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Thermal excitation contribution into the electromechanical performance of self-supported Gd-doped ceria membranes

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Abstract. Here we present the results of the study of electromechanical performance of the $Ce_{0.8}Gd_{0.2}O_{1.95}$ (CGO) self-supported thin circular membranes with aluminum and titanium as contact electrode materials. The electromechanical performance of both membranes was investigated using highly sensitive interferometric technique and showed two principal excitations mechanisms: common electrostriction and thermal contribution due to the Joule heating. Operating the membranes at frequencies about MHz results in significant contribution of the thermal excitation due to a large power dissipation for every electrode. The excitation of the membrane with aluminum electrodes at the frequencies about 1 Hz leads to the formation of the Schottky barrier at the interface with CGO. That is why the electromechanical response was almost independent on frequency and electric field. Membrane with titanium electrodes showed a prevalence of electrostriction effect with weak frequency dispersion and significant enhancement of the response with temperature.

1. Introduction

The area of microelectromechanical systems (MEMS) is extensively growing during the past forty years. The leading MEMS materials are mainly piezoelectrics in light of their superior sensing and actuating performances: $Pb(Zr,Ti)O_3$ (PZT) and $(1–x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ ceramics, thin and thick films [1, 2]. However, the significant electromechanical (EM) response was found only in a few compositions of the morphotropic phase boundary and all of them contain lead, which has negative effect on the human health not only during use, but also during production and recycling [3, 4]. Recently, several multifunctional materials based on the oxygen ionic conductors have been suggested as a substitution of lead containing piezoelectrics, such as (Y, Nb)-stabilized δ-Bi_2O_3 [5], partially hydrated Y-doped barium zirconate $BaZrO_3$, and (Sr,Mg) doped $LaGaO_3$ [5]. Besides, this approach is also attractive due to the absence of hysteresis of the EM response, which limits the creeps and sticking in the final devices [6].

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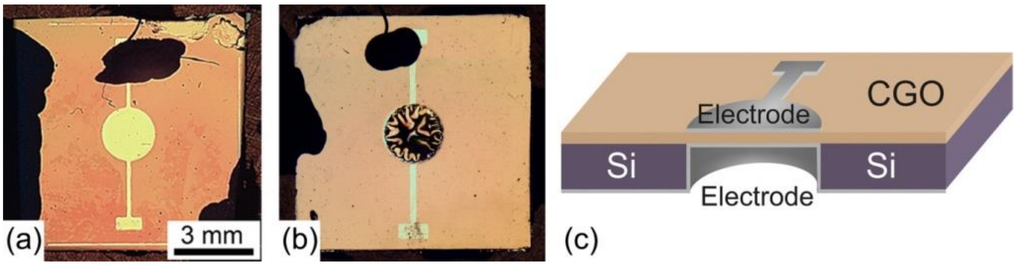

Figure 1. Optical images of CGO self-supported membranes with (a) Ti and (b) Al contacts. (c) Schematic of the membranes.

Gd-doped cerium oxide (CGO) was shown to have a very large electrostriction response [7]. This ionic conductor material is well studied from the point of usage in the solid fuel cells, while its non-typical EM properties were not studied. It was not considered for years as EM material due to its low dielectric constant and expected low electrostriction response according to the Newnham conception [8]. However, recently, the measurement of its EM performance by the cantilever approach revealed the electrostriction coefficient about 3×10^{-16} m^2/V^2 at frequencies below a few Hz [7]. This provides perspectives for its application in MEMS. However, the physical nature of the observed properties has not been completely understood [9].

Here we focus on the problem of thermal excitation appearing as a result of Joule heating that can contribute to the EM performance of CGO self-supported membranes. We have demonstrated that the electrode material [10] becomes even more important in the high operating frequency range (100 Hz-10 kHz). The principally different behavior of the membranes with Al and Ti electrodes at low frequencies is attributed to the formation of Schottky-barriers at the Al electrode/material interface, while at frequency about few MHz both membranes become thermally excited.

2. Experimental

A 1.5-μm-thick layer of $Ce_{0.8}Gd_{0.2}O_{1.9}$ (>99.99% pure, 3-inch ceramics target, 3.175 mm thick) was deposited by RF magnetron sputtering on a Si wafer (intrinsic, 2-inch, 275 μm thick, [100] oriented, double-sided polished, University Wafer, Inc.) covered by a 100 nm thick layer of Al and bottom electrode of Al or Ti (100-nm-thick, >99.999%, Tzamal D-Chem Ltd.). The top Al or Ti electrode, 200-nm-thick, was deposited by magnetron sputtering and patterned lithographically. Annealing at 430 °C for 4 h was carried out under vacuum of about 130 μPa. The cylindrical notch in the Si aligned with the top electrode was fabricated by dry reactive ion etching using back-side patterning of a 1 μm thick Al film that served as a mask [9]. Optical images and schematics of the membrane are shown in Figure 1. The top contact was connected to a copper wire and the bottom contact was connected to the metal pad using silver paint.

