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Gigantic electro-chemo-mechanical properties of nanostructured praseodymium doped ceria

Victor Buratto Tintia,b, Ahsanul Kabira, Jin Kyu Hanb, Sebastian Molinc, Vincenzo Espositoa,*

Some oxygen defective fluorites are non-Newnham electrostrictors, i.e., the electromechanical response does not depend on their dielectric properties. Here, we show gigantic electrostriction in nanocrystalline 25 mol% praseodymium doped ceria (PCO) bulk ceramics. The material was fabricated with a field-assisted spark plasma sintering (SPS) process from high-purity nanoscale PCO powders (<20 nm). The SPS process consolidates the powders into a single-phase, highly dense material with a homogeneous microstructure and large grain boundary extension. Various thermally and chemically stable ionic defects are incorporated into the nanostructure, leading to superior electrical conductivity. The material shows an electrostriction strain coefficient ($M_{33}$) of ~$10^{-18}$ m$^2$/V$^2$ at frequencies below 100 Hz at room temperature. Such performance is comparable and even superior to Newnham's electrostrictors, such as ferroelectric ceramics and polymeric actuators. Comparative analysis with polycrystals suggests that nanostructured PCO possesses electromechanically active nanodomains of Pr$^{3+}$-V$^0$ pairs. Such results are unexpected and open novel insights on non-Newnham electrostrictors.

In addition to the electrical properties at high temperatures, Lubomisky et al. have recently reported a "non-classical" electromechanical response in ceria-based compounds.13,14 In general, electrostriction is a property exhibited by all-dielectric materials, and it arises from cooperative ionic displacement induced by an external electric field. According to the proposed atomistic model, such a response depends on oxygen defects and their concentration in the host lattice. Oxygen vacancies induce a local electromechanical active distorted domain in the fluorite lattice that is centred at the [Ce$^{4+}$-7O$_{V}$] complex.5,12,16,17 Under an electric field, point defects in the distorted lattice reorient, leading to a local atomic displacement with a macroscopic giant electromechanical strain.12

Recently, global environmental measures restrict the manufacture and use of lead-based materials in various consumer items. The restrictions created an urgency to find alternatives to PZT and related compounds, which are currently the main marketed of piezoceramics.16–20 The high performance of these new "non-classical" electrostrictors enables applying these metal oxide as competitors of the classical PZT ceramics in electromechanically active devices.21 Metal oxides are already known for their wide range of properties and relevancy.22–24 However, these new electrostrictors based on ceria can profoundly impact the electromechanical application, which has been dominated by mainly piezoelectric materials.19,25 These new ceria based materials could be used for sensors, actuators, micro-pumps, manipulators and a wide range of MEMS.13,18,26

Several experiments reported for thin films and bulk ceramics show the electrostrictive strain coefficient ($M_{33}$) of $10^{-17}$–$10^{-19}$ m$^2$/V$^2$. This

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**Introduction**

Cerium oxide and its derivatives have been extensively investigated over the past few decades due to their wide range of technical applications in solid oxide fuel cells (SOFCs), oxygen gas sensors, automobile catalysts, non-classical electrostrictors, among others.1–3 Ceria crystallises into the cubic fluorite ($Pm\bar{3}m$) structure, showing no phase transformation from room temperature up to its melting point (2600 °C).4 The material is typically doped with rare-earth acceptor cations (M$^{3+}$), which create extrinsic oxygen vacancies, V$^0_O$, to balance the ionic lattice electrically. One remarkable property of ceria is the change of the host cation valence state (Ce$^{4+}$ to Ce$^{3+}$) under low oxygen partial pressure. Chemical reduction introduces extensive oxygen non-stoichiometry and quasi-free localised electrons, i.e., small polaron electronic defects, eventually resulting in mixed ionic-electronic conductivity (MIEC).5 Characteristically, such point defects control intrinsic properties of ceria. Some examples are ionic conductivity$^6$, mass transport$^7$–$10$, mechanical properties$^{11}$, and electrostriction$^{12}$–$15$. The chemical reduction of the host cation is strongly dependent on the properties of the dopant.$^9$

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range is at least one order of magnitude higher than Newnham empirical law for ceria.\textsuperscript{2,27,28} However, the factors influencing the electromechanical response remains unclear.

