Key-features in processing and microstructure for achieving giant electrostriction in Gadolinium doped ceria thin films

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Abstract

Gadolinium doped ceria is a well-known oxygen ion conduction material for solid fuel cell electrolytes. With its centrosymmetric average lattice and relatively low bulk dielectric constant it does not look interesting for electromechanical applications. However, a giant electrostriction (ES) effect was recently found in $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ thin films. It was explained by the dynamic response of oxygen vacancies to an external electric field. In this work, the giant ES response has been reproduced in sputter deposited thin films. The proper transverse bulk ES coefficient has been derived from the measured clamped value. For this purpose, the Young's modulus was measured by nanoindentation. The highest ES coefficient was found as $9.0 \times 10^{-19} \text{ (m/V)}^2$ for the strain coefficient, and $2.3 \times 10^{-7} \text{ N/V}^2$ for the effective stress coefficient. Specific growth conditions must be chosen in order to obtain a microstructure exhibiting the giant ES effect. There is evidence for a higher oxygen deficiency than needed to compensate the gadolinium dopants (Gd'). It was observed that the nature of the bottom electrode impacts on the size of the effect. The highest response was obtained at films grown on Al bottom electrodes. To learn more on the mechanisms of the giant ES effect, a bipolar cycling was performed to test the delay time for the ionic reorientation in changing the sign of polarization, as observed in the stress loop. The maximal response was observed below 100Hz in this bipolar mode, showing that the time for 180° reorientation amounts to several milliseconds.

1. Introduction

Recently, very intriguing properties were discovered in thin films of doped fluorite structures such as HfO_2 , ZrO_2 , and CeO_2 . Intriguing, because one would expect only from more complex materials to display ferroelectricity or incipient ferroelectricity, but not from simple dielectrics. It was found that Si doped HfO_2 exhibits remarkable ferroelectric properties^[1], which are so attractive that such films are investigated for non-volatile memories^[2]. Another astonishing effect was discovered by Korobko and coworkers at Gd-doped ceria (CGO) thin films^[3], normally investigated as solid electrolyte membrane in micro solid oxide fuel cells^[4]. They found that the electrostrictive response of CGO was very much larger than that expected for a compound with a relatively low dielectric constant. A huge electrostrictive stress was created upon application of an electric field. Their experiment yielded a generated compressive stress of -30 MPa at an electric field of 78 kV/cm (figure 2-f in ref.^[3]), or a stress coefficient of $5.0 \times 10^{-7} \text{ N/V}^2$. The same authors reported even higher values. The size, and also the fact that a compressive stress is generated – in contrast to the piezoelectric effect in thin films that produces a tensile stress at equal geometry – makes this finding extremely interesting for actuators in micro electro-mechanical systems (MEMS). Since in addition, it is a lead free material, there are excellent prospects for such applications.

While ferroelectricity in the hafnia films is ascribed to the occurrence of a non-centrosymmetrical phase due to the impact of mechanical constraints of the sandwiched film, and the local epitaxy to the TiN electrodes,^{[5][6]} the high electrostriction in the ceria films is ascribed to a high density of oxygen vacancies V_O that are introduced by the choice of dopant atoms and concentrations. Indeed the used $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}(\text{V}_\text{O})_{x/2}$ compound with $x=0.20$ leads to a large oxygen vacancy concentration of 5 at%. Electrostriction (ES) was explained by the lability of Ce- V_O pairs leading to the possibility to reorient them with an electric field. Korobko et al^[3] could also make plausible that bond reorientation and length change in an electric field would lead to a compressive stress. Verifying this hypothesis is somehow challenging and one has to study the defect density and more particularly the content of oxygen vacancies on the final response. In addition, one has also to take into the account that the electrostrictive coefficients of thin films cannot be directly compared to ones of bulk materials as the films are part of a layered composite structure.

In this paper, the electrostriction coefficients in thin film configuration is explained both

in the clamped and free body case. It is shown that the giant ES effect in CGO thin films is related to defects, which are produced during rather specific deposition parameters such as a low deposition temperature, an optimal ion bombardment and high deposition rate. The ES effect in ordinary CGO thin films was determined as well. It was found at our optimized films that the giant ES effect means an amplification by a factor 30 to 70 as compared to the ES effect in ordinary CGO thin films. Furthermore, it was discovered that the giant effect depends on the electrode type on which the CGO film is grown, and that the giant ES properties are increasing with lower stiffness. Finally, our work suggests a defect reorientation when changing the sign of the electric field. This reorientation needs several milliseconds time, and could be attributed to a 180° defect polarization change.