Highly sensitive (resolution about 0.1 pm) Michelson interferometer with phase locking and stabilizing PID-feedback loop was employed for the detection of vertical displacements in the middle of membrane. More details of the experimental setup were discussed in [11]. Dielectric measurements were done with QuadTech 7600 Plus (IET Labs, Inc.) RLC-meter.

3. Results and discussion

It is well known that electrostriction is an intrinsic property of all dielectrics whether they are polar or not. It originates from the interaction of the external electric field with the polarization of the unit cell induced by this field. Therefore, the electrostriction response is quadratic with respect to the applied electric field and, if the applied field is sinusoidal, the response could be detected at the second harmonic of excitation [12]. We have found that the EM response of the membranes with Al electrodes in the frequency range from 2 Hz to 1 kHz is much lower than that of the same membranes with Ti electrodes. In the same experimental conditions, the difference was almost an order of magnitude (Fig. 2). Both membranes revealed a decrease of amplitude in the frequency range

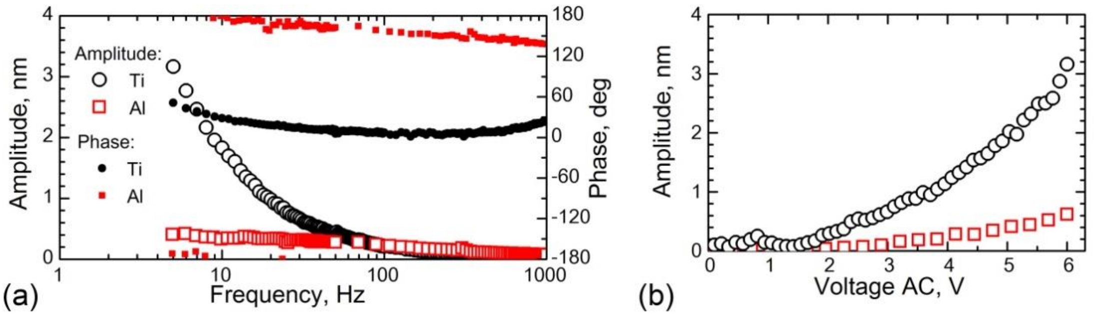

Figure 2. (a) Frequency (under 6 V AC) and (b) AC voltage (at 5 kHz) dependences of 2nd harmonic EM response in membranes with Al and Ti electrodes.

1Hz–1kHz. The phase of the EM response measured by the lock-in technique was different for different membranes. Membrane with Ti electrodes revealed close to zero value, while the one with Al electrode had a phase lag about 120-180 degrees with respect to the excitation voltage. The phase lag was also decreasing with frequency for both types of the membranes.

The increase of EM amplitude at low frequencies allowed measuring displacement-voltage dependences under slowly changed saw-type voltage (Fig. 3). The membranes with Al electrodes showed weak frequency dependence in the range of 2-50 Hz and almost temperature-independent behavior. The response was strongly asymmetric being about 30% lower, if the negative potential was applied to the top electrode. The asymmetry also depended on frequency. On the contrary, membranes with Ti electrodes demonstrated strong decrease of the EM signal with frequency (about an order in the studied frequency range). Moreover, membranes with Ti electrodes demonstrated strain hysteresis, while in the membranes with Al contacts hysteresis was observed only at high applied driving voltage.

