

COMMUNICATION

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *Mater. Adv.*, 2020,
1, 2717Received 3rd August 2020,
Accepted 6th October 2020

DOI: 10.1039/d0ma00563k

rsc.li/materials-advancesElectromechanical dopant–defect
interaction in acceptor-doped ceria†Ahsanul Kabir,^a Victor Buratto Tinti,^a Maxim Varenik,^b Igor Lubomirsky^b and
Vincenzo Esposito^a

Oxygen defective cerium oxide $\text{CeO}_{2-\delta}$ exhibits a non-classical giant electromechanical response that is superior to that of lead-based electrostrictors. In this work, we report the key-role of acceptor dopants, with different size and valence (Mg^{2+} , Sc^{3+} , Gd^{3+} , and La^{3+}), on polycrystalline bulk ceria. Different dopants tune the electrostrictive properties by changing the electrosteric dopant–defect interactions. We find two distinct electromechanical behaviors: when the interaction is weak (dopant–vacancy binding energy ≤ 0.3 eV), electrostriction displays a high coefficient (M_{33}), up to 10^{-17} (m V^{-1})², with strongly time-dependent effects. In contrast, we observe no time-dependent effects when the interaction becomes strong (≥ 0.6 eV).

Over the last four decades, oxygen defective ceria has been widely used in multiscale applications from electrochemical devices to automotive catalysts, gas sensors, *etc.*^{1–3} Furthermore, a recent discovery demonstrated that ceria thin films display an unconventional electromechanical strain at room temperature.^{4–7} For example, the reported electrostriction coefficient (M_e) is around 6.5×10^{-18} (m V^{-1})² for $[\text{V}_\text{O}^\bullet] = 5\%$, *i.e.* 20 mol% Gd-doped ceria (GDC).⁴ Such a value is extremely high for a material with low dielectric constant ($\epsilon_r^{\text{GDC}} \approx 30$)⁸ and high elastic modulus ($Y^{\text{GDC}} \approx 200$ MPa).⁹ Surprisingly, in contrast to conventional inorganic ceramic materials, ceria thin films expand perpendicularly to the applied field direction. These properties are also investigated in bulk ceria and other oxygen defective fluorites ($\text{Bi}_2\text{O}_{3-\delta}$), illustrating similar outcomes.^{10–15} The atomistic origin of this uncommon behavior is associated with the presence of charge compensating oxygen vacancies ($\text{V}_\text{O}^\bullet$) in the ceria lattice.^{16,17} The $\text{V}_\text{O}^\bullet$ creates an electroactive elastic dipole ($\text{Ce}_{\text{Ce}}-\text{V}_\text{O}^\bullet$) having a long bond

length and six anomalous reduced ($\text{Ce}_{\text{Ce}}-\text{O}_\text{O}$) bonds when compared to the bond length of undoped ceria, leading to the development asymmetric charge distribution and anisotropic local dipolar elastic field around the host lattice.¹⁸ Upon interaction with an electric field, this distorted fluorite lattice ($\text{Ce}_{\text{Ce}}\text{O}_\text{O}-\text{V}_\text{O}^\bullet$) complex becomes a more ideal-like fluorite structure and successively induces a considerable local strain and *vice versa*.^{16,17} Although governed by the $\text{Ce}_{\text{Ce}}-\text{V}_\text{O}^\bullet$ complex, the local configuration of an oxygen vacancy is a crucial feature controlling electrostriction in bulk ceria.^{16,19} Literature reports of both computational and experimental studies demonstrate that the configuration of oxygen vacancies in the lattice strongly depends on dopant size and valence, *i.e.*, electrostatic (attractive) and elastic (repulsive) interaction between the cation and vacancy.^{20–22} Fig. 1a schematically represents a simple configuration of dopant cations concerning nearby oxygen vacancies in a unit cell of ceria. In general, the acceptor dopant prefers to occupy the next neighbour (1nn) or next-nearest neighbour (2nn) lattice site of an oxygen vacancy. The electrostatic interaction favors the 1nn site while elastic