2. Electrostriction coefficients in thin films

In general, all materials undergo a change in dimensions when they are subjected to an electric field. In non-piezoelectric materials this is due to the electrostrictive effect generating a strain that is proportional to the square of electric field^[7]. The electrostrictive coefficients in bulk materials are usually derived for two special situations. Either the body is free to elongate or shrink in all directions at zero stresses (constant stress (T) condition), or the body is kept at zero strain in all directions (constant strain (S) condition). However, thin films are part of a composite structure with the substrate, meaning that the film is clamped in the plane to the substrate (strain S_1 and S_2 must be continuous across the interface), but free to move out of plane ($T_3=0$). This leads to the definition of coefficients at mixed border conditions: constant strain in the plane, and constant stress out of plane, as in the case of piezoelectric thin films^[8]. The searched thin film coefficient is obtained from the constitutive equations (equations 1-3) by setting $T_3=0$, and $S_1=S_2=0$:

$$S_1 = s_{11}T_1 + s_{12}T_2 + M_{31}^{(T)}E_3^2 = 0 \quad (1)$$

$$S_2 = s_{12}T_1 + s_{11}T_2 + M_{31}^{(T)}E_3^2 = 0 \quad (2)$$

$$\Rightarrow T_1 + T_2 = -\frac{2M_{31}^{(T)}E_3^2}{s_{11} + s_{12}} \quad (3)$$

The coefficients s_{ik} denote the components of the elastic compliance tensor, $M_{31}^{(T)}$ the electrostriction coefficient at constant stress, following the same notation as for the piezoelectric

78 tensors (first index refers to electric field, and the second index represents the strain com-
 79 ponent represented in the reduced index notation). Since the film is isotropic in the plane,
 80 the two stress components must be equal in magnitude. This leads to the definition of an
 81 effective, electrostrictive thin film coefficient, as shown in equation 4 ((S) and (T) stand for
 82 constant strain, and stress, respectively):

$$T_1 = -\frac{M_{31}^{(T)}}{s_{11} + s_{12}}E_3^2 = -M_{31,f}^{(S)}E_3^2 \quad (4)$$

83 where T_1 is the in-plane stress, and E_3 the electrical field perpendicular to the plane of the
 84 film. $M_{31,f}^{(S)}$ is a practical coefficient that is directly measured in beam bending experiments.
 85 In order to compare this coefficient with the standard strain coefficient $M_{31}^{(T)}$, one needs to
 86 know elastic properties, i.e $s_{11}+s_{12}$. In cubic or isotropic materials, the latter are expressed
 87 in terms of Young's modulus Y and the Poisson's ratio ν , giving the relation as shown in
 88 equation 5:

$$M_{31}^{(T)} = (s_{11} + s_{12})M_{31,f}^{(S)} = M_{31,f}^{(S)} \frac{(1 - \nu)}{Y} \quad (5)$$

89 The M_{31} coefficients were found to be positive^[3]. The effect thus produces compressive
 90 stress in the clamped case, and a positive strain in the free body case.

91 3. Experimental

92 3.1. Thin film synthesis and sample fabrication

93 $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ thin films were grown by RF magnetron sputtering on polycrystalline
 94 metal electrodes of Pt, Al, and Cr. Passivated silicon wafers served as substrates. All elec-
 95 trodes were deposited at 320 °C. CGO was deposited after a vacuum break. Details of the
 96 CGO process are given in table 1. The electromechanical properties were assessed by beam
 97 deflection techniques. The beams had full wafer thickness (525 μm) and were obtained by
 98 dicing. The dicing marks were formed together with the top electrodes by sputter deposition
 99 of Pt/Cr through a shadow mask (figure 1).

100 3.2. Structural characterization

101 The texture of the films was determined by Bruker D8 advanced X-ray diffractometer.
 102 The Al and Pt electrodes had (111) texture as is expected for FCC sputtered metals, while Cr

Table 1: Sputter process conditions for CGO thin film deposition

Target (100 mm dia)	$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$
Base pressure	$< 5 \times 10^{-4}$ mTorr
Sputter pressure (Ar)	10-20 mTorr
Growth temperature	RT - 400 °C (HT)
Ar gas flow	15 sccm
RF magnetron power	200 W
Film thickness	$2 \mu\text{m}$ ($\pm 10\%$)

Figure 1: Sample structure for electromechanical characterization of the CGO thin films. The beams had dimensions of $15.0 \times 1.50 \times 0.38$ mm and were clamped across the narrow part of the top electrode (left side). The dot on the right hand side serves to reflect the light of the proximity sensor of the electromechanical measurement setup.

electrodes texture had (110) texture, also, expected for a BCC metal. The film microstructure was investigated in cross-section by using a FEI Tecnai Osiris Transmission Electron Microscope (TEM) at 200 kV. A chemical mapping by EDX (energy-dispersive X-ray spectroscopy) measurement was done. Chemical composition was measured using Merlin scanning electron microscopy (SEM) at 3 kV.