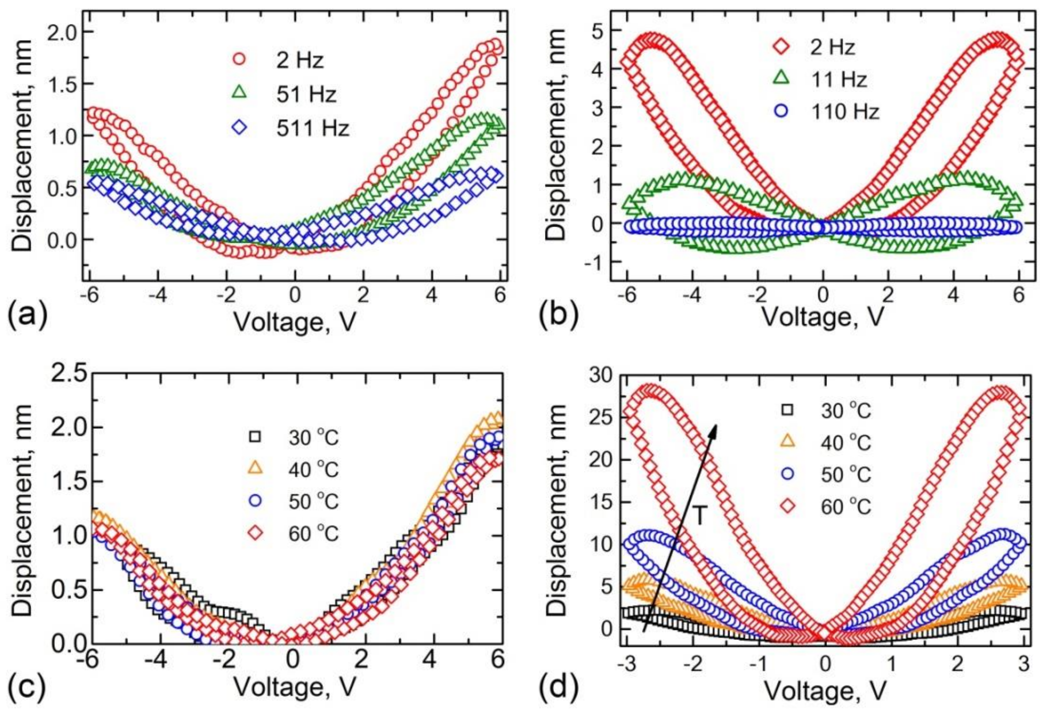

Figure 3. (a,b) Frequency and (c,d) temperature dependent displacement-voltage loops of the CGO membranes with (a, c) Al and (b, d) Ti electrodes.

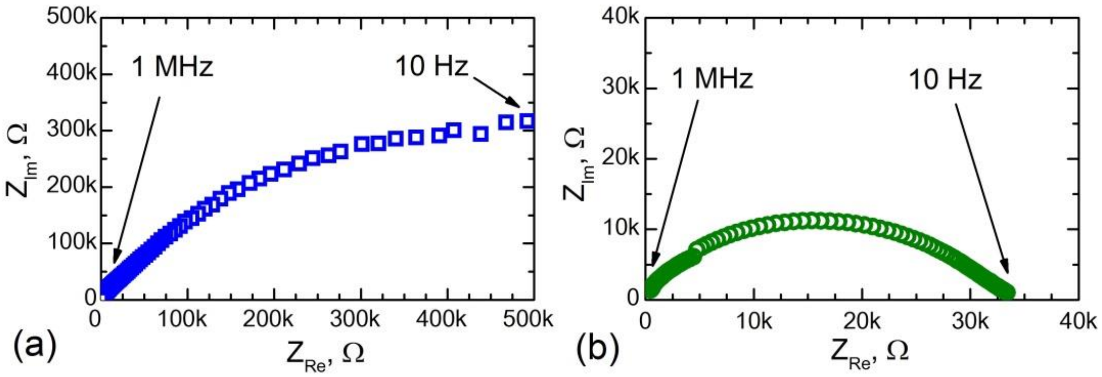

Figure 4. Cole-Cole diagrams of membranes with (a) Al and (b) Ti electrodes.

We used the impedance spectroscopy to verify the contact quality and electric field distribution (Fig. 4) within the membranes. The impedance spectra of membrane with Al electrode demonstrated clear Schottky-barrier behavior at low frequencies [13]. The existence of the Schottky-barrier resulted in voltage drop at the CGO/Al interface and additional barrier resistance. The impedance of the films was about 120 Ohms at 1 MHz under 5 V applied voltage, which implies that the dissipated power was about 200 mW. The dissipated power can be a source of heating by a few degrees, which can result in detectable strain due to thermal expansion. Both electrostriction and Joule heating are proportional to the electric field squared, which makes difficult to distinguish them.

The appearance of the Schottky barrier in CGO with Al contacts can explain the difference in displacement-voltage dependences (Fig. 3). Indeed, the blocking nature of the Al contacts dominates the overall resistance at all frequencies and temperatures.

