

# Impact of high-energy milling synthesis on the electrostriction performance of $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$

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## ABSTRACT

Electrostrictors have the capacity to unidirectionally convert electrical energy into a mechanical response. The best electrostrictors known so far have a high content of toxic lead (Pb) in their composition. To solve this environmental issue, research efforts shifted to lead-free electrostrictor compositions, such as the ceria-based compounds. Ceria-based materials present “giant” electrostriction, and amongst them,  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  can be a suitable lead-free substitute. To advance in the implementation of green chemistry principles for electromechanically active materials and to determine the ramifications of its employment on functional properties of fluorite-based  $\text{CeO}_2$  -  $\text{ZrO}_2$  mixed oxides, we successfully synthesized a  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid solution using a high-energy milling-assisted method. Nanometric milled powders exhibit the fluorite structure and a homogeneous dispersion of Zr in the ceria matrix that is preserved after sintering dense pellets. Soft X-ray absorption measurements reveal the predominance of  $\text{Ce}^{4+}$  species and the limited presence of oxygen vacancies in  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ . Impedance spectroscopy measurements reveal highly resistive behavior, characterized by a strong overlap of grain and grain boundary contributions. The  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  dielectric constant measured at room temperature is twice that of undoped ceria,  $\epsilon_r \approx 66$ , which is related to improved electromechanical response. Longitudinal electrostriction measurements support this assessment, reaching values of up to  $1.7 \cdot 10^{-17} \text{ m}^2 \text{ V}^{-2}$  near the kHz frequency.

## 1. Introduction

In recent years, ceria-based ceramics have been widely investigated due to “giant” or “nonclassical” electrostriction, a second-order electromechanical coupling phenomenon linked to defective oxides [1]. Such materials present a phenomenological electrostriction coefficient ( $M_{33}$ ) at least two times higher than the theoretical value predicted by Newham’s law, which makes them useful in the field of electromechanically active materials, e.g., sensors, actuators, transducers, in the field of micro-electromechanical systems in bulk form or thin film, applying different tactics to obtain superior performance such as doping or interface mismatch/strain engineering [2–9]. Initially, much attention was focused on aliovalent-doped ceria compositions such as Gd- and Sm-doped ceria [10–13]. In these materials, oxygen vacancies are responsible for creating “static” elastic dipoles, which are reoriented by

an applied electric field and believed to be the mechanism responsible for “giant” electrostriction in defective oxides, being paramount over structural factors such as grain size and dopant concentration [14]. This means that cerium-oxygen vacancy pairs and their local environment are the driving force for the unusual stress response in non-stoichiometric ceria-based materials [15–17]. However, recent research has shown that, although trivalent-doped compositions can exhibit performances that rival those of lead-based alternatives, this is only the case for a limited frequency range [10,11,18]. A great recent development, however, has proved to be a possible solution to this critical limitation. For isovalent-doped ceria, namely  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , exceptional performance extends over a wide range of frequencies, from 0.15 to 3000 Hz, and a strain superior to 200 ppm can be achieved without reaching saturation [2]. Additionally, from an environmental perspective, using Zr as a dopant instead of less abundant rare earth

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elements such as Gd and Sm is also advantageous. In isovalent-doped ceria, instead of “static” elastic dipoles, “dynamic” elastic dipoles are observed, which originate from bond anharmonicity. This finding helped to showcase further that “giant” electrostriction involves multiple complex factors linked to defect chemistry in the form of oxygen vacancies and n-type polarons, for example [19]. In the case of dynamic elastic dipoles, the different bond lengths due to the isovalent dopants cause the formation of dipoles only under an applied electric field. This mechanism was further investigated by extensive X-ray Absorption Spectroscopy (XAS), which was able to confirm that bond anharmonicity is the reason for the exceptional  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  electromechanical performance since no deviation from the fluorite structure can be observed even in the vicinity of  $\text{Zr}^{4+}$ , which confirm that bond anharmonicity is the cause of local field anisotropy when an electric field is applied [4]. This makes  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  a great contender to substitute lead-based materials such as  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – $\text{PbTiO}_3$  (PMN-PT), a solid solution in which the best electrostrictors are based. Unfortunately, lead-based compositions present two major drawbacks: first, they are not fully compatible with current silicon-based microchip technology, and second, lead is highly toxic. It is widely known that lead poses a great health concern, and there is a global effort to mitigate its use. Lead content in such compositions can reach up to 60 wt%; Moreover, green chemistry principles apply not only to the materials themselves, by minimizing the use of hazardous chemicals, but also to the techniques employed in their synthesis, carrying out more environmentally friendly chemical processes [20]. High-energy milling is an exceptional example of a synthesis method that adheres to several principles of green chemistry; for instance, no harmful chemicals are required as solvent, and no harmful byproducts are generated during the process. In mechanosynthesis, the kinetic energy of the grinding beads, high-mechanical-resistance spheres, as they collide with each other and with the materials being ground, supplies the necessary energy for chemical reactions to occur. This method even allows the synthesis of compositions that would not be obtained by traditional synthesis methods [21]. In addition, mechanosynthesis promotes homogenization and yields highly sinterable powders with high surface specific area, which is beneficial because minimizes the risk of cationic segregation. In this sense, high-energy milling can be an eco-friendly alternative to produce doped ceria-based ceramics; however, it is necessary to determine how critical properties are affected by this processing. Most studies regarding the high-energy milling of Ce-rich  $\text{CeO}_2$ – $\text{ZrO}_2$  mixed oxides are restricted to the impacts on the catalytic properties [22,23]. In the present study, we investigated the high-energy milling-assisted synthesis of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , aiming to apply the principles of green chemistry in the synthesis of electromechanically active ceramics. The influence of synthesis on the structural, microstructural, and electrical properties of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  is assessed to demonstrate potential applications as electromechanical material.

## 2. Experimental section

$\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  ceramics were prepared by a high-energy milling-assisted synthesis method. First,  $\text{ZrO}_2$  (99 %, Sigma-Aldrich) and  $\text{CeO}_2$  ( $\geq 99$  %, Sigma-Aldrich) were weighed according to the desired stoichiometry and homogenized in a Turbula® (Willy A. Bachofen AG, Switzerland) mixer for 2 h. After homogenization, the powders were milled for up to 10 h using a planetary mill (Pulverisette 6, Fritsch, Germany) to form the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid solution. For high-energy milling, the following conditions were employed: a 250 mL zirconia jar, 3 mm zirconia beads as the grinding media, 500 revolutions per minute (rpm), and a 7:1 ball-to-powder ratio (BPR).