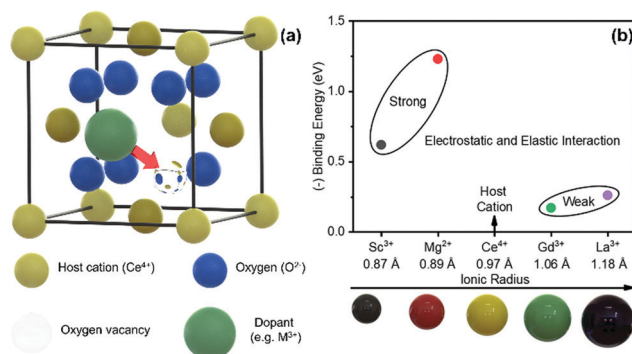


Fig. 1 (a) Schematic illustration of a unit cell of fluorite structured ceria, showing electrosteric interaction between the acceptor dopant and charge compensating oxygen vacancy. (b) Computationally calculated binding energy (1nn) values of variously doped ceria as a function of dopant radius. The data are taken from V. Butler *et al.*²⁴

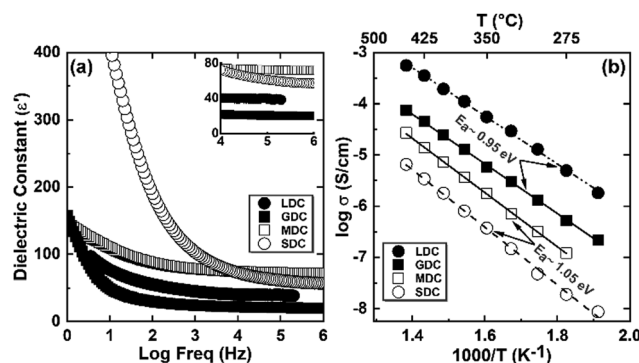
^a Department of Energy Conversion and Storage, Technical University of Denmark, Kgs, Lyngby 2800, Denmark. E-mail: ahsk@dtu.dk, vies@dtu.dk

^b Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 761001, Israel

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ma00563k

Nanoscale ceria powders with a composition of $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ where $x = 0.10$ and 0.05 for trivalent ($\text{M} = \text{Sc}^{3+}$, Gd^{3+} , La^{3+}) and divalent ($\text{M} = \text{Mg}^{2+}$) dopant, respectively were prepared using a combination of co-precipitation and nitrate route.²⁵ At first, the appropriate amount of metal nitrate salts was dissolved in boiling nitric acid (5 N) under mild stirring and slowly cooled. Then pure ceria (CeO_2) powder, as synthesized by the co-precipitation method described in 16 was dispersed in ethanol. Sequentially, a metal nitrate solution was transferred into the suspension. After that, the chemically modified suspension was ball-milled with zirconia balls (2 mm diameter) for 10 hours at 50 rpm, oven-dried at $100\text{ }^\circ\text{C}$, and finally calcined at $500\text{ }^\circ\text{C}$ for 2 hours. Next, the powder was softly crushed with an agate mortar and pestle and sieved using a $150\text{ }\mu\text{m}$ mesh. For the pellet preparation, the powders were uniaxially cold-pressed (12 mm diameter) under a pressure of 200 MPa for half a minute and sintered at $1450\text{ }^\circ\text{C}$ for 10 hours in atmospheric air. The apparent density of the resultant pellet was measured by the Archimedes method in the water medium. The crystallographic phase and microstructure were characterized by X-ray powder diffraction (XRD, Bruker D8) and scanning electron microscopy (SEM, Zeiss Merlin), respectively. For the dielectric and electrochemical measurements, silver paste (electrode) was brushed onto the parallel face of the sample and dried at $600\text{ }^\circ\text{C}$. The electrochemical experiments were performed using the two probe method with a frequency response analyzer (FRA-EIS, Solartron 1260) at $25\text{--}450\text{ }^\circ\text{C}$ in a frequency range from 1 Hz to 10 MHz in the air with an alternating potential of 100 mV. The room temperature impedance (dielectric) measurement was carried out with a dielectric analyzer (Novocontrol) in a high voltage mode (10 VAC) with frequencies between 1 MHz and 1 mHz. The electromechanical strain was estimated at room temperature under ambient conditions (relative humidity 25–50%) with a proximity sensor of the