3.3. Measurement setup

The cantilever beams were mounted on X-Y-Z stage controlled by micro screw drives. The top and bottom electrodes were accessed via micromanipulators. The films had been subjected to sinusoidal bipolar excitation (zero DC offset). The displacement at the tip was tracked using a MTI 2000 “fotonic” sensor (see figure 2). From the cantilever deflection, the curvature and thus the film stress is derived. Division by the square of the electric field yields the effective stress ES coefficient $M_{31,f}^{(S)}$. If not stated differently, the values given in this paper

115 correspond to a the maximal effect obtained with a sweeping frequency of 66 Hz. A detailed
 116 description of our setup and procedure (derivation of large-signal response) was published
 117 by Mazzalai et al^[9]. This method is a standard one for evaluating converse piezoelectric
 118 coefficients in piezoelectric thin films method.

Figure 2: Schematic of the cantilever-tip displacement measurement setup, used for electrostrictive characterization (after^[9]).

119 3.4. Nanoindentation

120 In order to derive $M_{31}^{(T)}$, the elastic modulus (Y) is needed. We determined it by means of
 121 nanoindentation. Elastic properties can also be indicative of the oxygen vacancy concentra-
 122 tion, as in flourite-structured oxide materials the elastic modulus decreases with increasing
 123 concentration of oxygen vacancies^{[10][11][12]}. A Nano Indenter XPTM (MTS Nano Instru-
 124 ments) with a three-sided diamond Berkovich indenter was used for the nanoindentation
 125 experiments. The compliance of the set-ups as well as tip shape was calibrated using fused
 126 silica standard^[13]. A linear loading and unloading profile with peak load of 25mN and dwell
 127 duration of 20s was applied. The loading and unloading durations were 20s each. The ther-
 128 mal drift was measured at 10 % of peak load value during unloading for 60 s. 20 indents
 129 were performed for each sample. The maximum displacement depths were less than 10% of
 130 film thickness in order to avoid elastic substrate effects from affecting the measured modulus
 131 values^[14]. The elastic modulus was calculated using the method proposed by Oliver and
 132 Pharr^[13]. The Poisson ratio needed for the calculation was taken as 0.334 as found in the lit-
 133 erature for ceramic electrolyte layers of CGO 80/20^[15]. The same work published a modulus

Y=187 GPa, which is close to the values obtained in this work. As no single crystal compliance tensors are measured so far for CGO 80/20, we could not calculate modulus values for a specific thin film texture. In the same work, a modulus decrease of 6.5 % was obtained when increasing the Gd content from 10 to 20 %, thus increasing the V_{O} concentration by 2.5 %. Very similar values were derived from density functional theory for pure ceria, i.e. 8 % decrease for a 3% vacancy concentration^[12]. In this case the vacancies are apparently compensated by electrons, which are most likely trapped by Ce^{4+} ions, thus becoming negative Ce^{3+} point defects. The existence of these were shown by electron paramagnetic resonance in earlier works on reduced CGO^[16].

4. Results and discussion

4.1. Microstructure effect

According to the mechanism described by Korobko et al^[3], a (111) film texture is important for obtaining maximum electrostriction effect. Fluorite thin films grow in fact most naturally with this texture, as known from most FCC structures, as a result of nucleating the densest plane parallel to the surface. This is also valid for the iso-structural YSZ thin films, at which deviation from this rule, i.e. growth of (200)-oriented grains, could be attributed to strong ion bombardment during sputter deposition^[17]. Within our experimental matrix, we found that high temperature (HT) grown films on Pt showed more prominent (111) texture than those grown at RT (figure 3-a). Nevertheless, as shown in figure 3-b, RT films show a much stronger effect. The origin of such behavior must lie in the different microstructure, and particularly the higher defect density of low temperature processed films. As oxygen vacancies were proposed to play an essential role in the giant ES effect^[3], the formation of additional oxygen vacancies during RT deposition is a likely mechanism. In order to verify this, we performed simultaneous SEM-EDAX measurements of the RT deposited film, and at a piece of the same sample subjected to a post-anneal in oxygen ($T=600\text{ }^{\circ}\text{C}$ for 15 minutes), table 2. It was found that the former had $1.5\pm0.5\%$ less oxygen content. In agreement to EDAX, nanoindentation results show elastic modulus of 205 GPa and 185 GPa for HT and RT prepared films on Pt(111), respectively. This variation in principle can be attributed to higher oxygen vacancy content in RT films. This 10 % decrease would be compatible with an increase of oxygen vacancies of 3 to 4 %. The lower measured value with SEM-EDAX is probably caused by an insufficient re-oxidation of the post-annealed sample. It appears that

