Giant Electrostriction in Gd-Doped Ceria

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Materials developing mechanical stress in response to the application of an external electric field are of great importance for a wide range of applications from actuators for portable cameras to transducers for audio-speakers and sonars. The electromechanical response of modern inorganic piezoelectrics and electrostrictors generally reaches a few MPa of stress per 1 kV•cm^{-1} of applied electric field and does not exceed an upper limit of ≈150 MPa either in bulk ceramics or in thin films.[1–5] While over the last several decades, these materials have become highly reliable and technologically mature, the magnitude of the mechanical stress generated in response to a given electric field is probably close to their limit. In piezoelectrics, stress develops due to the deformation of a non-centrosymmetric lattice under the application of an electric field. In commercial electrostrictors–materials with centrosymmetric lattices and very large dielectric constants–an external electric field distorts the unit cells of the lattice, rendering them locally non-centrosymmetric. In both cases, the electromechanical stress develops due to a small displacement of atoms within each unit cell. Increasing the magnitude of the response would lead to more powerful actuators, and permit a decrease in the operating voltage; therefore, the search for novel mechanisms of electromechanical response in solids remains an important objective for both fundamental and applied science. Here, we demonstrate that Gd-doped CeO$_2$ exhibits an anomalously large electrostriction effect and, in some cases, can generate stress in excess of 500 MPa, which surpasses that generated by the best electromechanically active materials. We have determined that the stress develops in response to the rearrangement of cerium-oxygen vacancy pairs and of their local environment, which is a fundamentally different mechanism from that of materials currently in use. In this view, one can suggest that Gd-doped ceria is a representative of a new family of high-performance electromechanical materials.

Gd-doped ceria, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$, an oxygen ionic conductor used as the electrolyte in solid oxide fuel cells,[6–9] retains the CeO$_2$ fluorite lattice but with 5% of the oxygen sites vacant. A cubic centrosymmetric lattice and a relatively low dielectric constant (ε < 30)[10,11] would seem to make Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ uninteresting for electromechanical applications. However, recent comparative studies of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ thin films by extended X-ray absorption fine structure spectroscopy (EXAFS) and by X-ray diffraction (XRD) showed that at room temperature, the fluorite symmetry is maintained only on a scale larger than a few unit cells[12] (Earlier EXAFS measurements demonstrated that at 10 mol% Gd doping, this distortion is not apparent[13]). Local distortions near the oxygen vacancies, V_o, which prefer Ce rather than Gd as near neighbors,[12] cause a reduction in the mean Ce-O bond length and an increase in the Ce-V_o distance compared to the average fluorite structure obtained by XRD measurements. Using the cation-1 site in the *Ia-3* structure of Ce$_{0.6}$Gd$_{0.4}$O$_{1.7}$ as a model,[14] the presence of a [Ce_{Ce}–V_o] pair results in elongation along the Ce_{Ce}–V_o direction, while six of the seven oxygens move towards the Ce at the center of the cube (**Figure 1**). The volume of the unit cell may also increase by 0.2–0.4%.[15,16] Notably, about 41% of all Ce ions have at least one vacancy as a neighbor. The Ce-O bond length and the Ce-V_o distance are labile: as a result, the undistorted fluorite-like units and the distorted *Ia-3*-like units can transform into each other under externally applied mechanical stress. Therefore, thin films of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ are able to "adapt",[16,17] similar to a "soft ball" when squeezed.

The atomic arrangement in Figure 1 has two notable features: i) the local elastic field around the [Ce_{Ce}–V_o] pair is anisotropic and ii) the presence of the vacancy makes the local charge distribution asymmetric; therefore, application of an electric field can induce anisotropic ion displacement. Here, we present experimental confirmation that the interaction of [Ce_{Ce}–V_o] pairs with an applied electric field in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ generates a very large electromechanical effect.