To assess the effects of milling on the material structure, X-ray diffraction (XRD) measurements were performed at intervals of 0, 2, 6, and 10 h of milling, on samples CZ0, CZ2, CZ6, and CZ10, respectively. After milling, green bodies were obtained from the CZ10 powder by uniaxial pressing, applying approximately 100 MPa.

Polyvinylpyrrolidone (PVP, Sigma-Aldrich MW 55.000) was used as a binder in a 2 wt% ethanol solution. Following uniaxial pressing, the shaped pellets were isostatically pressed, applying 1400 bar for 3 min using an isostatic press (WT Indústria, Brazil). A pre-sintering step at 500 °C for 1 h, using a heating rate of 2 °C/min, was performed to eliminate the binder (PVP). Sintering was carried out at 1500 °C for 2 h, with a heating and cooling rate of 5 °C/min.

The apparent density of the sintered pellet was measured using Archimedes' method, using distilled water as the auxiliary medium. To evaluate the effect of milling on phase formation, XRD data for the milled powders were collected in reflection mode using Bragg-Brentano geometry, with  $\text{CuK}\alpha_1$  radiation and nickel filter, utilizing a D8 Focus diffractometer (Bruker, Germany). To determine the long-range order structure of the sintered samples, powder specimens were placed between cellulose acetate foils, and XRD data were collected using a STADI-P diffractometer (STOE, Germany) operating in transmission mode with  $\text{AgK}\alpha_1$  radiation. Quantitative analysis of the diffraction patterns was performed using Rietveld refinement with TOPAS Academic software (version 7.25), in accordance with IUCr recommendations [24,25]. Background scattering was fitted using a sixth-order Chebyshev polynomial, and peak profile analysis employed a Thompson-Cox-Hastings pseudo-Voigt profile function. Crystallographic information file (CIF) collection code number 152478 from the Inorganic Crystal Structure Database (ICSD) was used as the structural model for  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , site occupancy was kept constant ( $\text{Ce} = 0.9$ ,  $\text{Z} = 0.1$ , and  $\text{O} = 1$ ), peak broadening was treated as a result of both crystallite size and microstrain contributions [26].

Analysis of the high-energy milled powder was conducted using a Talos F200X G2 (Thermo Scientific) Transmission Electron Microscope (TEM) to obtain Energy-Dispersive X-ray Spectroscopy (EDS) mapping in scanning mode (STEM-EDS), Selected Area Electron Diffraction (SAED) measurements, and high-resolution (HRTEM) images. To analyze the microstructure and semi-quantitatively determine the homogeneity of the sintered samples, Scanning Electron Microscopy (SEM) in secondary electron mode (SE) and EDS mapping were employed using a JSM-6010LA JEOL microscope. All microscopy images were analyzed with ImageJ (version 1.54g), and the grain size of sintered samples was calculated by applying the linear intercept method [27].

To further investigate the structure after sintering, Raman scattering measurements (Horiba Jobin-Yvon/Instruments S.A., T64000) were performed in the range of 200 to 1200  $\text{cm}^{-1}$ , using a Verdi G5 laser (Coherent Inc.) with a 532 nm excitation source.

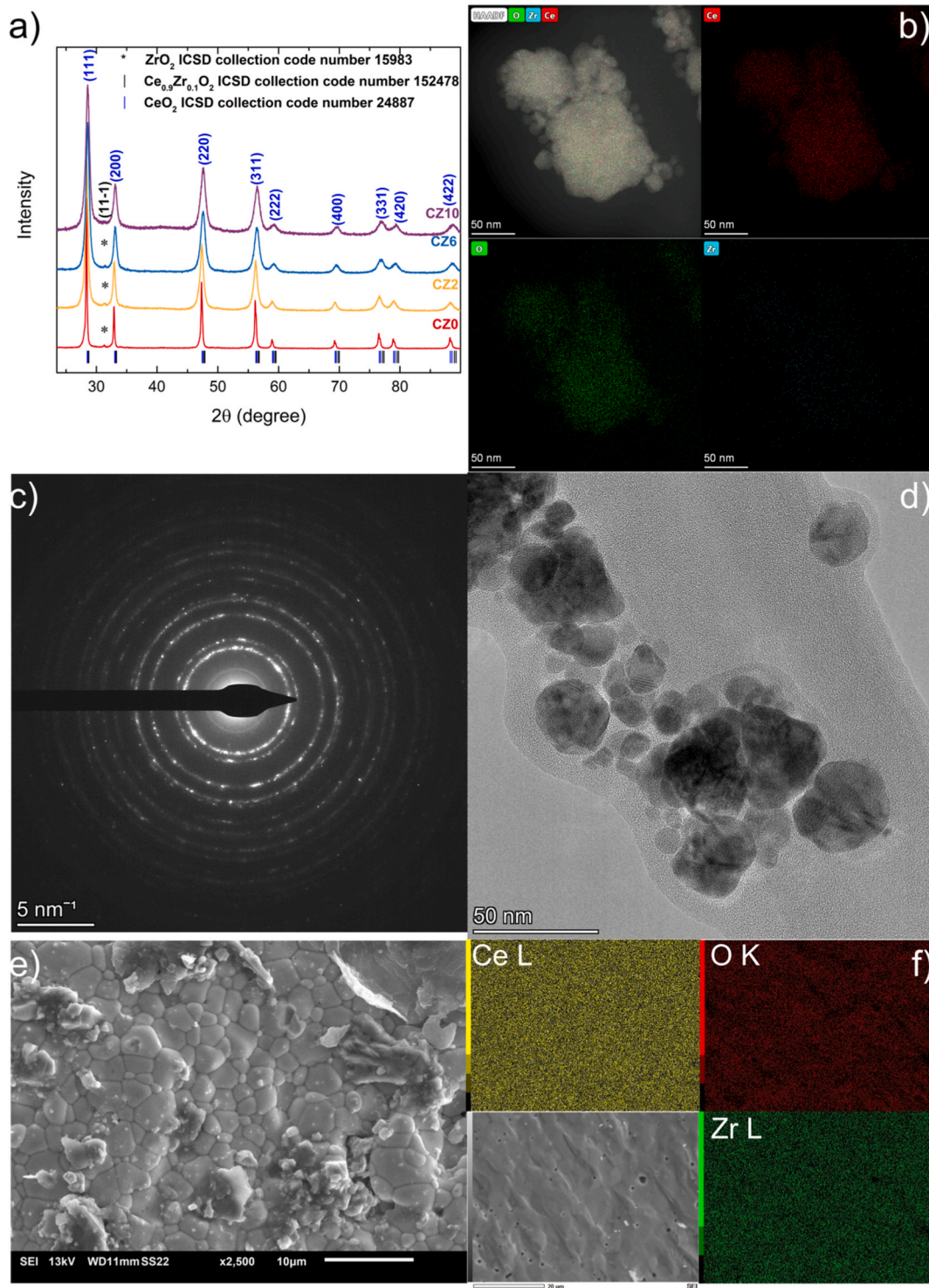
To determine the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio and investigate oxygen vacancy formation, soft X-ray absorption spectroscopy (XAS) measurements at Ce  $\text{M}_{4,5}$  and O K-edges were performed at the LNLS IPÊ beamline (SIRIUS – CNPq, proposal 20250691), collecting in total electron yield mode (TEY) with a resolution of 0.1 eV, in fluorescence mode. X-ray absorption near-edge structure (XANES) data treatment was performed using normalization with the autoXAS Python package [28]. For this, pre-edge was fitted and subtracted from the data. Next, the post-edge was fitted, and the data was divided by this fit. As a pre-processing step, multiple scans were averaged to improve the signal-to-noise ratio, and commercial ceria (Sigma-Aldrich,  $\geq 99\%$ ) was used as the standard foil for data normalization of the Ce  $\text{M}_{4,5}$  spectra. The peaks fitting and deconvolution were carried out as described by Santucci et al. [29].

