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Electro-chemo-mechanical effect in Gd-doped Ceria thin films with a controlled orientation

Simone Santucci**, Haiwu Zhang¹, Simone Sanna¹, Nini Prydsº, Vincenzo Esposito*¹

Gd-doped ceria fluorites (CGO) exhibits prominent electro-chemo-mechanical properties and giant-electrostriction at room temperature has been recently disclosed in both CGO polycrystalline films and bulk. The electrochemical properties in CGO depend on oxygen vacancy defects of the fluorite lattice. Early experiments suggest that defects along the [111] crystallographic direction promote high atomic distortion. These factors result in the largest electrostriction response ever measured. However, only out-of-plane electrostriction (i.e. M⊥) in [111] CGO oriented thin films has been reported so far, and several questions remain open about electrostriction mechanism in the oxygen-defective fluorite. Here, we present electromechanical performances along with different crystallographic directions. We grow thin films by pulsed laser deposition on single crystals substrates to obtain longitudinal, and shear deformations (i.e. M∥ and M shear) of highly coherent (100), (110) and (111) oriented CGO thin films. As a result, we find an order of magnitude higher electrostrictive coefficient along [100]. Such an analysis gives a new insight into the mechanism of CGO electrostriction.

Introduction

Ceria-based materials apply in a wide range of applications such as solid oxide fuel cells (SOFCs)¹-³, oxygen sensors ³⁴ and storage⁵, catalysts⁶-² and memristors⁸-¹⁰. Ceria oxide, i.e. CeO₂, is capable of accommodating a high amount of oxygen vacancies (V̅O) into the lattice, which results in a remarkable versatility as ionic conductor and catalyst¹¹-¹³. At temperatures superior to 1200 °C, highly ionic and low oxygen partial pressure (P O₂ = 2.5 x 10⁻¹⁸ atm)¹⁴, ceria undergoes a chemical reduction of Ce⁴⁺ to Ce³⁺ releasing oxygen gas and consequently increasing the defects concentration, δ = (V̅O)¹⁵,¹⁶. Acceptor doping, e.g. by substitutional rare-earth cations with a 3+ valence state (i.e. Gd, Nd, Sm, La), stabilizes the structure and leads to high ionic mobility²,⁷,¹⁷-²¹. At room temperature, doped ceria showed outstanding electromechanical properties due to local distortion in the vicinity of oxygen vacancies.²² Studies carried out on Gd-doped ceria (CGO) thin films²²-²⁶, bulk²⁷,²⁸ and membranes²⁹-³¹, show an average electrostriction coefficient of M∥ = 6 · 10⁻¹⁸ (m² V⁻²)²², which is comparable to the state-of-the-art materials such as Pb(Mg₁₋ₓNB₂ₓ)O₃ (M∥ = 2 · 10⁻¹⁸ m²V⁻²)³². For classical electrostrictors, Newnham et al. provided a relationship in which the logarithm of performances depends on (S/e), with S elastic compliance and e dielectric constant.³³ However, Yavo et al.³⁴ showed that CGO electromechanical properties are conflicting with Newnham law. The electrostriction coefficient is two-three orders of magnitude higher than similar materials³⁵, meaning that a different mechanism is in play. In the same study, they also showed high electrostriction in (Y, Nb)-stabilized BiO₃ bulk. These findings suggest that such features are common to some defective fluorite structures, representing a new family of electromechanical functional materials.
Fig. 1. Vacancy neighbor structure of CeO$_2$ and related structures. a) Ce$_{ce}$-7O-V$_0$ unit, structure of the current model for electrostriction in CGO. Black vector: V$_0^-$ - Ce$_{ce}$ - O$_6$ electroactive triplet and distortion direction. Blue vectors: consequent 6O displacement b) 4-units complex composed of four Ce$_{ce}$-7O-V$_0^-$ distorted units with central vacancy. Near-empty site oxygen atoms, i.e. 6O, are numbered. Red lines highlight the bond direction of Ce atoms with oxygen 1 and 2. c) 60 octahedron structure composed of six near-empty site oxygen atoms, base structure for our new model.