In order to achieve sufficiently strong internal electric fields, we prepared Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films with thicknesses d = 400–700 nm. The films were deposited on either 150 μm thick glass or 250 μm thick n-Si^{++} cantilevers that were 8-10 mm wide and 30–50 mm long (**Figure 2**a). The films were sandwiched between conductive electrodes (n-Si^{++} and/or 100 nm thick Cr, Al, Ti or Au) (Figure 2b) (Supporting Information, section 1). The stress developed in the Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films under bias caused the cantilever to bend. Changes in the bending curvature could be accurately measured by CCD tracking of the displacement of the reflected laser beam (Figure 2a). From these data, the stress was calculated[18] (Supporting Information, section 2). A mechanical force gauge (0.5 mN resolution) monitored the force generated by the cantilever directly.

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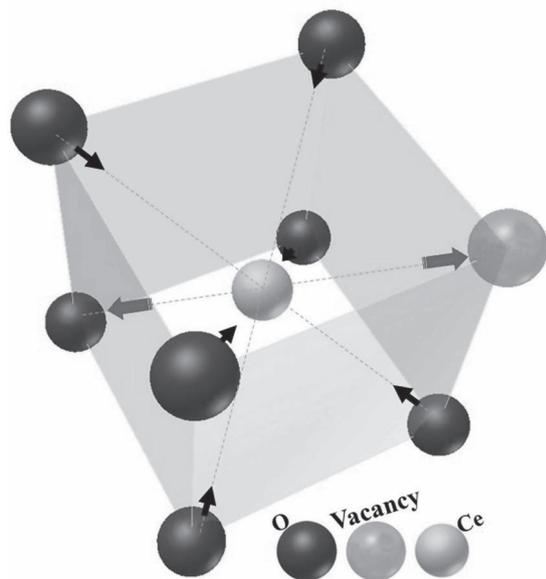**Figure 1.** Ball scheme of $Ce_{0.8}Gd_{0.2}O_{1.9}$: The oxygen coordination surrounding a Ce ion with a single oxygen vacancy, modeled after the type 1 cation site in the *Ia-3* lattice of $Ce_{0.6}Gd_{0.4}O_{1.7}$ (Figure 2 in ref [14]). In comparison with the fluorite-like unit, the local coordination shell of the Ce ion in the *Ia-3*-like unit, elongates along the $Ce-V_O$ direction and contracts in the directions perpendicular to it.

In general, electromechanical response is proportional to the first, second or higher power of the electric field.[19] To understand the mechanism acting in $Ce_{0.8}Gd_{0.2}O_{1.9}$, we applied a combination of constant (DC) and alternating (AC) voltage with frequency, $f = 10^{-2}–10^3$ Hz, $U_{applied} = U_{AC} \cdot \cos(2\pi \cdot f \cdot t) + U_{DC}$ (t is time), and examined the magnitude and harmonic content of the mechanical response. Irrespective of the polarity of the applied voltage, $Ce_{0.8}Gd_{0.2}O_{1.9}$ films develop compressive stress, indicating expansion within the plane of the substrate. The mechanical response to the bias with [$f = 10$ mHz; $U_{AC} = 3.5$ V; $U_{DC} = 0.4$ V] contains two harmonics–10 mHz and 20 mHz (Figure 2c), with amplitude ratio of $\frac{A_{10mHz}}{A_{20mHz}} = 0.542 \pm 0.010$, as determined by Fourier analysis. The amplitude of the first harmonic increases linearly with U_{AC} or U_{DC}; whereas the amplitude of the second harmonic is proportional to U^2_{AC} and independent of U_{DC} (Figure 2c–f). This behavior is a characteristic of electrostriction, where the stress, σ, is proportional to the square of the applied field $E^2 = \{U_{applied}/d\}^2$:

$$\sigma \propto \{U_{AC} \cdot \cos(2\pi f t) + U_{DC}\}^2 = U^2_{DC} + \frac{U^2_{AC}}{2}$$
$$+ 2U_{AC} \cdot U_{DC} \cdot \cos(2\pi f t)$$
$$+ \frac{U^2_{AC}}{2} \cos(2 \cdot 2\pi f t) \qquad (1)$$