Therefore, we decided to use amplitude modulated signal with 1MHz carrier to probe the response of the membranes at different frequencies. In the case of amplitude modulation, the electric field is equal to:

$$E_{AM} = A \cdot \cos(\omega_c t)\,(1 + M \cdot \cos(\omega_m t)), \quad (1)$$

where A is the amplitude of carrier signal, M is the amplitude of modulation, ω_c is the carrier frequency, and ω_m is a modulation frequency. For modulation depth of 100% (A equals to M) the strain may now be expressed as:

$$S = \frac{dL}{L} = ME^2 = M \cdot \left(A \cdot \cos(\omega_c t) + \frac{AM}{2}(\cos(\omega_c t - \omega_m t) + \cos(\omega_c t + \omega_m t))\right)^2 = \\ = \frac{3MA^2}{4} + MA^2\cos(\omega_m t) + \frac{MA^2}{4}\cos(2\omega_m t) + \frac{3MA^2}{4}\cos(2\omega_c t) + \cdots, \quad (2)$$

where dL is the absolute deformation of sample, L is the thickness of sample, M is the electrostriction coefficient. Thus, the electrostriction response could be observed on the first harmonic of the excitation.

The measurements of the EM response at the 1[st] harmonics were done in the 100% modulation regime (modulation coefficient $h = 1$) in a modulation frequency range 5Hz-1kHz and voltage amplitude up to 1 V (Fig. 5, black line). Amplitudes of normalized displacements from both membranes were higher than those in low frequency; however, in the case of Al electrodes this increase was more significant (Fig. 5). Analysis of the phase allowed us to make an assumption about important contribution into EM response at high and low frequencies. Phase lag in the case of electrostriction effect is supposed to be close to zero, because it is, generally, the elastic response, while Joule heating must have retardation due to a limited cooling rate. In the case of Al electrode and low frequency, we expect no electrostriction due to the Schottky barrier at the electrode. Indeed, we have in that case the highest value of the phase lag manifesting the general Joule heating input in the

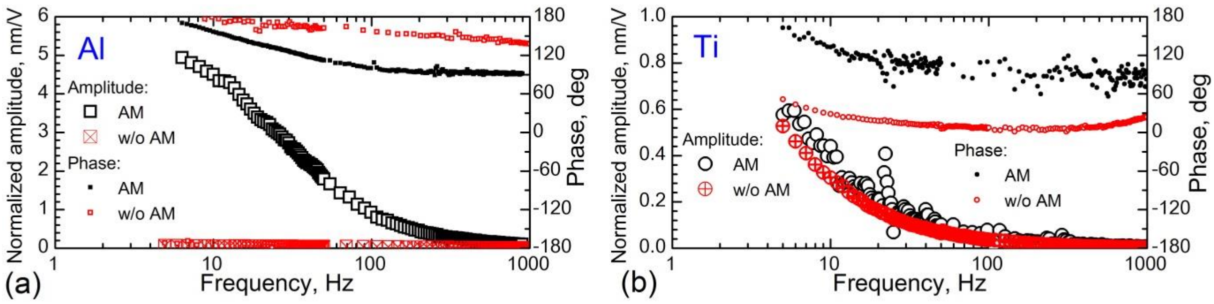

Figure 5. Frequency dependences of EM response depend on amplitude modulation (black) or 2nd harmonic detection (red, 6 V driving voltage) regimes of membranes with (a) Al and (b) Ti electrodes. 1 MHz carrier frequency and 1 V of voltage amplitude were used for amplitude modulation regime.

EM response. On the contrary, the membrane with Ti electrode demonstrated the minimal phase lag at low frequency, likely, because of the domination of the electrostriction. At high frequency, the phase lag became close to 60 degrees for both membranes indicating mixing of the signals from electrostriction and Joule heating. Actually, Al electrodes became non-blocking for the high frequency range of applied voltages, while membrane with Ti electrode at high frequency became heated due to increase of its resistance. That is why the mixed regime was realized in a high frequency range and phase lag became similar for both membranes.

Thus, the electrode providing the voltage for the membrane significantly limited the frequency range, where the CGO self-supported membrane could be operated in a regime with dominant electrostriction effect without essential heating.

4. Conclusion

We demonstrated the existence of two principal excitation mechanisms of the self-supported Gd-doped cerium oxide $Ce_{0.8}Gd_{0.2}O_{1.95}$ (CGO) thin circular membranes: electrostriction effect and Joule heating. Al electrodes apparently formed a blocking interface with CGO, probably a Schottky barrier. Therefore, at low frequencies no field was applied at CGO and at high frequencies, the barrier became electrically transparent because of the high electrical capacitance. As a result, at low frequencies the response of the membranes with Al contacts was very small, but at high frequencies it was dominated by the Joule heating. The resistance of the titanium electrodes was much smaller and a large fraction of the electric field fell on the CGO layer already at low frequencies. In this case, the electrostriction became a dominant excitation mechanism. Operating the membranes at high frequencies (> 0.1 MHz) caused a mixed regime of excitation.

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