To perform electrochemical impedance analysis (EIS), electrical contacts were created by covering the parallel faces of the sintered samples with silver paint and heat-treating them for 15 min at 600 °C, using a heating and cooling rate of 1 °C/min in a muffle furnace (EDG). An Inconel home-made sample holder, which allows for the measurement of multiple samples, was used to conduct the EIS measurements. This setup was placed inside a tubular furnace that enabled a controlled temperature program; samples were measured in air. The EIS measurements were performed using a Solartron (1260A), covering frequencies from 1 MHz to 1 Hz with 10 points per decade and applying a

100 mV AC voltage, at temperatures ranging from 200 to 500 °C. The impedance data were fitted using ZView software (Scribner), considering the overlapped contributions of grain and grain boundary, represented by a resistor and a constant phase element (CPE) in parallel. From the impedance data, the real dielectric permittivity ( $\epsilon'$ ) and loss tangent ( $\tan \delta$ ) were obtained through calculations described elsewhere [13].

The longitudinal electromechanical response was assessed using the electrostriction strain coefficient ( $M_{33}$ ) measurement. The sample was

placed between two copper electrodes, with a mirror-polished magnet positioned on the top of the upper electrode. Measurements were performed at room temperature using a single-beam laser interferometer microscope (SIOS NA analyzer) and a lock-in amplifier (Ametek 7230 DSP). Voltage was applied using an *Aim-TTi* signal generator. The electrostrictive strain was calculated as the ratio between the displacement and the thickness of the ceramic sample. Each data point was acquired over 120 s, and the final value represents the time-averaged



**Fig. 1. (colored).** Structural and microstructural characterization of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ . (a) XRD measurements for all milling times,  $\text{CuK}\alpha$  radiation in reflection mode. (b) STEM-EDS for the CZ10 sample. (c) SAED for the CZ10 sample. (d) HRTEM for the CZ10 sample. (e) 2500 magnification SEM imaging of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sintered pellet surface. (f) Cross-section fracture EDS mapping of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sintered pellet.

response.

### 3. Results and discussion

XRD analysis of the milled powders, samples CZ0, CZ2, CZ6, and CZ10, reveals the dynamics of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid-solution formation through mechanosynthesis (Fig. 1a). The homogenized ceria and zirconia powders (CZ0) present two distinct phases as expected: one corresponding to  $\text{CeO}_2$  in the cubic symmetry (fluorite), indexed with CIF collection code number 24887 from the ICSD, indicated by blue vertical bars, and one corresponding to monoclinic zirconia, indexed with CIF number 15983, marked with an asterisk in Fig. 1a [26,30,31]. As milling time increases, diffraction peaks broaden, and the peak related to the monoclinic zirconia phase reduces in intensity and is completely absent after 10 h of milling (CZ10 in Fig. 1a). In addition, Zr incorporation into ceria can also be observed by the lattice parameter variation as a function of Zr concentration for all milling times, Fig. S1. Peak broadening can be linked to crystallite size reduction and microstrain increase, while the monoclinic zirconia phase disappearance is the result of Zr incorporation into ceria, which also causes the diffraction peaks to shift to higher diffraction angles, due to zirconium's smaller ionic radius. In the diffraction pattern of sample CZ10, only peaks corresponding to the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  fluorite phase are observed, as indicated by the ICSD collection code number 152478, crystallographic planes are shown in blue [32]. It is evident that, with the incorporation of Zr into ceria's structure due to the high-energy milling, the lattice parameter  $a$  decreases due to the substitution of the bigger  $\text{Ce}^{+4}$  (0.97 Å) cation for the smaller  $\text{Zr}^{+4}$  (0.84 Å), and the diffraction peaks shift to higher  $2\theta$  until the solution formation is complete, considering the XRD technique sensitivity, CZ10 [33]. This finding is consistent with previous works concerning Ce-rich  $\text{CeO}_2$  -  $\text{ZrO}_2$  solid-solution synthesis by high-energy milling [22,23].

Further characterization of the CZ10 sample was carried out by TEM (Fig. 1b and c) to investigate  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid-solution formation via mechanosynthesis. STEM-EDS mapping analysis demonstrates that a 10-h milling time was effective in producing a homogeneous powder, as evidenced by the uniform dispersion of zirconium within the ceria structure. In Fig. 1b, each element is represented by a color: red for cerium, green for oxygen, and blue for zirconium. No clusters related to segregation can be observed. Additionally, the combined image displays the homogeneous dispersion of the cations more clearly. This is significant because milling was solely responsible for the solid-solution formation, as corroborated by the XRD measurement shown in Fig. 1a. The SAED pattern from the CZ10 sample (Fig. 1c) displays Debye-Scherrer rings, which are characteristic of polycrystalline materials. By calculating the interplanar spacing ( $d_{hkl}$ ) from the SAED pattern, it is possible to determine that the obtained values closely match those from CIF collection code number 152478 for  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , as shown in Table 1 with the respective crystallographic planes indexed to a fluorite structure. This finding helps to further strengthen the idea of solid solution formation.

HRTEM imaging of the powder milled for 10 h, CZ10, shown in Fig. 1d, confirms its nanometric scale, with an average particle size of 13 (4) nm and predominantly rounded shape. The visible parallel lattice fringes further confirm the crystallinity of the milled powder. As seen in S2, the HRTEM images detail the exposed face of the (111)

crystallographic plane. It is important to note that, considering the solubility of Zr into the lattice structure, adequate sintering programs for CZ0, CZ2 and CZ6 samples most likely would yield single phase ceramics in the fluorite structure. In this study, however, we aim to gauge the potential of mechanosynthesis as a tool to obtain complete solutions.