The effect of microstructure on electrostriction is generally weak.\textsuperscript{2} Previous publications on both nano- and micro-crystalline ceramics indicate that electrostriction strongly relies on the grain boundary chemistry rather than its extension.\textsuperscript{2,3} Conversely, other experiments show that electrostriction in polycrystalline ceria strongly depends on the dopant type.\textsuperscript{20} Trivalent and divalent dopants such as Gd\textsuperscript{3+}, Sm\textsuperscript{3+}, Ca\textsuperscript{2+}, Sc\textsuperscript{3+} are reported in the literature.\textsuperscript{15,29-31} Tetra-valent cations, e.g. Zr\textsuperscript{4+} and Pr\textsuperscript{4+}, are common in ceria solutions for other applications. However, iso-valent dopants remain unexplored in electrostriction. The lack of extrinsic oxygen vacancy in the iso-valent composition should exhibit limited electromechanical response. Notably, the Pr-doped ceria (PCO) case presents some interesting aspects.

PCO has been studied extensively as a model system for the defect chemistry of ceria.\textsuperscript{5,32} In highly doped PCO, defects commonly coexist in two oxidation states, the Pr\textsuperscript{4+} and Pr\textsuperscript{3+} ions.\textsuperscript{5,32,33} The oxygen defect concentration is stable at intermediate oxygen partial pressures, from 10\textsuperscript{−5} to 10\textsuperscript{−15} atm. However, with the increase of pO\textsubscript{2}, the Pr\textsuperscript{3+} oxides to Pr\textsuperscript{4+}. The oxidation leads to a decrease in the oxygen vacancy concentration following equation (1).\textsuperscript{5,32}

\[
[V_o] = \left[ Pr_{Ce} \right]^{2/3} \left[ O_2 \right]^{1/3} \left[ K_o \right]^{1/3} \exp \left( \frac{-\Delta G}{3kT} \right) P_{O_2}^{-1/6}
\]

At high temperatures, the PCO conductivity is directly proportional to the $V_o$ concentration, inducing a dominant oxygen ionic conductivity. Following Brower's formalism, the equation (1) indicates that the PCO conductivity varies with a $-1/6$ slope at high pO\textsubscript{2}.\textsuperscript{32} Moreover, the Pr valance switch phenomena (Pr\textsuperscript{3+}$\rightarrow$Pr\textsuperscript{4+}) at high temperatures lead to chemo-mechanical expansion through lattice expansion, which can cause micro/macro-level cracking to mechanical failure.\textsuperscript{33} Also, the presence of mixed ionic-electronic properties in Pr\textsuperscript{3+}/Pr\textsuperscript{4+} can induce electronic leaks under intense electrical fields. Thus, electronic conductivity increases by augmenting the dopant concentration.\textsuperscript{5} As a consequence of such effects, the PCO does not seem a promising candidate for non-classical electrostriction, thus remaining unexplored.

In this work, we approach the relationship between the electro-chemo-mechanical properties of 25\% molar Pr-doped ceria consolidated by conventional sintering and field-assisted sintering, i.e., spark plasma sintering (FAST/SPS). We selected a high dopant content to emphasise the isovalent dopant concentration's influence in the Pr\textsuperscript{4+} and the Pr\textsuperscript{3+} states. Recent results show that up to 15-20\% doping molar ratio is the threshold to obtaining superior electromechanical performance.\textsuperscript{29} Higher dopant content can induce defect-dopant association, defect clusters nanodomains, and micro-segregation, which eventually induce oxygen vacancy concentration order.\textsuperscript{15} In PCO, we do not expect vacancies' ordering. Yet, as Pr\textsuperscript{4+} creates no extrinsic oxygen vacancy, we have chosen a higher dopant concentration to increase the chance of oxygen vacancy formation via a facile Pr reduction from Pr\textsuperscript{4+} to Pr\textsuperscript{3+} via microstructural tailoring, e.g., in nanocrystals and grain boundaries.