As measured, the sintered pellets are highly dense and above 95% of the theoretical density, agreeing with the microstructural analysis (Fig. S1, ESI[†]). The grains are thermodynamically relaxed and have an average size between 3 and 5 μm , regardless of the composition. The XRD pattern of the samples corresponds with the reference profile of pure ceria (Fig. S2, ESI[†]), illustrating a single-phase cubic fluorite structure without any additional phases. The dielectric constant of a material has a significant role in controlling electrical properties, *i.e.*, dopant-defect interaction and defect cluster.²⁶ The distinction of the dielectric constant (ϵ') concerning applied frequency is estimated from the imaginary part (Z'') of the complex EIS spectra and represented in Fig. 2a at room temperature. As can be seen, ϵ' is relatively constant from high to intermediate frequencies (up to ~ 10 kHz) for all samples. However, ϵ' increases significantly at lower frequencies, which is associated with increased capacitive effect, leading to accumulation of charge at the high-energy barrier site.²⁷ As estimated, the GDC and LDC samples have a lower ϵ' value than those of SDC and MDC compounds (see Table 1), indicating that electrostatic interaction between dopant and defect is small in the former. Characteristically, the dielectric constant increases with increasing temperature (Fig. S3, ESI[†]), since the polarization of charge carriers increases at higher temperatures. From the EIS spectra, the electrical conductivity of the sample is measured using the Nyquist formalism,² which allows separation of the grain, grain boundary, and electrode



This journal is © The Royal Society of Chemistry 2020

suggesting that SDC and MDC compounds can be used for prospective frequency insensitive electrostriction applications. Table 1 demonstrates the comparative analysis of the dielectric constant, relaxation frequency, and electrostriction coefficient between the investigated samples.

In this work, variously doped ceria compounds having equivalent oxygen vacancy concentration were fabricated by conventional sintering at higher temperatures. The resultant dense pellets illustrate relaxed grains of micron size. As expected, the samples show a highly deviated dielectric relaxation and total electrical conductivity based on the local configuration of oxygen vacancies built in the materials. Moreover, all of these compounds demonstrate an unconventional electrostriction response. Interestingly, the sample having weak dopant-defect interaction in the lattice generates a frequency-dependent electrostriction behavior. Whereas, the material with strong dopant-defect interaction exhibits a frequency-independent steady electrostriction coefficient from low to high frequencies. To sum up, the local oxygen vacancy configuration and its association with the dopant cation is a crucial factor controlling the electromechanical response in cerium-based compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the DFF-Research project grants from the Danish Council for Independent Research, Technology and Production Sciences, grant number 48293 (GIANT-E), and the European H2020-FETOPEN-2016-2017 project BioWings, grant number 801267. The authors would like to thank Rana Al Tahan for her assistance in impedance measurements.