From SEM imaging of sintered samples (Fig. 1e), the average grain size was calculated to be 2.25(31)  $\mu\text{m}$ ; the image also reveals a very dense structure with limited porosity. In the EDS mapping of the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sintered pellet, fracture cross-section, each element is represented by a different color, which helps to visualize the dispersion of the elements, i.e., Ce in yellow, Zr in green, and O in red (Fig. 1f). From the image, a homogeneous dispersion of zirconium in the ceria matrix can be observed, and no cationic segregation is seen.

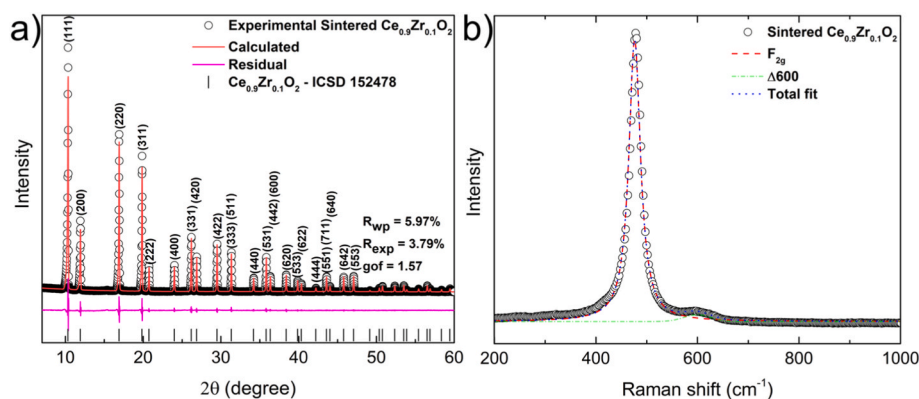
Sintering at 1500 °C yields crystalline samples with the fluorite structure maintained, as shown in the diffraction pattern in Fig. 2a. All diffraction maxima were indexed using the ICSD collection code number 152478, which is identical to that of the CZ10 sample [26,32]. Rietveld refinement results demonstrate excellent agreement between the calculated data (solid red line) and experimental data (black circles), as well as favorable numerical indicators: goodness of fit (gof), expected R-factor ( $R_{\text{exp}}$ ), and weighted-profile R-factor ( $R_{\text{wp}}$ ), all within acceptable values, as presented in Table 2 [34]. The lattice parameters obtained from the Rietveld refinement show a clear contraction of the unit cell for the Zr-doped ceria sintered sample in comparison with pure ceria, 155.90 and 159.03 Å<sup>3</sup>, respectively. The calculated unit cell volume, in fact, falls very close to the one from CIF 152478 and reported values for the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid solution [35]. Unit cell volume can also serve as an indicator of oxygen vacancy presence in the fluorite structure when combined with additional characterization techniques. For an eightfold coordination of the A site,  $\text{Ce}^{3+}$  presents an ionic radius 15% bigger than  $\text{Ce}^{4+}$ , causing the expansion of the unit cell, which is not observed in the diffraction data of sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , suggesting that  $\text{Ce}^{3+}$  presence is limited in these samples, which is also observed in XANES data measured at the Ce M<sub>4,5</sub> and O-K edges. Additionally, the crystallite size, calculated from the Gaussian broadening, is 58.96(56) nm for the sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sample, indicating a clear effect of the high-energy milling process. The low microstrain values obtained from the Rietveld refinement, as shown in Table 2, also indicate that the structure obtained from the thermal treatment is not highly defective.

The heat treatment observed yielded pellets with a relative density of 93.7%, which is consistent with the sintering method employed [36]. The theoretical density value was obtained from the Rietveld refinement, and the calculated density is presented in Table 2.

Further investigation into the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sintered pellet structure was conducted using Raman spectroscopy (Fig. 2b), as it is a powerful technique for determining perturbations and distortions in the crystal structure, and also for identifying phases present and defects such as strain/stress in ceramics [37]. In the obtained spectrum, it is possible to identify two distinctive bands, one assigned to the optical phonon mode  $F_{2g}$  related to the 8-fold oxygen coordinated cerium cation [Ce-O<sub>8</sub>] in the cubic crystal, and a second one assigned to a non-active Raman mode triggered by point defects such as oxygen-defect presence and oxygen coordinated dopant cations, at 476.1 and 599.4 cm<sup>-1</sup>, respectively [13, 38]. The  $F_{2g}$  band is highly sensitive to perturbations in the symmetry of cerium and oxygen sites, which aids in determining the incorporation of dopants into the fluorite structure [39]. Due to Zr doping, a blue shift occurs in the  $F_{2g}$  band, which typically appears at 463.9 cm<sup>-1</sup> for undoped ceria [35]. This phenomenon is caused by the shorter Zr-O bond, which is stiffer than the Ce-O bonds, increasing the vibrational frequency and, consequently, the wavenumber at which the  $F_{2g}$  mode is registered [13]. In addition, the peak related to the  $F_{2g}$  mode exhibits a significant broadening, from 11.1 cm<sup>-1</sup> for undoped ceria to 27.9 cm<sup>-1</sup> for  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , which is consistent with substitutions in the A site [40]. Broadening could also be attributed to a decrease in grain size such as in the case for nanometric ceria; however, the ceria sample considered here has an average grain size of 3.46(42)  $\mu\text{m}$ , in the same scale of

**Table 1**  
Calculated d-spacing values from the SAED pattern of the CZ10 sample.

| Crystallographic Plane | 1/Radius (nm <sup>-1</sup> ) | $d_{hkl}$ (Å) | $d_{hkl}$ CIF 152478 (Å) |
|------------------------|------------------------------|---------------|--------------------------|
| (111)                  | 3.356                        | 2.979         | 3.108                    |
| (200)                  | 3.888                        | 2.571         | 2.692                    |
| (220)                  | 5.462                        | 1.830         | 1.903                    |
| (311)                  | 6.354                        | 1.573         | 1.623                    |
| (222)                  | 6.696                        | 1.493         | 1.554                    |



**Fig. 2. (colored).** Structural characterization of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sintered pellets. (a) Rietveld refinement, XRD data obtained in transmission mode  $\text{AgK}\alpha$  radiation. (b) Raman measurement.