the processing conditions have to be manipulated in a way to increase the concentration of oxygen vacancies - or eventually of another unknown defect forming at the same time and promoting as well the giant ES effect.

Figure 3: a) XRD pattern, and b) Generated electrostrictive in-plane stress change as a function of the applied electric field swept at 66 Hz of a high (HT) and a room (RT) temperature deposited CGO thin film grown at 15 mT Ar pressure on Pt (111) bottom electrodes.

Table 2: Normalized atomic concentration of Cerium (Ce), Gadolinium (Gd), and oxygen (O) for films grown on Pt bottom electrode for as-deposited and annealed (in oxygen at 600 °C for 15 min) samples.

Sample	Ce	Gd	O
Pt (RT)	20.8±0.3	6.1±0.3	73.1±0.3
Pt(RT)+Annealing	20.2±0.3	5.6±0.3	74.2±0.3

168 Three different bottom electrodes, namely Pt, Al, and Cr, were used to investigate their
169 influence on CGO electrostriction response. The electrodes were exposed to air prior to CGO
170 deposition, resulting in thin oxide layer formation on Al and Cr electrodes. The STEM-
171 EDAX line scans shown in figure 4 show evidence of the oxide scales of Al and Cr at their
172 interfaces, as the oxygen atoms extends into these electrodes.

173 The growth mechanism of CGO on Pt electrodes is expected to be quite different in com-
174 parison to the one on Al and Cr electrodes. Figure 5 compares CGO films grown on the
175 mentioned electrodes. Cross-section TEM dark field images, figure 5 (a-c), demonstrate that
176 films grown on Al and Cr bottom electrodes have a columnar structure with fiber shaped
177 grains, whereas in case of Pt, the grains are larger and also show large grains overgrowing
178 smaller (111)-oriented ones at the interface (as evidenced by high resolution TEM images,
179 not shown here). The ring-shaped diffraction patterns 5 (d-f) confirm the polycrystalline na-
180 ture. The film on Pt electrodes exhibits a more "spotty" pattern (figure 5 (b)), which confirms
181 the presence of larger crystals. In case of Al and Cr bottom electrodes, the SAED patterns
182 (figure 5 (a,c)) with arcs are indicating better preferentially oriented films. Furthermore, the
183 films grown on Al bottom electrodes are showing arcs with greater intensity, confirming that
184 this film is having a better (111) texture, as already observed by X-ray diffraction. From
185 this technique, (111)-texture indexes of 78%, 75%, and 56% were derived for Al, Cr, and Pt
186 electrodes, respectively. The surprising point is the stronger (111) texture on Cr (110) than
187 on Pt (111). This could be due to the oxide layer on Cr that prevents epitaxial attachment to
188 the metal surface.

Figure 4: Line scans at the interface film-electrode obtained from STEM-EDAX Hyper-maps for CGO films grown on Al (a) Pt (b) and Cr (c) bottom electrodes deposited at room temperature. The Gd signal inside the Pt-electrode (b) and, the Gd and O signals inside Cr-electrode (c) are due to peak overlapping with the respective elements.

Figure 5: Dark field TEM images for the CGO thin films grown on Al, Pt and Cr bottom electrodes, which are sorted from left to right respectively.