From the pre-cosine multipliers in Equation (1) the theoretical harmonic amplitude ratio for the data in Figure 2c should
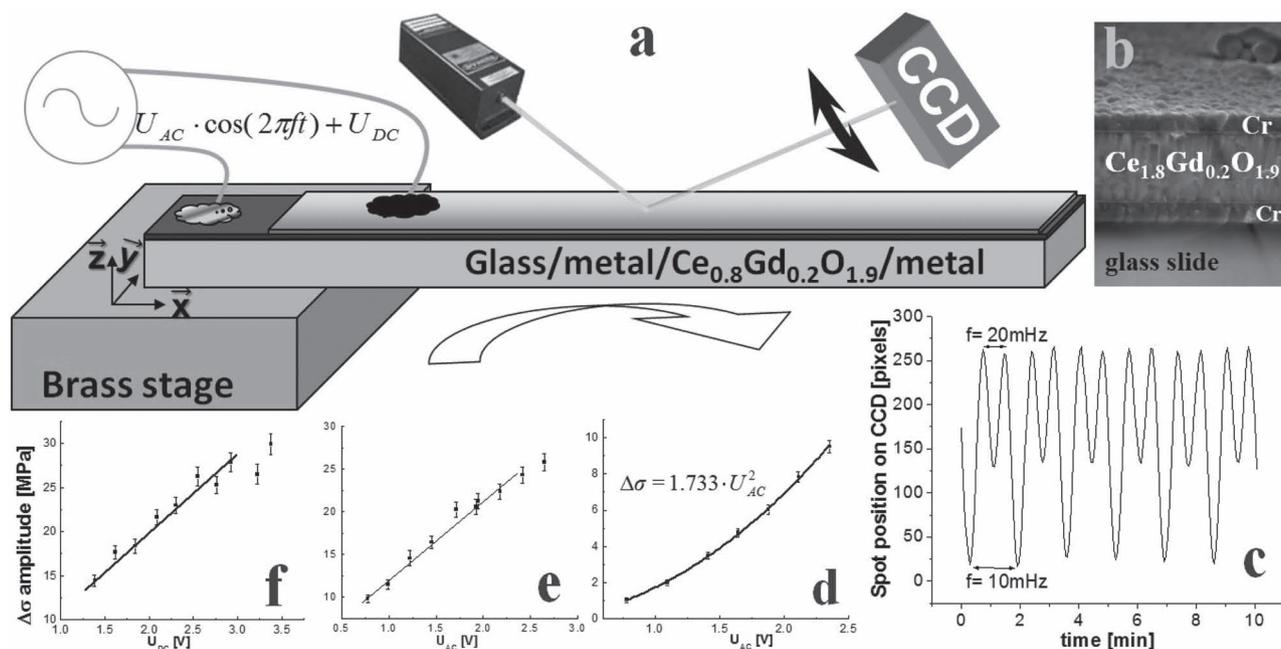

Figure 2. Experimental observation of large electrostriction in $Ce_{0.8}Gd_{0.2}O_{1.9}$. a) The experimental setup: the test sample is deposited onto a singly-clamped uniform cantilever, bias voltage is applied to the electrodes and the changes in the cantilever curvature are tracked by measuring the displacement of the reflected laser beam on a CCD camera. b) SEM image of the cross-section of a [100 nm Cr/450 nm $Ce_{0.8}Gd_{0.2}O_{1.9}$/100 nm Cr] structure on a 40 mm×8 mm×150 μm glass substrate. c) Electromechanical response for applied bias with $f = 10$ mHz, $U_{AC} = 3.5$ V, $U_{DC} = 0.4$ V, measured with a CCD camera. The response has both first and second harmonics. (d-f) Amplitude of the in-plane stress as a function of: d) U_{AC}, with U_{DC} switched off, $f = 10$ mHz, second harmonic. e) U_{AC}, $f = 10$ mHz, $U_{DC} = 1.53$ V, first harmonic. f) U_{DC}, $f = 10$ mHz, $U_{AC} = 1.56$ V, first harmonic. The quadratic dependence of the second harmonic of the mechanical response on U_{AC} and the linear dependence of the first harmonic on U_{DC} and U_{AC} identify electrostriction (Equation (1)).

be: $A_{1st}/A_{2nd} = \frac{2U_{AC} \cdot U_{DC}}{U_{AC}^2/2} = \frac{4 \cdot 0.4 \, AV}{3.5 \, V} = 0.457$, which is close to the experimentally observed value.