A similar octahedron structural representation is used to describe the effect of local distortion in piezoelectric ABO$_3$ perovskites. In such a structure, the oxygen atoms arrange as an octahedron with a centred B-ion that induces stress. For piezoelectric perovskites, Li et al. also showed a trend of the distortion magnitude as a function of the electric field to the crystalline directions. Such an analysis shows that an electric field parallel to <100> allows oxygen to release the stress imposed by the cation easily along the octahedron axis, favouring atomic distortion. By comparison, the displacement along the <110> directions results in an overall counteracting of the surrounding, leading to a decreased electromechanical response. In the same way, <111> directions show an even weaker distortion effect. On the other hand, the trend is the opposite in fluorite structures such as CaF$_2$.

In this work, we use pulsed laser deposition (PLD) technique to grow (100), (110), and (111)-oriented CGO grain boundaries free thin films on (100)-oriented SrTiO$_3$ (STO) and (110) YSZ and (100) NdGaO$_3$ (NGO) respectively. To study the electrostriction effect, we analyze both the longitudinal ($M_{11}$) and the shear ($M_{12}$) responses of the films as a function of the crystallographic orientation and the direction of the electric field. Then, we compare the experimental results with the microscopic model based on ABO$_3$ octahedron applied to CGO. As a result, we are able to provide new...
insight into the electrostrictive mechanics in the defective fluorite structure.

**Experimental**

Film and electrodes deposition

We fabricated Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ target from powder pressed at 140 MPa and then sintered at 1723 K for 10 h. XRD investigation indicates a pure fluorite phase of the target. One micron thick films of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ are grown on STO(100), NGO(100) and YSZ(110) substrates by PLD using a KrF the excimer laser ($\lambda = 248$ nm), at 20 Hz repetition rate, 120 mJ energy and fluency of about 1.8 J cm$^{-2}$ (deposition rate was ~0.07 Å/pulse). During the deposition, we fixed the background oxygen pressure at $10^{-3}$ mbar, with a temperature of 600 °C. Such condition is optimal to grow high-quality fluorite structured CGO with single orientation. After deposition, the samples were kept in the chamber with the temperature slowly decreasing (-3°C/min) for reoxidation and release the stress. We sputtered Au top electrodes with a Bal-tec SCD 005 Sputter Coater at room temperature. The substrates’ size was 5 x 2.5 mm and 0.1 mm thick.

Samples characterization

We analysed the crystallographic properties of the grown samples using X-ray diffraction with a Rigaku Smartlab diffractometer. We carried out θ-2θ and rocking curve scans, and the crystalline quality of the film was established by evaluating the full-width-half-maximum (FWHM). Grazing incident angle scans with θ-2θ = 248 nm, at 20 Hz repetition rate, were performed on CGO/NGO to exclude the reflection of the substrate, and then sintered at 1723 K for 10 h. XRD investigation indicates a pure fluorite phase of the target. One micron thick films of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ are grown on STO(100), NGO(100) and YSZ(110) substrates by PLD using a KrF the excimer laser ($\lambda = 248$ nm), at 20 Hz repetition rate, 120 mJ energy and fluency of about 1.8 J cm$^{-2}$ (deposition rate was ~0.07 Å/pulse). During the deposition, we fixed the background oxygen pressure at $10^{-3}$ mbar, with a temperature of 600 °C. Such condition is optimal to grow high-quality fluorite structured CGO with single orientation. After deposition, the samples were kept in the chamber with the temperature slowly decreasing (-3°C/min) for reoxidation and release the stress. We sputtered Au top electrodes with a Bal-tec SCD 005 Sputter Coater at room temperature. The substrates’ size was 5 x 2.5 mm and 0.1 mm thick.