Figure 7 shows the in-plane stress change generated in CGO films for the different electrodes. The highest $M_{31,f}^{(S)}$ coefficient was found in films grown on Al bottom electrode where we have the best (111) texture and narrower, fiber type grains. With an identical process we have obtained electrostriction stress coefficient of 1.4×10^{-07} (N/V²) on Al, as compared to 3.3×10^{-08} (N/V²), and 3.7×10^{-08} (N/V²) for Pt and, Cr bottom electrodes, respectively. These results clearly demonstrate the effect of microstructure on the ES response. ES strain and stress coefficients, (111)-texture indexes, and elastic moduli of films mentioned in this report are listed in table 3. CGO films with Al bottom electrode are showing a roughly 10 % lower young modulus, as compared to high temperature grown films on Pt electrodes, and even considering the measurement error, a lowering of 5 % remains as significant value. Meanwhile, one can also consider the porosity as reason of elastic modulus change^[18], which is definitely not the case here as can be seen in the STEM-HAADF (high angle annular dark field) image of figure 6, showing a dense microstructure. Pores would appear as dark regions or dark spots in the HAADF image. A 5 to 10 % reduction in elastic modulus corresponds to an oxygen vacancy concentration of 2 to 4 %, according to literature works cited earlier on this article^{[15][12]}. The important finding is that the giant ES effect is not caused by the oxygen vacancies present to compensate the charged Gd point defects - as proposed by Korobko et al^[3] - but by additional oxygen vacancies that need to be compensated by electrons close to the conduction band, and normally thought to be trapped in Ce³⁺ states^[16]. Possibly, such vacancies are reorienting more easily, as they are not interacting with a Gd³⁺ ions staying at a fixed positions. Moreover, in contrast to earlier findings^[19] our results show that the bottom electrode plays a major role in determining the electrostriction coefficient, and thus needs to

be selected carefully, as it may change the response by a factor of 5.

Figure 6: High angle annular dark field (HAADF) TEM image of CGO thin film grown on Al bottom electrode at room temperature.

Table 3: The electrostriction stress coefficient, $M_{31,f}^{(S)}$, strain coefficient $M_{31}^{(T)}$, (111) texture index, and elastic modulus of CGO films deposited at room temperature on three different bottom electrodes (B.E.), Al, Pt, and Cr. $M_{31}^{(T)}$ was derived according to eq. 5, and with an electric field sept at 66 Hz. (* The Al(5.8) film will be discussed in following section)

B.E.	$M_{31,f}^{(S)}$ (N/V ²) $\times 10^{-07}$	$M_{31}^{(T)}$ (m ² /V ²) $\times 10^{-19}$	(111)-Texture index (%)	Elastic modulus (GPa)
Al (RT)(6.4)	1.4	5.4	78	180 $\pm$ 7
Pt (RT)	0.33	1.2	56	185 $\pm$ 9.5
Cr (RT)	0.37	1.3	75	190 $\pm$ 6.5
Al (RT)(5.8)*	2.3	9	70	180 $\pm$ 8.5
Pt (HT)	0.12	0.4	84	205 $\pm$ 8

4.2. Ion bombardment effect

Besides electrodes and deposition temperature, other processing variables also impact the ES properties. In sputter deposition, ion bombardment is an important parameter, and influences for instance piezoelectricity of AlN thin films^{[20][21]}. Ion energy and flux density

Figure 7: In-plane stress change as function of electric field for CGO films deposited on different bottom electrodes (Al, Pt, and Cr) at room temperature, 15mT working pressure. The characterization frequency was 66 Hz.

are influenced by all process parameters. We varied substrate-target (S-T) distance and the sputter gas pressure to investigate their effect on the ES response. Plasma effects, such as ion bombardment, as well as deposition rate increase with decreasing S-T distance and pressure. As presented in table 4, at a large S-T separation of 10 cm resulted in low ES response (-16 MPa stress at $E = 850$ kV/cm). Smaller S-T distance of 6.4 cm resulted in a film that yielded -12 MPa in-plane stress in a field of only 90 kV/cm ($M_{31,f}^{(S)} = 1.4 \times 10^{-07}$ (N/V²). Further lowering of the distance to 5.8 cm lead to even stronger ES properties (-8 MPa at 59 kV/cm, $M_{31,f}^{(S)} = 2.3 \times 10^{-07}$ (N/V²), however at the expense of an increased leakage. This film also exhibited a lower modulus ($Y = 180$ GPa), so one may assume that this film contains more oxygen vacancies. When we are going closer to the target, the deposition rate increases. Therefore, there is less time at the surface of the growing film to annihilate oxygen vacancies by oxygen uptake, as the diffusion distances are very limited at room temperature. A further lowering of the S-T separation leads to a loss of the (111) texture - the (111) texture index decreases from 78% to 15% - accompanied by a strong decrease in ES properties. Moreover, at lower distance the negative O-ions coming from the target have more energy and implant easier in the film. Three different sputter pressures of 10, 15 and 20 mT were applied. The ES coefficients $M_{31,f}^{(S)}$ were measured as 4.6×10^{-09} , 1.4×10^{-07} , and 8.1×10^{-09} (N/V²), respectively (table 4). The highest electrostrictive response was achieved with 15 mT