**Table 2**

Data obtained from Rietveld refinement of sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ .

| Composition                                | Rietveld refinement quality factors                              | Lattice parameters                                                      | Crystallite size (nm) | Microstrain (%) | Density ( $\text{g}/\text{cm}^{-3}$ ) |
|--------------------------------------------|------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------|-----------------|---------------------------------------|
| $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ | $R_{\text{wp}} = 5.97\%$<br>$R_{\text{exp}} = 3.79\%$ gof = 1.57 | $a = 5.38201(5) \text{ \AA}$<br>$\text{vol} = 155.895(4) \text{ \AA}^3$ | 58.96(56)             | 0.019(2)        | 7.1249 (2)                            |

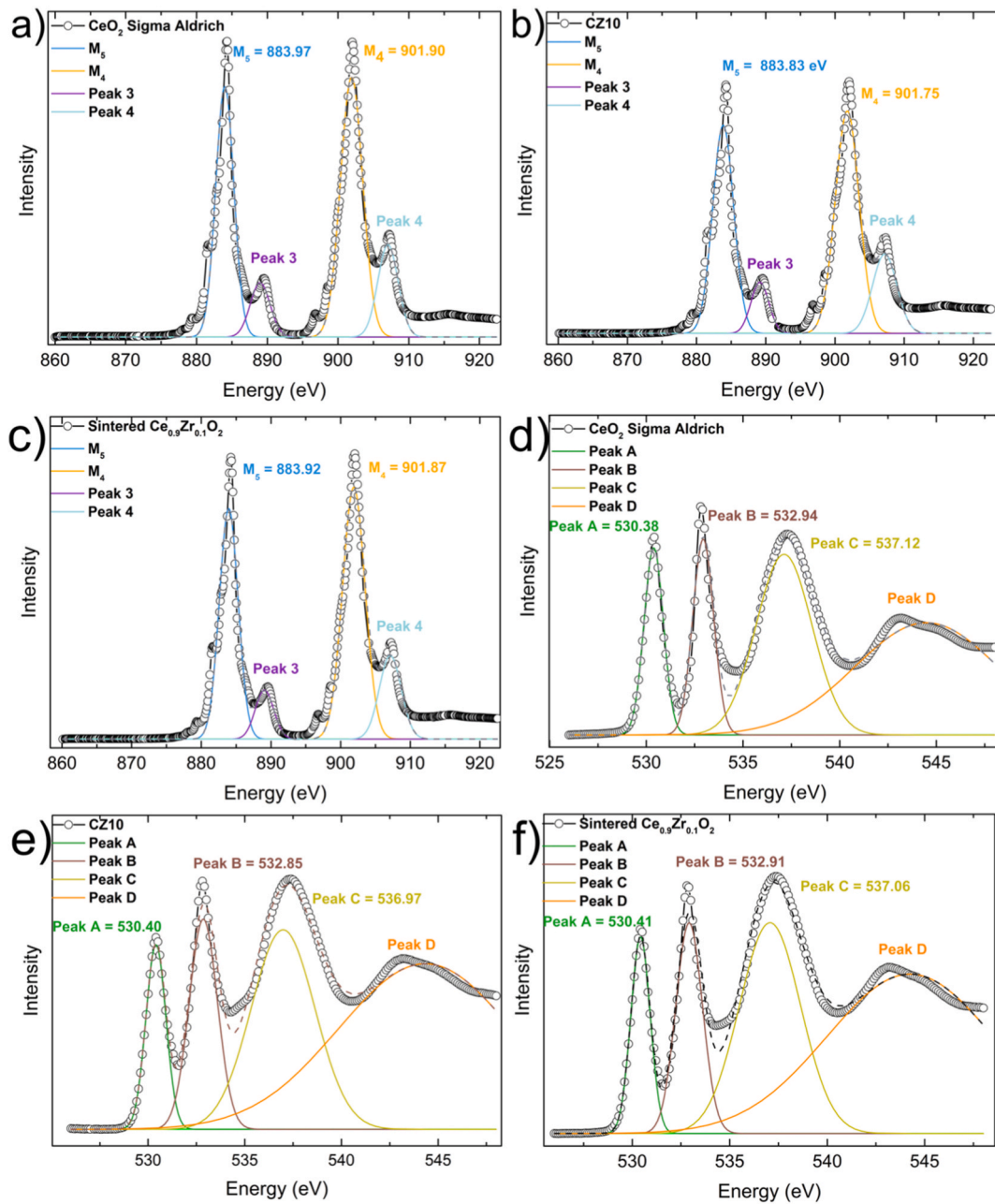
$\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , 2.25(31)  $\mu\text{m}$ ; thus, the A site disturbance can be assigned as the main factor for the  $\text{F}_{2g}$  band broadening [41]. These factors, in conjunction with the XRD data, indicate the successful incorporation of Zr into the fluorite structure in sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  pellets [39].

Additional structural investigation performed through soft XAS measurements of Ce  $\text{M}_{4,5}$  edges of standard ceria ( $\geq 99\%$ , Sigma-Aldrich), CZ10, and sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  gives information on cerium oxidation states of milled and sintered samples (Fig. 3a–c). For isovalent-doped ceria-based electrostrictors, a limited  $\text{Ce}^{3+}$  species concentration is desired since the coexistence of “static” and “dynamic” elastic dipoles is not favorable to superior electrostriction properties [4]. So, determining the valence states of Ce is crucial for electrostriction applications in ceria-based materials. Moreover,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  can be assessed by XAS measurements through the quantification of  $\text{M}_4$  and  $\text{M}_5$  spectral peak relative intensities, as well as the  $\text{I}_{\text{M}_5}/\text{I}_{\text{M}_4}$  ratio [42]. These peaks correspond to Ce  $3d_{3/2}$  and Ce  $3d_{5/2}$  core levels electronic transition into the unoccupied 4f orbital, which incidentally gives information on this orbital. Both peaks display satellite peaks at the high-energy side, related to the anti-bonding state, peaks 3 and 4, as well as pre-peaks, both of which are regular features in cerium absorption spectra [42,43]. From Table 3, it is evident that the  $\text{M}_4$  integrated intensity is higher than that of  $\text{M}_5$  for all samples investigated, including the standard ceria measured for comparison. This suggests that the  $\text{Ce}^{4+}$  oxidation state is prevalent, with  $\text{I}_{\text{M}_5}/\text{I}_{\text{M}_4}$  falling close to the 0.93 value reported for  $\text{Ce}^{4+}$  [44]. In addition, no white line shift can be observed for both  $\text{M}_4$  and  $\text{M}_5$  spectral peaks when comparing all samples. The  $\text{I}_{\text{M}_5}/\text{I}_{\text{M}_4}$  ratio of standard ceria, in comparison with CZ10 and the sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  samples, reveals no significant change, which further confirms the prevalent  $\text{Ce}^{4+}$  oxidation state.