**Electrostriction setup**

The electromechanical characterization is carried out on a cantilever with planar top electrodes. The samples had one side glued to a base, and the other one free to move. The experiment was performed at room temperature. The method used to calculate the electrostriction coefficient is reported in detail in the Supplementary Information. We performed the measurements with a single-beam laser interferometer SIOS NA analyzer. The experimental setup and instruments are described elsewhere. We added some new features here described. The interferometer resolution is 5 pm, but the background noise is usually higher, and it is not possible to observe displacements smaller than 3-4 nm. We coupled an Ametek 7230 DSP Lock-in Amplifier to the interferometer. This instrument allows us to extract an oscillating signal from the raw measurement of SIOS NA analyzer. Since lock-in detection spots only periodically signal with a specific set frequency, the measured response is not affected by mechanical drift or external noises. As a consequence, when an oscillating field is applied, the resolution increases to values around 0.1-0.2 nm. These values are used as error bars in our measurements. Supplementary information reports further details of the instrument as well as measurement data as an example (Fig. S2). An AIM-TTI TGP 3100 function generator connected with a Trek 2220 amplifier, are used to apply a sinusoidal electric field to the samples. The voltage amplifier has been added to increase the electric field needed to trigger electrostriction on samples with planar electrodes. The contacts are made with tungsten tips. Oscillation in electrostrictive materials always takes place with double of the frequency of the applied field. For this reason, the source generator and the lock-in amplifier were set at 0.5 Hz and 1 Hz respectively. The displacement measured in this work is always related to the II harmonic contribution to the oscillation amplitude. A schematic of the updated experimental setup is reported in the supplementary information (Fig. S3).

![Fig. 2. Structural characterization of CGO on NGO. a) 8-20 scans of CGO on NGO at the top, CGO on STO and CGO on NGO at the bottom. Inset: 8-20 scan in grazing angle mode. b) rocking curve at (220) peak of CGO on STO, (200) peak of CGO on NGO and (111) peak of CGO on NGO. c) cross section images by SEM: from the top CGO on NGO, CGO on NGO and CGO on NGO.](image-url)
Results and discussion:

Structural characterization

Fig. 2. Structural characterization of CGO(111)/NGO (100), CGO(100)/STO(100) and CGO(110)/YSZ(110) thin films. a) θ-2θ scans of CGO(110)/YSZ(110) at the top, CGO(100)/STO(100) and CGO(111)/NGO(100) at the bottom. Inset: θ-2θ scan in grazing angle mode. b) rocking curve at (220) peak of CGO on YSZ, (200) peak of CGO on STO and (111) peak of CGO on NGO. c) cross-section images by SEM: from the top CGO(110)/YSZ(110), CGO(100)/STO(100) and CGO(111)/NGO(100).

We deposited highly coherent CGO thin films on several single-crystal substrates. Fig. 2 shows the results of both the structural characterization, i.e. XRD pattern in θ-2θ scan mode, rocking curve and the microstructure of the samples thin films by scanning electron microscope (SEM) images. Depending on the orientation of the substrates, the films are grown in a single orientation, i.e. CGO(110)/NGO(100), CGO(100)/STO(100) and CGO(111)/NGO(100) (Fig. 2a). The inset of CGO(111)/NGO(100) plot shows a grazing angle scan to exclude the presence of CGO (200). For the CGO(110)/STO(110), the cubic cell aligns along the [110] direction of the STO substrate and grows 45° in-plane tilted (Fig. 5S) 5, resulting to an epitaxial relationship <110>CGO/<100>STO in both in- and out-of-plane directions.

NGO is a perovskite with an orthorhombic cell. A pseudocubic structure with lattice parameter a ≈ 3.86 Å can be extracted 52. Considering an NGO substrate with (200)orthorhombic orientation, a good crystallographic match is the (111) face of CGO 52 with in-plane relationship [001]NGO//[0-11]CGO and [010]NGO//[1-21]CGO. Finally, YSZ and CGO have similar cell parameters, CGO grows on (110) YSZ with the in- and out-of-plane relationship <100>CGO/<100>YSZ and <110>CGO/<110>YSZ 48,49. More details of the film/substrate geometry can be found in the supplementary information. Fig. 2b shows the rocking curve scans of CGO(111)/NGO (100), CGO(100)/STO(100) and CGO(110)/YSZ(110) with FWHM values of 0.42°, 0.32°, and 0.33° respectively. Such low values indicate a high order of crystallinity. The cross-section of films (Fig. 2c) also shows a homogenous and continuous microstructure without the signature of vertical grain boundaries, i.e. columnar grains. The samples are grown with a thickness of t_f = 1 μm, ruling out the contribution from substrate-induced strain, which is relieved after a few nanometers 53. The lattice parameter of the CGO, as determined from the XRD, indicates that the structures are fully relaxed pure fluorite.

