bulk ferroelectric Curie point. The sign of this shift depends on the experimental conditions of sample preparation.

## 1. Introduction

Anodic aluminium oxide films formed by the electrochemical oxidation of aluminium have been widely studied to protect and decorate the surface of aluminium and to make inorganic membranes. In recent years, nanoporous anodic aluminium oxide with relatively regular pores, narrow distributions of pore sizes and interpore spacings has become a popular template system for the synthesis of various nanostructures. This trend originated from the discovery of Masuda and Fukuda a novel process so-called two-step anodization in 1995 [1]. They reported that the pore regularity can be improved by a long anodization time under appropriate conditions, known as 'self-ordering regimes'. Hexagonally arranged arrays with circular pores can be obtained under these regimes.

Porous alumina templates have advantages as a basis for nano-patterning. These are the fundamental nanometer scale of the pores, the control of their size over large areas achievable by varying the anodizing parameters, their high aspect ratio and highly regular structure of the pore arrays.

The arrangement and size of alumina pores are controlled by the applied voltage, temperature, type and concentration of the electrolyte. In this paper dielectric properties of  $\text{NaNO}_2$  within porous alumina fabricated under different anodizing parameters were studied.

## 2. Experimental

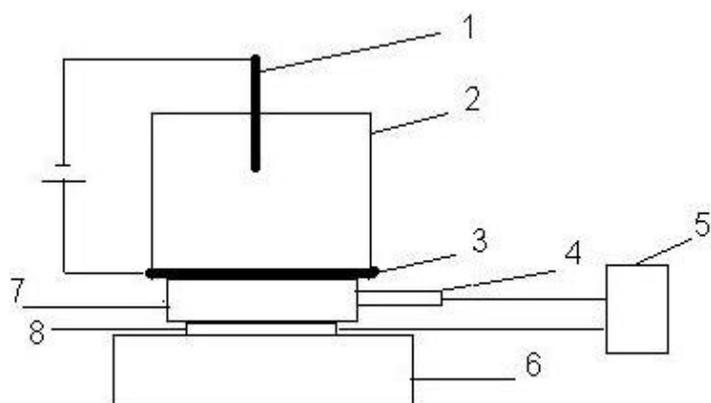
Porous alumina was fabricated by the electrochemical method. Two-step anodization was used. Experimental setup was designed according to diagram described in [2]. It is shown in figure 1. The electrochemical cell consisted of two-electrode system, the lead electrode acting as the cathode and Al sheet acting as the anode. The Al sheet was inserted between the electrolyte container and heat-conducting substrate. During anodization, the surface of aluminium heated up, leading to a requirement for a cooling system. Cooling system was based on Peltier element. The temperature was measured by semiconductor temperature sensor with digital interface. Temperature sensor was integrated into the heat-conducting substrate and allowed to measure temperature with the accuracy of



0.5 °C. Temperature regulation was carried out with the help of microprocessor control system. The microprocessor control system was based on the microcontroller Atmega16 from Atmel. The microcontroller measured the temperature in the reaction zone and maintained the set temperature by varying the supply voltage of Peltier element. In this system PID regulation algorithm was used.

The anodized sample was cleaned and inserted into 40% solution of sodium nitrite for several days. Then the sample was wiped with moist cloth and dried.

AFM-images were obtained by the scanning probe microscope Nanoeducator from NT-MDT.



1 – lead electrode, 2- electrolyte container, 3- aluminium sheet, 4 – temperature sensor, 5- microprocessor control system, 6- cooling radiator, 7- heat-conducting substrate, 8- Peltier element.