234 Ar pressure. An optimal ion bombardment is thus needed to induce the giant electrostriction
 235 effect.

Table 4: ES stress coefficient $[N/V^2]$ as function of substrate-target (S-T) separation and chamber pressure for the films grown on Al bottom electrode at room temperature

S-T separation Chamber Pre.	10 cm	6.4 cm	5.8 cm	5.2 cm
10 mT		4.6×10^{-09}		
15 mT	2.2×10^{-09}	1.4×10^{-07}	2.3×10^{-07}	3.4×10^{-10}
20 mT		8.1×10^{-09}		

236 Finally, as had been presented in this report, in order to obtain an extraordinary ES re-
 237 sponse, one has to be careful about: i) Film microstructure and texture, ii) Ion bombardment,
 238 iii) Bottom electrode, and iv) Deposition temperature. Ideally, the process condition has to
 239 be manipulated in a way that results in high oxygen vacancy content while maintaining the
 240 (111) texture.

241 4.3. Time delays in ion reorientation

242 If the giant ES effect is due to bond reorientation and local defect rearrangements, it is
 243 expected to be slower than a piezoelectric response, which is a pure lattice effect with small
 244 ion displacements from the equilibrium positions, and which may work up to the 100 GHz
 245 region. Three films with high giant ES have been characterized over a frequency range from
 246 22 to 1052 Hz (Figure 8). The observed ES response was indeed strongly dependent on the
 247 frequency. A hysteresis was observed, and the amplitude decreases with frequency above
 248 100 Hz. Thus, for a 180 degree redirection of the polarization, the giant ES effect needs at
 249 time in the ms time range to explain the observed time lag. The apparatus has been checked
 250 with Aluminum nitride (AlN) samples to see that there is no hysteresis at these frequencies.

Figure 8: In-plane stress change generated by an electric field as a function of frequency for CGO films deposited on three different electrodes, a) Al , b) Pt, and c) Cr. All films were deposited at room temperature with 15mT working pressure and 6.4 cm S-T separation (same as in table 2).

Conclusions

We have shown that specially prepared CGO thin films show the phenomenon as described by Korobko et. al, and that our films achieve electrostrictive strain coefficients of up to $M_{31}^{(T)} = 9.0 \pm 0.5 \times 10^{-19} \text{ (m}^2/\text{V}^2\text{)}$. The particular microstructure required for the giant ES effect was obtained by employing a low deposition temperature, a higher ion bombardment, and an higher deposition rate, as compared to the usual process for an electrolyte membrane fabrication. All these parameters ranges are known to produce a higher defect density. In the end, we obtained a 70 fold increase of the ES coefficient as compared to ordinary CGO thin films. There is evidence that a higher oxygen vacancy concentration than introduced by the Gd doping is needed. We found by SEM-EDAX investigations that this excess concentration is 1 % or higher. These additional oxygen vacancies are compatible with the observed lowering of the stiffness, a maximal concentration of less than 4%. We also have shown that the bottom electrode has a crucial impact on the efficiency of the microstructure. Best electrostrictive responses have been obtained for films deposited on Al bottom electrodes, i.e., $M_{31,f}^{(S)} = 2.3 \times 10^{-07} \text{ (N/V}^2\text{)}$. This could indicate that a reduction of CGO at the interface plays a role for increasing oxygen vacancy concentration. Additional defects, and most likely the mentioned oxygen vacancies compensated by Ce^{3+} , are in fact needed to explain why ordinary CGO with the vacancies compensating the Gd dopants do not lead to the giant ES effect. We also have observed a strong frequency dependence of the ES response in case of bipolar operation. The change of sign of the electric field is leading to hysteretic behavior in terms of a voltage shift of the stress curve. There is an obvious time delay in increasing and decreasing the giant ES effect in a time varying electric field, supporting the hypothesis advanced in the literature that bond reorientation in the electric field, eventually accompanied by a vacancy hop, is at the origin of the effect. The involved time delays are typical for space charge effects in the response of dielectric materials. The large impact on electrostrictive stress shows that the effect is in the bulk of the material, and not just at the interfaces. Further investigations are needed to elucidate the precise acting mechanisms of this behavior, leading to a phenomenon comparable to best electrostrictive materials known so far. These special giant ES $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ thin films thus show a promising potential as a new electromechanical material for actuators.

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