Notes and references

- 1 H. Inaba and H. Tagawa, *Solid State Ionics*, 1996, **83**, 1–16.
- 2 V. Esposito and E. Traversa, *J. Am. Ceram. Soc.*, 2008, **91**, 1037–1051.
- 3 A. Kabir, S. Colding-Jørgensen, S. Molin and V. Esposito, *Mater. Lett.*, 2020, **279**, 128513.
- 4 R. Korobko, A. Patlolla, A. Kossoy, E. Wachtel, H. L. Tuller, A. I. Frenkel and I. Lubomirsky, *Adv. Mater.*, 2012, **24**, 5857–5861.
- 5 M. Hadad, H. Ashraf, G. Mohanty, C. Sandu and P. Muralt, *Acta Mater.*, 2016, **118**, 1–7.
- 6 S. Santucci, H. Zhang, S. Sanna, N. Pryds and V. Esposito, *APL Mater.*, 2019, **7**, 071104.
- 7 S. Santucci, H. Zhang, S. Sanna, N. Pryds and V. Esposito, *J. Mater. Chem. A*, 2020, **8**, 14023–14030.
- 8 S. Kim and J. Maier, *J. Electrochem. Soc.*, 2002, **149**, J73.
- 9 E. Wachtel and I. Lubomirsky, *Scr. Mater.*, 2011, **65**, 112–117.
- 10 N. Yavo, O. Yeheskel, E. Wachtel, D. Ehre, A. I. Frenkel and I. Lubomirsky, *Acta Mater.*, 2018, **144**, 411–418.
- 11 N. Yavo, A. D. Smith, O. Yeheskel, S. Cohen, R. Korobko, E. Wachtel, P. R. Slater and I. Lubomirsky, *Adv. Funct. Mater.*, 2016, **26**, 1138–1142.
- 12 A. Kabir, J. R. Bowen, M. Varenik, I. Lubomirsky and V. Esposito, *Materialia*, 2020, **12**, 100728.
- 13 A. Kabir, M. E. Cachaza, E. M. Firolaliso, D. Ke, S. Grasso, B. Merle and V. Esposito, *J. Eur. Ceram. Soc.*, 2020, **14**, 5612–5618.
- 14 A. Kabir, J. Kyu Han, B. Merle and V. Esposito, *Mater. Lett.*, 2020, **266**, 127490.
- 15 M. Varenik, J. C. Nino, E. J. Wachtel, O. Yeheskel, N. Yavo and I. Lubomirsky, *ACS Appl. Mater. Interfaces*, 2020, **12**, 39381–39387.
- 16 E. Wachtel, A. I. Frenkel and I. Lubomirsky, *Adv. Mater.*, 2018, 1707455.
- 17 Y. Li, O. Kravynis, J. Kas, T. C. Weng, D. Sokaras, R. Zacharowicz, I. Lubomirsky and A. I. Frenkel, *AIP Adv.*, 2016, **6**, 055320.
- 18 A. S. Nowick, B. S. Berry and J. L. Katz, *J. Appl. Mech.*, 1975, **42**, 750.
- 19 A. Kabir, S. Santucci, N. Van Nong, M. Varenik, I. Lubomirsky, R. Nigon, P. Muralt and V. Esposito, *Acta Mater.*, 2019, **174**, 53–60.
- 20 J. Koettgen, S. Grieshammer, P. Hein, B. O. H. Grope, M. Nakayama and M. Martin, *Phys. Chem. Chem. Phys.*, 2018, **20**, 14291–14321.
- 21 S. Omar, E. D. Wachsman and J. C. Nino, *Solid State Ionics*, 2008, **178**, 1890–1897.
- 22 H. Zhang, I. E. Castelli, S. Santucci, S. Sanna, N. Pryds and V. Esposito, *Phys. Chem. Chem. Phys.*, 2020, 1–8.
- 23 S. Anirban, T. Paul, P. T. Das, T. K. Nath and A. Dutta, *Solid State Ionics*, 2015, **270**, 73–83.
- 24 V. Butler, C. R. A. Catlow, B. E. F. Fender and J. H. Harding, *Solid State Ionics*, 1983, **8**, 109–113.
- 25 F. Kern, R. Gadow and A. Kabir, *Ceram. Mater.*, 2017, **69**, 279–285.
- 26 S. Anirban and A. Dutta, *RSC Adv.*, 2015, **5**, 95736.
- 27 K. P. Padmasree and A. F. Fuentes, *Mater. Chem. Phys.*, 2019, **223**, 466–472.
- 28 D. R. Ou, T. Mori, F. Ye, T. Kobayashi, J. Zou, G. Auchterlonie and J. Drennan, *Appl. Phys. Lett.*, 2006, **89**, 171911.
- 29 R. Gerhardt-Anderson and A. S. Nowick, *Solid State Ionics*, 1981, **5**, 547–550.
- 30 A. Kabir, H. Zhang, S. Colding-Jørgensen, S. Santucci, S. Molin and V. Esposito, *Scr. Mater.*, 2020, **187**, 183–187.