Electrostriction effect and discussion

We evaluated the electromechanical performances measuring the longitudinal M_{11} and the transverse M_{12} electrostriction coefficients. We used the cantilever vibration method 53 on samples with in-plane top electrodes (Fig. S1). In CGO(111)/NGO(100), we used two different electrodes configuration, as described in Supplementary Information (Fig. S4). By doing this, we can apply electric field along [-211] and [0-11] directions. In the same way, we apply voltage in CGO(110)/YSZ(110) along [001] and [1-23] in-plane directions, as depicted in Fig. S6. Fig. S1b shows a typical map of the 2nd harmonic component of vertical displacement d in different positions on the sample. The X-scans and Y-scans indicate a distortion both parallel and perpendicular to the electric field, respectively.
To measure the longitudinal electrostriction coefficient $M_{12}$, we measure the displacement $d$ in a fixed position for different electric fields. The scans along the width of the sample (Y-scans) allow evaluating the shear component $M_{12}$ (see the experimental section for details).

Fig. 3 shows the electromechanical response of CGO thin films for both longitudinal and shear directions. Indications of the electric field direction are also reported. Fig. 3a shows the performances of CGO(110)/YSZ in response to the electric field along [001] direction. The longitudinal electrostriction coefficient is found to be $M_{12} = 4.93 \times 10^{-17}$ mV$^{-2}$ and $3.50 \times 10^{-18}$ mV$^{-2}$, respectively. Fig. 3c,e show the response of CGO(100)/STO and CGO(111)/NGO to the electric field along [110] direction with a longitudinal electrostriction coefficient of $2.22 \times 10^{-17}$ mV$^{-2}$ and $1.9 \times 10^{-18}$ mV$^{-2}$, respectively. Fig. 3g shows the electric field in CGO(111)/NGO sample with in-plane electrodes is along [-211] direction with an $M_{12} = 2.03 \times 10^{-18}$ mV$^{-2}$. In CGO(110)/YSZ with electrodes along the [-223] direction, the electrostriction is annihilated, and the oscillations are so weak to be comparable with the background noise. Therefore, we cannot calculate the electrostriction coefficient, and we report it as minimal noise value $M_{12} = 6.72 \times 10^{-19}$ mV$^{-2}$. Each measurement lasted between 5 and 10 minutes. We did not find evidence of degeneration of performances with time, evidencing sound mechanical integrity of the device.

According to equation S4, the electrostriction coefficient is dependent on CGO Young’s modulus ($Y$), which we assumed 200 GPa $^{22,23,33-35}$. $Y$ values can change depending on the $hkl$ texture, but such measurements are still not available in the literature. However, Goldsby et al. reported the elastic compliances of CeO$_2$ by the first-principle simulation for different $hkl$ $^{56}$, showing a maximum difference of 30% from the average value. Moreover, Young’s modulus was obtained in fluorite structure YSZ $^{57,58}$, showing similar values along with all the crystal directions. Kurpaska et al. in particular, reported $Y$ ranging from 235 GPa along <110> to 216 GPa along with <111> $^{59}$. Fujikane et al., on the other hand, showed variable $Y$ depending on the experimental technique. They considered the nanoindentation method as the most trustable as they obtained $Y$ with a maximum difference of 21% or 9% for elastic and elastoplastic deformation, respectively. Taking into account these results, we decided to use the approximated $Y$ presented in the literature for thin-film configuration.

Fig. 3b, f, h show the full Y-scans for $M_{12}$ analysis as a result of laser profilometry measurements. We applied 13 kV/cm at 1 Hz of frequency. The transverse electrostriction coefficient represents the component of stress that is perpendicular to the electric field. As the electrostriction effect takes place at both in- and out-of-plane directions, we describe the crystal distortion in terms of vertical and lateral directions. Fig. 3b shows the transverse electrostrictive response of CGO(110)/YSZ with a measured value of $M_{12} = 0.26 \times 10^{-17}$ mV$^{-2}$ considering the vertical (z) and in-plane (y) directions [110], [1-10], [0-11]. On the other hand, for the CGO(100)/STO sample, the electrostriction coefficient is $M_{12} = 1.2 \times 10^{-17}$ mV$^{-2}$ along [100], [1-10], [0-11]. As depicted in Fig. 3d, CGO(111)/NGO shows an electrostriction coefficient of $M_{12} = 1.9 \times 10^{-18}$ for [111].