Figure 1 Experimental setup

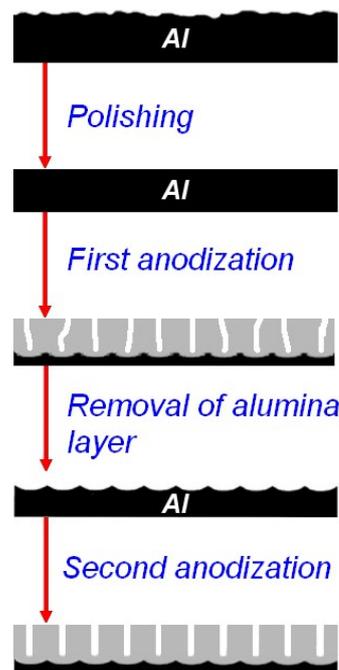


Figure 2 Two- step anodization

Figure 2 illustrates the procedure of fabricating alumina templates using two-step anodization.

The first anodization was carried out at a constant voltage of 40 V in 0.3 M oxalic acid at 8 °C or at a constant voltage of 160 V in 0.1 M phosphoric acid at 3 °C for about 10 hours.

In the first anodization step pores initiate at almost random positions and order thereafter by self-adjusting during the anodizing process of long duration, pore arrangements on the surface are disordered and have a broad size distribution. Ordered pore domains can only be obtained at the bottom of the layers. So, the pores produced in the first anodization step are not parallel to one another. To fabricate ordered nanopore arrays, the first porous oxide film, which contains the barrier layer at the bottom, is selectively dissolved in mixture 20 g/l  $\text{CrO}_3$  and 35 ml/l  $\text{H}_3\text{PO}_4$  at 80 °C. The barrier layer is not flat but consists of periodically arranged crests and troughs. These fluctuations result in a dimpled and undulating surface that has the same spatial ordering as the barrier layer. After the removal of the porous film, the periodic concave patterns that remain, as shown schematically in figure 2, act as a self-assembled template for the second anodization process. In the second anodization step the same parameters are used as in the first anodization step.

AFM-image of the aluminium surface after removal of the porous oxide is shown in figure 3. AFM-image of the porous alumina after the second anodization step is shown in figure 4. The average pore size is about 200 nm.

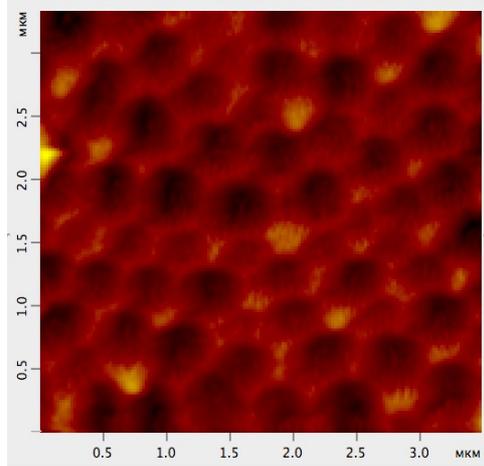


Figure 3 AFM-image of the aluminium surface after removal of the porous oxide (160 V, 0.1 M phosphoric acid, 3 °C)

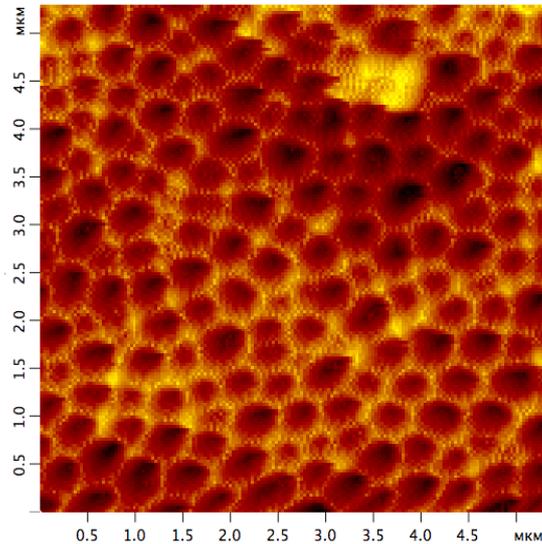


Figure 4 AFM-image of the porous alumina after the second anodization step (160 V, 0.1 M phosphoric acid, 3 °C)

### 3. Results

Dielectric measurements of the filled porous alumina were carried out at the frequency of 1 kHz by an E7-13 impedance meter. The temperature dependences of sample capacity  $C(T)$  and sample conductivity  $G(T)$  were measured upon continuous warming with a heating rate of 1 to 2 degrees per minute. Silver (sputtered on the surface of the porous alumina with ATC ORION SERIES SPUTTERING SYSTEM) or graphite were used as electrode materials.