Additionally, the presence of oxygen vacancies was investigated using O K-edge soft XAS measurements. XANES data of O K-edge give information on the hybridization between the oxygen 2p, cerium 4f, and Zr 4d orbitals (Fig. 3d–f) for standard ceria, CZ10, and sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sample. O K-edge XANES data present all the characteristics of successful solid solution formation between  $\text{CeO}_2$  and  $\text{ZrO}_2$ , indicating that oxygen is in a distinctive chemical environment from  $\text{CeO}_2$  and  $\text{ZrO}_2$  separately, i.e., O K-edge XANES data of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  is not a direct sum of  $\text{CeO}_2$  and  $\text{ZrO}_2$  features [45]. Peak A is usually stronger in pure ceria than in doped ceria because it is linked to the hybridization of  $\text{Ce}^{4+}$  species and oxygen, which is the case here; peaks B and C, on the

other hand, are very sensitive to structural changes [45,46]. The decrease in intensity of peak A for the milled and sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  samples compared to standard ceria (Table 3) might indicate partial occupation of the  $4f^0$  orbital, i.e., the presence of  $\text{Ce}^{3+}$  species [45]. In Table 3, information on peak intensity and the ratio between the intensity of peaks B and C is given. No significant change in peak position is observed between samples, suggesting no considerable difference in hybridization for the oxygen orbitals. Peaks B and C give an insight into the structure of ceria-based materials, these peaks correspond to the 5d- $e_g$  and 5d- $t_{2g}$  levels, respectively, and are directly linked to the oxygen vacancy ordering in non-stoichiometric ceria [42,45]. Specifically, the increase in relative intensity of the B peak compared to C,  $\text{I}_B/\text{I}_C$  ratio, may be linked to cation segregation and oxygen vacancy ordering in ceria-based ceramics [42,46]. Thus, the results obtained here may indicate the presence of oxygen vacancies; however, comparing the  $\text{I}_B/\text{I}_C$  ratio in zirconia-doped samples (CZ10 and sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ ), and the standard ceria sample, it is possible to infer that the amount of oxygen vacancies is limited, which is corroborated by Raman and Rietveld analysis.

From the EIS measurements, Nyquist and Arrhenius plots were obtained, shown in Fig. 4a and b, respectively. For comparison, data for Gd-doped ceria (GDC) and  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$  were plotted alongside  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  in Fig. 4b [13,47]. Nyquist plots for all measured temperatures display two distinctive electrical components: a single semicircle arc, associated with mixed contributions from both the grain and grain boundaries, which overlap and cannot be separated into high- and low-frequency contributions, and the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ /electrode interface contribution at lower frequencies. The second component was not fitted because it is not related to the sample's properties, but rather an interfacial feature. The equivalent circuit for the impedance data and additional data obtained from the fitting can be verified in the supplementary material, Fig. S3, and Supplementary Table S1. As temperature increases, conductivity increases, which is consistent with the increased mobility of charge carriers. The Arrhenius plot (Fig. 4b) clearly demonstrates that  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  is considerably more resistive than other ceria-based electrostrictors such as GDC. The extrinsic oxygen vacancies confer GDC a high ionic conductivity. In contrast, the conductivity exhibited by  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  aligns well with values reported for a similar isovalent-doped ceria composition,  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ , both presenting similar activation energies, 0.98 for the latter and 1.06 eV for the



**Fig. 3.** (colored). XANES data of Ce  $M_{4,5}$  and O K-edge. (a, d) Standard ceria. (b, e) High-energy milled sample, CZ10. (c, f) Sintered  $Ce_{0.9}Zr_{0.1}O_2$ .

**Table 3**

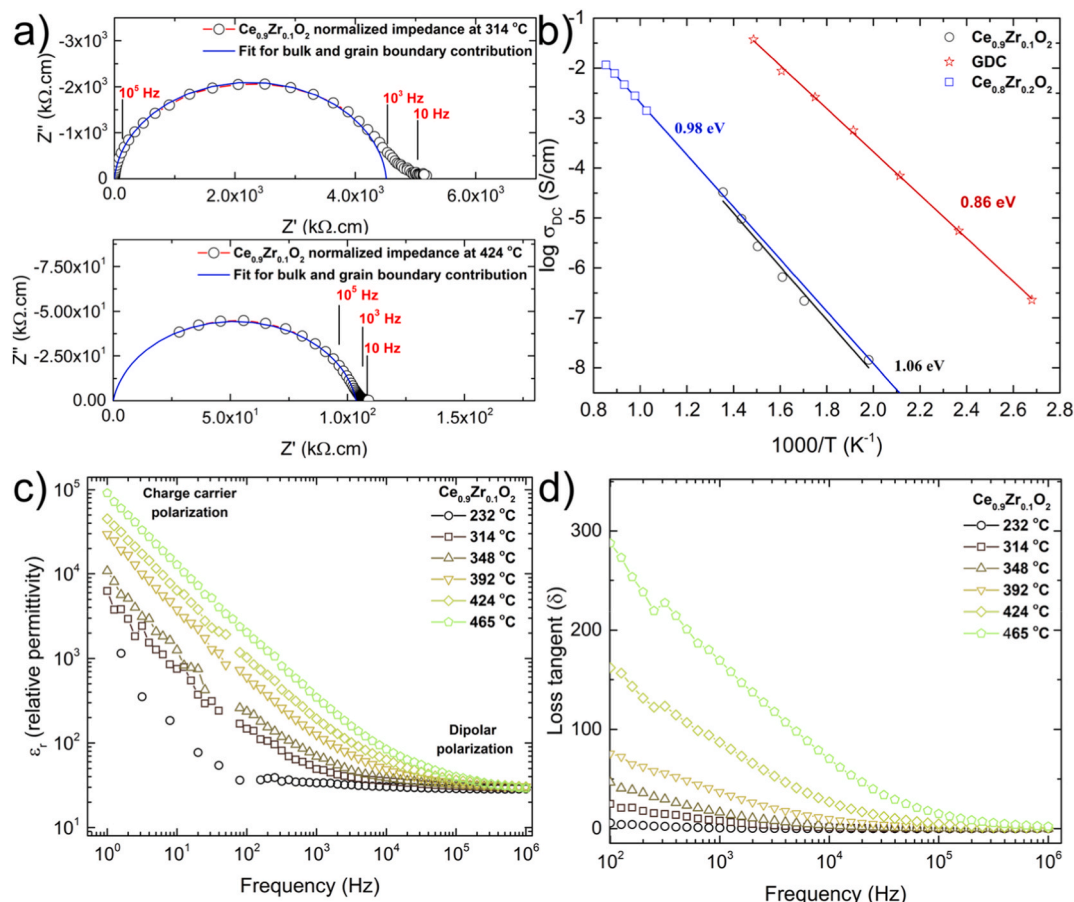
Integrated  $M_5$  and  $M_4$  intensities, calculated  $I_{M5}/I_{M4}$  ratio for cerium,  $I_A$ ,  $I_B$ ,  $I_C$ , and  $I_B/I_C$  ratio for the oxygen K-edge.