The same electrostrictive behavior was observed irrespective of the nature of the electrode, which excludes electrochemical reactions as a cause. Furthermore, oxygen diffusion cannot explain the observed effect: voltage-induced redistribution of oxygen through the film thickness would create an oxygen-depleted layer that expands and an oxygen-rich layer that contracts.[20,21] The stress in these layers would cancel and the cantilever would remain unbent. The magnitude of the electromechanical response remains almost constant below ~100 Hz. Above this frequency, the mechanical resonance of the cantilever interferes with the measurements (Supporting Information, Figure S2).

The strength of the electrostriction effect is characterized by the electrostriction coefficient M_e:

$$\sigma = Y \cdot M_e \cdot E^2 \qquad (2)$$

where Y is the Young's modulus.[22] Values of M_e range from ~10^{-24} m^2/V^2 in materials with low dielectric constants ($\varepsilon < 50$), to 10^{-16} m$^2 \cdot$V^{-2} for materials with high dielectric constant ($\varepsilon > 1000$) used in mechanical actuators. For Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$, $M_e^{CGO} = 6.47 \pm 0.43 \times 10^{-18}$ m$^2 \cdot$V^{-2} (Supporting Information, section 3), which is unusually high for a material with dielectric constant of $\varepsilon_r^{CGO} \approx 30$.[10,11] For example, for MgO ($\varepsilon^{MgO} \approx 10$) $M_e^{MgO} = 2 \cdot 10^{-21}$ m$^2 \cdot$V^{-2} and for the relaxor ferroelectric 3% Ca-doped PMN (PbMn$_{1/3}$Nb$_{2/3}$O$_3$) ($\varepsilon^{CaPMN} \approx 4000$) $M_e^{CaPMN} = 3.5 \cdot 10^{-18}$ m$^2 \cdot$V^{-2}.[23] The difference between known electrostrictors and Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ is also obvious in the maximum stress they can generate. The commercial electrostrictor TRS™ PMN15 displays the largest electromechanical effect at 6.5 kV·cm^{-1}, at which it generates stress of 16 MPa.[24] However, strain-free Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ can operate at >55 kV·cm^{-1} and repeatedly generate >63 MPa of stress.

To relate the electrostrictive behavior to the rearrangement of the $[Ce_{Ce} - V_O]$ pairs, we monitored the mechanical response of a freshly prepared sample to combined DC and AC voltage as a function of time. During 18 h, the magnitude of the response increases linearly with time from 5 MPa to ~20 MPa and then saturates (**Figure 3**, bottom inset). Either polarity of the DC applied voltage enhances the response. Subsequent application of voltage of opposite polarity does not reduce it. In this respect, the effect is totally different from the poling of ferroelectrics.[25] We have also found that heating of "poled" samples for 10 h at 150 °C, weakens the response by more than 50%. However, it can be fully restored by applying voltage at room temperature. This observation is consistent with our earlier findings that the local distortions in Ce$_{0.8}$Gd$_{0.2}$O$_{19}$ (Figure 1) disappear above 200 °C and reform at room temperature.[15] The nature of this "poling effect" is discussed below.