Our measurements deviate from the prediction of the single-cell model described by Yavo et al. $^{22,36,37}$ which suggests that the distortion is favoured if the electric field is along the [111] direction (see Fig. 1a). We propose here an alternative view of the effect, based on the previous one, but extended to the octahedron structure and supported by our experimental results. It is worth noticing that our interpretation is not necessarily in contrast with the model previously reported, as the primary effect is the same. We consider the broad environment of the oxygen vacancy and the anisotropic mechanical behaviour of electrostriction expands beyond the single-cell.

Fig. 4a shows the octahedron structure. Each of the oxygen atoms depicted withstands distortions from two $\mathbf{V}_{\text{O}}^\bullet$ - Ce$_{\text{O}}$ - O$_2$ triplets. As an example, the oxygen atom labelled as 2 (highlighted in the figure) is strained by the triplets labelled as A and B. Both distortions take place along diagonal directions, as depicted by the red arrows. Consequently, the resulting distortion is parallel to [100] direction.


Tab. 1. Longitudinal (M11) and shear (M12) electrostriction coefficient of CGO thin films depending on electric field direction and perpendicular orientation.a) (z and y denote the vertical and lateral orientation of the films, respectively). The values in the brackets are values calculated without subtracting the contribution of substrates (Fig. S7-8-9). *, **: el. conf. 2 (suppl. info).

<table>
<thead>
<tr>
<th>ORIENTATION (°)</th>
<th>LONGITUDINAL M11 (m²/V²)</th>
<th>SHEAR M12 (m²/V²)</th>
</tr>
</thead>
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<tr>
<td>CGO100/YSZ110</td>
<td>[001]</td>
<td>4.93 (9.11) ·10⁻¹⁷</td>
</tr>
<tr>
<td>CGO100/STO100</td>
<td>[011]</td>
<td>2.22 (2.45) ·10⁻¹⁷</td>
</tr>
<tr>
<td>CGO111/NGO100</td>
<td>[0-11]</td>
<td>3.50·10⁻¹⁸</td>
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<tr>
<td>CGO111/NGO100</td>
<td>[-211]</td>
<td>2.03·10⁻¹⁸</td>
</tr>
<tr>
<td>CGO110/YSZ110</td>
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<td>&lt;6.72·10⁻¹⁹</td>
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In this work, we fabricate highly coherent CGO thin films with (100), (110) and (111) orientation. These films are electromechanical tested using a planar electrodes geometry at different electric field directions for both longitudinal (M11) and transverse (M12) directions. The electrostrictive performances depend on the crystalline direction of the film, showing a maximum value of M11 = 4.93·10⁻¹⁷ m²/V² along <100> direction, followed by <110> and then <111>. To support the experimental results, we propose an extension of the current model, based on the octahedron structure of oxygen atoms neighbour of a V0 site. By such an interpretation, we explain the reason for the performance trend concerning crystal direction, giving new insight into the microscopic mechanism behind electrostriction in CGO.

Conclusions

In this work, we fabricate highly coherent CGO thin films with (100), (110) and (111) orientation. These films are electromechanical tested using a planar electrodes geometry at different electric field directions for both longitudinal (M11) and transverse (M12) directions. The electrostrictive performances depend on the crystalline direction of the film, showing a maximum value of M11 = 4.93·10⁻¹⁷ m²/V² along <100> direction, followed by <110> and then <111>. To support the experimental results, we propose an extension of the current model, based on the octahedron structure of oxygen atoms neighbour of a V0 site. By such an interpretation, we explain the reason for the performance trend concerning crystal direction, giving new insight into the microscopic mechanism behind electrostriction in CGO.

Conflicts of interest

There are no conflicts to declare.

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Gd-doped ceria electrostriction enhanced: The electrostriction effect in Gd-doped ceria is commonly thought to be maximum along <111> crystallographic directions as a result of a microscopic model. Based on experimental results on thin films with controlled in and out of plane orientation, this study uncovers new anisotropic properties of the effect, which is enhanced along with the <100> crystallographic directions by roughly one order of magnitude. Thus, we propose a new extended microscopical model to explain such new findings.