| Sample                         | $I_{M5}$ | $I_{M4}$ | $I_{M5}/I_{M4}$ | $I_A$ | $I_B$ | $I_C$ | $I_B/I_C$ |
|--------------------------------|----------|----------|-----------------|-------|-------|-------|-----------|
| CeO <sub>2</sub> (standard)    | 3.83     | 3.97     | 0.96            | 0.82  | 0.86  | 0.79  | 1.08      |
| CZ10                           | 3.21     | 3.43     | 0.94            | 0.74  | 0.84  | 0.80  | 1.05      |
| Sintered $Ce_{0.9}Zr_{0.1}O_2$ | 3.53     | 3.86     | 0.92            | 0.76  | 0.82  | 0.82  | 1.00      |

former. In fact,  $Ce_{0.9}Zr_{0.1}O_2$  is more resistive and has a higher activation energy than 3+ doped ceria ceramics, which is consistent with a low oxygen vacancy concentration in Zr-doped ceria [13].  $Ce_{0.9}Zr_{0.1}O_2$  shows a significantly higher activation energy of 1.07 eV compared to 0.86 eV for GDC, and considerably smaller activation energy than undoped ceria, 2.45 eV [41,48,49].

Relative permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan\delta$ ) were calculated as a function of frequency over a wide range of temperatures from the

impedance data (Fig. 4c and d, respectively), providing insight into the polarization mechanisms of  $Ce_{0.9}Zr_{0.1}O_2$ . In Fig. 4c, it is observed that  $\epsilon_r$  decreases as frequency increases. In the frequency range above ~10 kHz, the temperature dependence of the relaxation response is small, and  $\epsilon_r$  becomes nearly constant at ~1 MHz. The observed  $\epsilon_r$  decrease is a well-known behavior of dipolar polarization, whereby the induced electric dipoles are unable to follow the fast alteration of the applied ac field. It has been observed in ceria-zirconia mixed oxides and nanometric  $Ce_{0.75}Zr_{0.25}O_2$  solid solution [13,36,50]. At lower frequencies, the temperature dependence of the relaxation response is more pronounced, and at high temperatures,  $\epsilon_r$  increases considerably as the frequency decreases, indicating the presence of thermally activated mechanisms. Space charge, interfacial, polarization is commonly observed in ceria-based ceramics. It originates from grain boundaries that act as energy barrier sites blocking charge movement [50,51]. As frequency increases, interfacial polarization diminishes as the influence of charge carriers on the dielectric constant also decreases due to the



**Fig. 4. (colored).** Electrical characterization of sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sample. (a) Nyquist plots for selected temperatures. (b) Arrhenius plot. (c) Dielectric constant as a function of frequency. (d) Loss tangent as a function of frequency.

disappearance of the capacitive effect at the lattice sites with a high-energy barrier. Interfacial polarization usually manifests as a steep slope in  $\epsilon_r$  in the kHz range, followed by a plateau in lower frequencies. This step-like feature is more pronounced when the resistivity of the grain boundaries is considerably smaller than the bulk [13]. For the sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  in this work, such a step-like feature does not appear, rather a continuous increase in  $\epsilon_r$  as the frequency is reduced is observed in a wide frequency range, from 1 kHz down to MHz. Considering such a wide range and the fact that the mechanism is thermally activated, i.e., for a fixed frequency,  $\epsilon_r$  increases with temperature, such behavior can be attributed to charge carrier polarization that occurs in materials having significant ionic conductivity and electrodes that block ion exchange [52]. The prevalence of a bulk charge carrier polarization response over interfacial polarization at the grain boundaries is supported by the Nyquist plots in Fig. 4a that show that grain and grain boundary contributions have a large overlap, indicating that grains and grain boundaries possess similar electrical properties [53]. Interestingly, unlike what has previously been observed in aliovalent doped-ceria, where cationic segregation occurs, the relatively low conductivity of the sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  still allows for charge carrier polarization, and grain boundaries do not exhibit such restrictive blocking effects [13]. On the other hand, the samples' low conductivity, even at high temperatures ( $3.3 \times 10^{-5}$  S/cm at 465 °C), explains why  $\epsilon_r$  at approximately 1 Hz is up to two orders of magnitude lower than GDC at the same frequency [13]. Moreover, considering conductivity values of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  obtained by fast sintering when heat-treated in an oxygen rich atmosphere,  $\approx 10^{-17}$  S/m, it is clear that our sample is considerably more resistive even at higher temperatures [2].

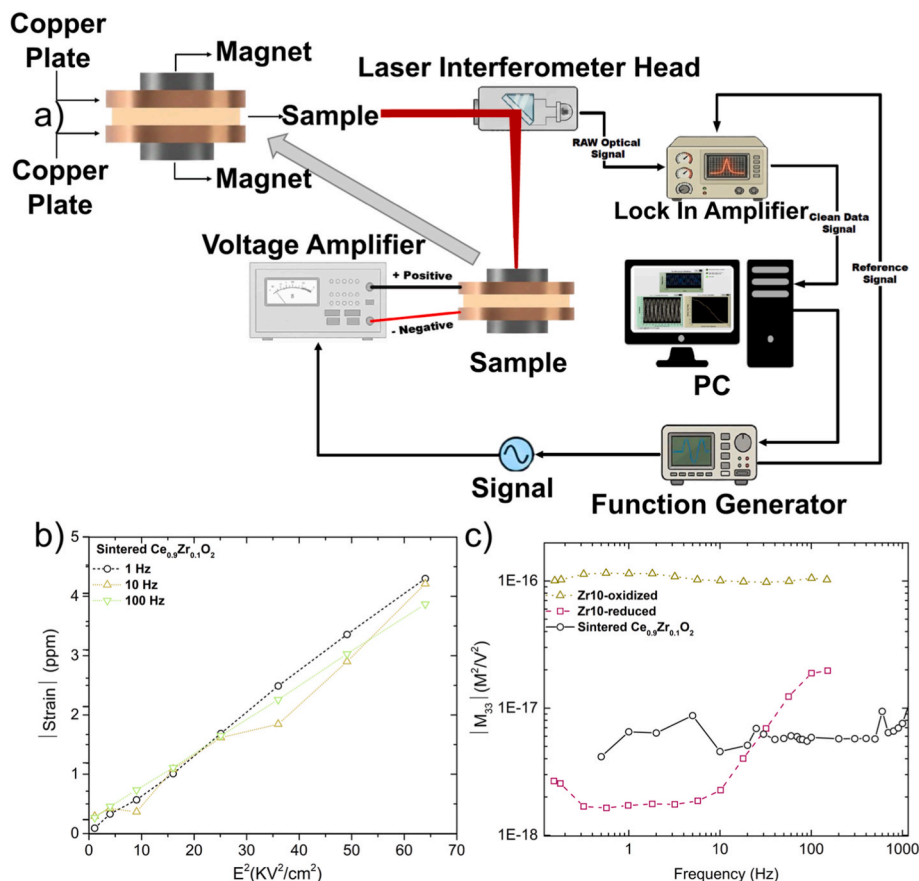
Impedance measurements also provide information on the