To characterize the effect of the applied electric field on the near neighbor environment of Ce (and Gd) ions in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$, we have used X-ray absorption near-edge structure (XANES) spectroscopy. We collected in situ XANES spectra of the Ce-L$_{III}$ absorption edge and the Gd-L$_{III}$ absorption edge prior to and during application of the electric field. Under electric field, the amplitude and integrated area of the prominent Ce-L$_{III}$ peaks at ~5731 and ~5738 eV (the "white line") increases
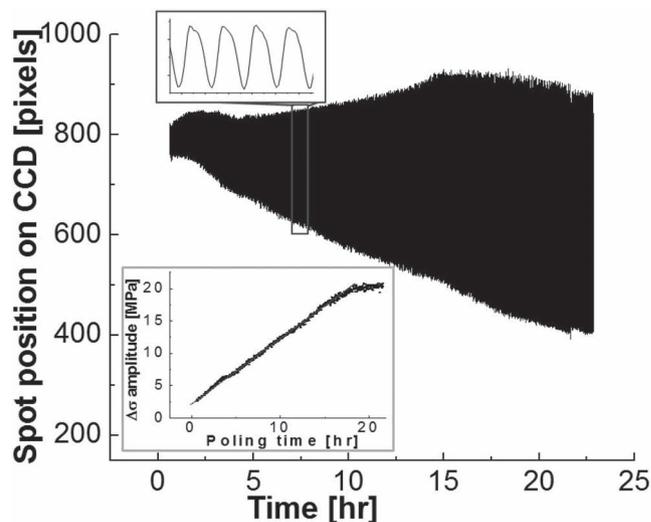

Figure 3. In situ monitoring of the poling process–position of the reflected laser beam; first harmonic, f = 10 mHz, U_{AC} = 1.97 V, U_{DC} = 3.04 V. Top inset: close-up on electromechanical fluctuations; Bottom inset: Calculated increase in stress amplitude during poling–linear behavior until saturation.

with time, reaches a maximum and then levels off (**Figure 4**a), whereas the amplitude of the Gd-L$_{III}$ peak at ~7250 eV is unaffected (Figure 4b). This spectral change shows that the near neighbor environment of Ce undergoes rearrangement: either increased atomic order and/or a more ionic character of the Ce-O bond,[26] implying that the average Ce-O bond length increases. From that we conclude that poling causes the distorted environment of the $[Ce_{Ce} - V_O]$ pair (Figure 1) to shift back towards that of the more symmetric fluorite structure, even though intuition might suggest that application of the electric field should increase the asymmetry.

We have presented mechanical and spectroscopic evidence that the unexpectedly strong electrostrictive behavior of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films is associated with the lability of the Ce-O bonds and $[Ce_{Ce} - V_O]$ pairs. Simple field-induced rotation of $[Ce_{Ce} - V_O]$ pairs is not consistent with these observations. Therefore, we offer a phenomenological explanation based on our XANES and EXAFS[12,27] measurements, the mechanical response data and the basic premise that a large electrostriction effect requires strongly anharmonic chemical bonds. Assuming that the electric field predominantly affects Ia-3-like units with the $[Ce_{Ce} - V_O]$ direction parallel to the field ($\vec{z}$, Figure 2a), its application will cause: (i) a decrease in the $[Ce_{Ce} - V_O]$ distance and (ii) an expansion in the perpendicular ($\vec{x}\vec{y}$) plane, thereby rendering these units more fluorite-like and, at the same time, generating in-plane mechanical stress. In those Ia-3-like units oriented such that the $Ce_{Ce} - V_O$ pairs are antiparallel to the field ($-\vec{z}$), the already highly stretched $Ce_{Ce} - V_O$ distance[12,14] would not increase. Since $[Ce_{Ce} - V_O]$ pairs in strain-free films are randomly oriented, the material response will therefore be independent of field polarity. During "poling", in-plane stress persists for many hours and the ability of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films to "adapt", i.e., respond to stress via reorientation of $[Ce_{Ce} - V_O]$ pairs becomes apparent.[16] Adaptation includes two processes:
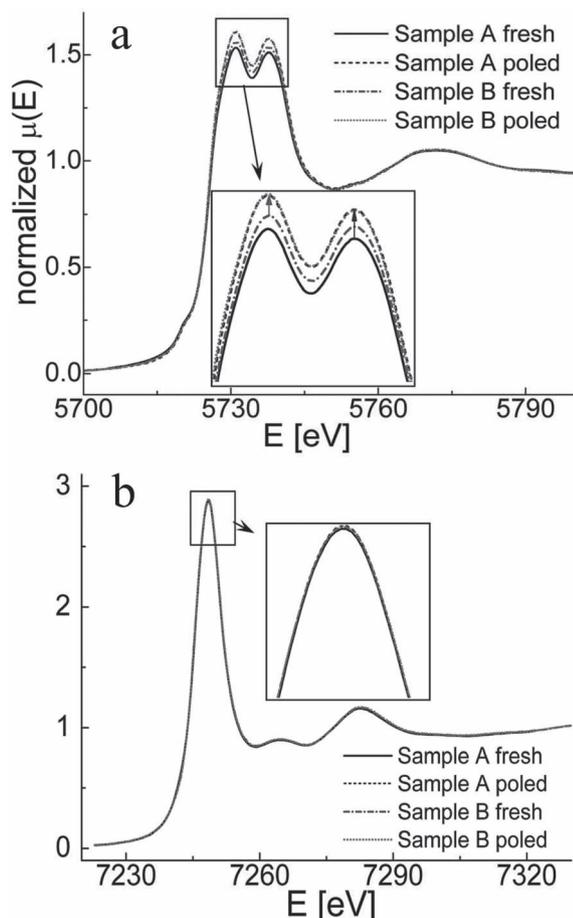
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Figure 4. XANES spectra a) Ce-L$_{III}$ absorption edge and b) Gd-L$_{III}$ absorption edge of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ prior to and during poling for two different [n-Si^{++}/Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$/Ti+Au] samples. Poling conditions: sample a) f = 10mHz, U_{AC} = 3V, U_{DC} = 4V, 5h; sample b) f = 51mHz, U_{AC} = 2V, U_{DC} = 2V, 9h (curves of the poled samples overlap).