The temperature dependences of capacity  $C(T)$  and conductivity  $G(T)$  of two samples under study are shown in figures 5 and 6. According to our preliminary results curves  $C(T)$  and  $G(T)$  have peculiarities at the temperatures near 425 K and 450 K.

Thus phase transition temperature in sodium nitrite within porous alumina is shifted compared to the bulk ferroelectric Curie point(437K) [3, 4].

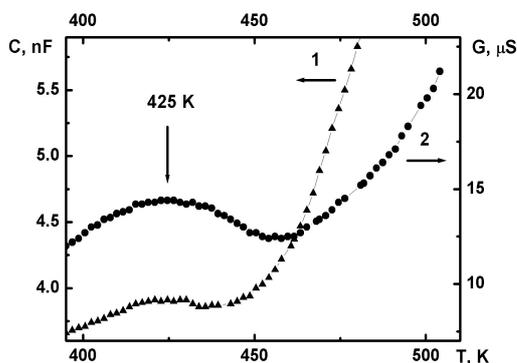


Figure 5 Temperature dependences of sample capacity (1) and sample conductivity (2). Conditions of sample preparation: 160 V, 0.1 M phosphoric acid, 3 °C.

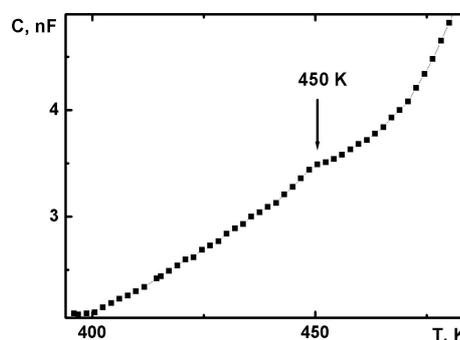


Figure 6 Temperature dependence of sample capacity. Conditions of sample preparation: 40 V, 0.3 M oxalic acid, 8 °C.

#### 4. Conclusion

Porous alumina was fabricated by the electrochemical method using two-step anodization.

Our dielectric studies of  $\text{NaNO}_2$  embedded into porous alumina showed that the phase transition temperature can be higher or lower than Curie point in bulk  $\text{NaNO}_2$  depending on the experimental conditions of sample preparation.

These results are in accordance with modern theoretical models based not only on the phenomenological approach to the size effect on phase transitions in ferroelectric particles [5], but also taking into account an influence of pore walls on ferroelectric properties of nanoparticles [6] as well as long-wave dispersion interactions [7].

#### Acknowledgments

The author is grateful to V.G. Solovyev (Pskov State University, Pskov, Russia) for help in carrying out the experiments.

This work was supported by the Ministry of Education and Science of Russian Federation according to the program “Development of Scientific Potential of Higher Educational Institutions”.

#### References

- [1] Masuda H, Fukuda K 1995 *Science* **268** 1466
- [2] Belov A N *et al* 2011 *Nanotechnology* **4** (28) 58
- [3] Gurevich V M 1969 *Electrical conductivity of ferroelectrics* (Moscow: Standards committee) pp 215-218
- [4] Strukov B A, Levanyuk A P 1995 *Physical principles of the ferroelectric phenomena in crystals* (Moscow: Science) p 30
- [5] Zhong W L, Wang Y G, Zhang P L *et al* 1994 *Phys. Rev. B* **50** 698
- [6] Tien Ch, Charnaya E V, Podorozhkin D Yu *et al* 2009 *Phys. Status Solidi B* **246** 2346
- [7] Alexeeva N O, Vanin A I, Pan'kova S V *et al* 2008 *Proc. Int. Conf. “Physics of Dielectrics (Dielectrics-2008)”* (St Petersburg: Herzen State Pedagogical University of Russia Press) vol 2 p 201