dissipative characteristics of dielectric materials, the dielectric loss. Such a characteristic is usually presented as the loss tangent,  $\tan\delta$ , and its spectral response also helps identify polarization mechanisms as shown in Fig. 4d. In the low-frequency regime, the dielectric loss is high, consistent with the high dielectric constant. In the low-frequency part of the spectra, a sharp increase in the dielectric loss is observed, associated with a resonant dipolar response. The loss tangent plots corroborate the presence of two distinct polarization responses: dipolar polarization at high frequencies and charge carrier polarization at low frequencies.

Finally, room temperature impedance measurements reveal a significant increase in the dielectric constant value, i.e., the  $\epsilon_r$  value of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  in comparison to undoped ceria, 66 and approximately 32, respectively. Such an increase is consistent with the Zr doping of ceria and might indicate superior electrostriction properties, which means that the high-energy milling synthesis method carried out in this project was successful, yielding dense  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  samples with high potential for electrostriction application, but synthesized through an eco-friendly synthesis process [2].

The electrostriction response was gauged in the form of the  $M_{33}$  coefficient, measurement setup is shown in Fig. 5a. The sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  responds to the second harmonic of the applied electric field and demonstrates an electrostrictive response, similar to previous reports [2]. As observed in Fig. 5b, electrostrictive strain is proportional to the square of the applied electric field for a wide frequency range, 1 to 100 Hz. No strain saturation was noticed within the investigated electric field ( $E \leq 8$  kV/cm).

$M_{33}$  values as a function of frequency can be observed for sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  plotted alongside reference 2 data for oxidized  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  (Zr10-oxidized), which presents a lower concentration of  $\text{Ce}^{3+}$  species,



**Fig. 5. (colored).** Electromechanical characterization of sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  ceramic. (a)  $M_{33}$  measurement setup. (b) Longitudinal electrostriction strain measured as a function of applied electric field squared. (c) Electromechanical strain ( $M_{33}$ ) as a function of frequency, second harmonic, for sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  pellets in comparison with reduced  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  (Zr10-reduced) and oxidized  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  (Zr10-oxidized) samples from reference 2.

and reduced  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  (Zr10-reduced), presenting a higher concentration of  $\text{Ce}^{3+}$  species, for comparison (Fig. 5c) [2]. From the Hz to the kHz range,  $M_{33}$  values are nearly constant, reaching a maximum of approximately  $1.7 \cdot 10^{-17} \text{ m}^2 \text{ V}^{-2}$  near the kHz frequency. Moreover, the  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  synthesized in this work still underperforms compared to more traditional lead-based ceramics, such as PNM-PT, Fig. S4 [2]. In fact, it falls below the values presented for the Zr10-oxidized sample in Ref. [2]. Comparing the  $M_{33}$  value obtained for the sintered  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  sample to Zr10-oxidized,  $\approx 10^{-16} \text{ m}^2/\text{V}^2$ , and Zr10-reduced samples,  $\approx 10^{-18} \text{ m}^2/\text{V}^2$ , and taking into consideration the dielectric constant value of the oxidized sample, 224(2), the synthesis process must be optimized to reach similar dielectric constant and  $M_{33}$  values [2]. Controlling the microstructure developed, i.e. smaller grains, similar to what has been observed in the reference 2,  $\approx 1 \mu\text{m}$ , could be a valid tactic, however, it should be taken into consideration that little change in electrostriction performance was observed in aliovalent-doped ceria ceramics when average grain size is varied in the micrometer range [11, 54,55]. In addition, high-energy milling yields samples with comparatively smaller crystallites, which impacts the dielectric constant and incidentally electrostriction performance. Moreover, even though measurements suggest a limited presence of oxygen vacancies, it is possible that, even in low concentrations, they have a significant detrimental effect on the electrostriction properties, which is substantiated by extensive studies showing the limited impact of grain size in the electrostriction coefficient. This assumption is further supported by comparing usual  $M_{33}$  values obtained for isovalent and aliovalent dopants in ceria, which shows that although performance falls short of the previously reported value for oxidized  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ , the sample produced by high-energy milling shows performance superior to

aliovalent-doped ceria for frequencies over 100 Hz (S5) [2].

#### 4. Conclusions

High-energy milling is a straightforward method for synthesizing the nanometric  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  solid solution in the fluorite structure, as evidenced by extensive structural and microstructural characterization of the high-energy milled powder. Sintering at  $1500^\circ\text{C}$  does not induce cationic segregation, and dense pellets are obtained by a short sintering program enabled by the enhanced surfaced area of the high-energy milled powder. XANES measurements confirm the predominance of  $\text{Ce}^{4+}$  species in the Zr-doped ceria solid solution and the limited presence of oxygen vacancies. Moreover, the sintering program adopted yielded dense and homogeneous samples, with high-energy milling favoring sintering, which creates a microstructure characterized by similar relaxation times for grain and grain boundary responses, as evident in the Nyquist plots over a wide range of temperatures. Room-temperature dielectric constant values indicate superior electrostriction properties, which are confirmed by  $M_{33}$  coefficient measurements. Thus, it was demonstrated that high-energy milling can be a powerful tool for obtaining  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  ceramics with high potential for electromechanical applications.

#### CRediT authorship contribution statement

**Larissa S. Marques:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization, Investigation, Methodology, Project administration. **Andre S. Ferlauto:** Writing – review & editing, Supervision, Investigation. **Fabio C. Fonseca:** Writing –

review & editing, Investigation, Formal analysis. **Ahsanul Kabir:** Writing – review & editing, Investigation, Formal analysis. **Dimitrios Koukoulis:** Investigation, Formal analysis, Writing – review & editing. **Khondoker N. Islam:** Writing – review & editing, Investigation, Formal analysis. **Vincenzo Esposito:** Writing – review & editing, Investigation, Formal analysis. **Daniel Z. de Florio:** Writing – review & editing, Investigation, Conceptualization, Formal analysis, Funding acquisition, Supervision.

## Synopsis

This article presents the impacts of high-energy milling-assisted synthesis on the functional properties of “giant” electrostrictor  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ .

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2026.04.099>.

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