average Ce-O distance is further reduced.[12] Because of the macroscopic anisotropy, an out-of-plane orientation for [Ce$_{Ce}$ − V$_O$] pairs would be favored. Indeed, we found that with ~60 kV/cm, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films with in-plane strain >0.2% can generate stress >500 MPa ($M_{e-strained}^{CGO} \approx 6.45 \pm 0.43 \times 10^{-17}\,\text{m}^2\cdot\text{V}^{-2}$), which is several times larger than that achieved in the best materials currently in use, and which is in fact limited experimentally by the failure of the Cr-glass interface (Figure 2b). The stress to voltage ratio in these films (>80 C·m^{-2}) is comparable to or greater than that of the best materials currently in use.[24]

We anticipate that our observation of the very large electrostriction effect in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ may contribute in a significant way to the search for new electromechanical materials. Since many solids with a large concentration of point defects have local distortions similar to those found in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$,[28] one may expect that such materials will indeed exhibit similar activity. In particular, oxygen ion conductors have negligible electronic conductivity at room temperature, their lattices tolerate very large distortions and their defect chemistry is very well studied.[29] Thus the next generation of electromechanically active materials may indeed come from the family of oxygen ion conductors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

(1) Field-induced in-plane compressive stress drives those *Ia-3*-like units oriented with [Ce$_{Ce}$ − V$_O$] pairs close to the film plane to acquire a fluorite-like arrangement where the in-plane dimensions are smaller while the Ce-O bonds are longer.[12] (2) The field-induced in-plane stress compresses the fluorite-like units and drives some of them to transform into *Ia-3*-like units with the [Ce$_{Ce}$ − V$_O$] pair oriented along $\pm\vec{z}$, i.e. properly aligned to contribute to the observed increase in the electromechanical response. This "poling effect", or field-induced stress adaptation, proceeds until a new equilibrium between the variously oriented *Ia-3*-like units and the fluorite-like units is achieved. Following removal of the field, the system returns close to its original state. This reverse process takes at least a few weeks at room temperature[15] due to the absence of any strong driving force.

By extension of the above reasoning, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ films in which the majority of [Ce$_{Ce}$ − V$_O$] pairs are oriented perpendicular to the film plane would exhibit an enhanced electromechanical effect. Our EXAFS studies showed that in films deposited with large in-plane compressive strain (>0.2%), the

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