Mainly, SPS is a non-equilibrium sintering process that enables fast mass diffusion due to direct (Joule) heating, typically forming a highly-dense nanostructured sample.\textsuperscript{34-36} This process also introduces physical and chemical properties different from the conventional approach, e.g., chemical reduction and metal oxides' defects. We here compare SPS-PCO with free sintered samples and reference Gd-doped ceria from previous literature. The different chemical and microstructural features introduced in the analysis highlight structural defects' role in electromechanical mechanisms.

**Experimental**

25 mol\% praseodymium doped ceria (PCO25) was synthesised from nanometric powders (ca 20 nm) by a co-precipitation method (see reference).\textsuperscript{37} The starting materials' purity and chemical composition was examined with energy-dispersive X-ray (EDX) analysis. Powders were sintered into pellets (PCO25-SPS) by spark plasma sintering (SPS, Dr. Sinter Lab) at 980 °C for 5 min dwelling under a uniaxial pressure of 70 MPa and vacuum atmosphere (6 x 10\textsuperscript{−6} Torr), with a heating rate of 100 °C/minute. A graphite die (Ø 16 mm) was used to fabricate 2 mm thick pellets. Graphite foil (0.1 mm thickness) was placed in the die as well as two spacers between the punch and the die to protect the punches from contamination. The temperature during sintering was monitored with a thermocouple attached to the outer wall of the die. The SPS samples were re-oxidised in synthetic air at 800° C for 10 hours to avoid chemically reduced metastable phases. Additionally, free-sintered samples were produced through exposure to a temperature of 1400 °C for 10 hours in air (PCO25-10h).

The sintered pellets' crystal structure and microstructure were investigated using X-Ray diffraction (XRD, Bruker D8) and scanning electron microscopy (SEM, ZEISS EVO MA10), respectively.

The electrical properties were measured by electrochemical impedance spectroscopy (EIS, Solartron 1260) from 200 °C to 600 °C with frequencies between 10\textsuperscript{5}-10\textsuperscript{6} Hz under a 100 mV AC voltage. A room-temperature conductive silver paste was brushed onto the sample parallel faces and dried at around 500 °C. To achieve different pO\textsubscript{2} during the electrical characterisation, O\textsubscript{2}, N\textsubscript{2}, and N\textsubscript{2}-H\textsubscript{2} mixtures were used. Equivalent RC circuit models were used to fit the data using ZView software. Two RC components associated with bulk and grain boundary were used to fit the high and intermediate frequency response (> 10 kHz). The low-frequency range (< 10 kHz) was not fitted since it is strongly influenced by the electrode and other interfacial contributions rather than the ceramic material property.

Electrostriction at room temperature was measured with a laser interferometer microscope (SIOS NA analyser) coupled with a lock-in amplifier (Ametek 7230 DSP). The samples were coated with gold (Au), and tungsten tips were used for the electrical contacts. Further
details of the set-up and measurement methods are in previous reports.\textsuperscript{37}

The Raman spectra were acquired with a Renishaw InVia Reflex Spectrometer System equipped with a confocal microscope under atmospheric pressure. The excitation wavelength used for PCO was 532 nm.\textsuperscript{38,39}

**Results and Discussion**

The PCO-25 starting powders consist of nanometric primary particles (<20 nm). Fig. 1 shows the main chemical, microstructural and structural properties of the PCO samples. As synthesised, the powders result in weakly bounded micro-sized agglomerates (Fig. 1a). The EDS maps (Fig. 1b-c) confirm the homogeneous distributions of elements in the starting powder and no impurities.

All sintered specimens show a low porosity volume, mainly consisting of isolated pores at the grain boundary (Fig. 1d-e). In line with the microstructure analysis, all sintered samples' apparent density measured by the Archimedes' method is above 95% of the theoretical values. For the PCO25-10h sample, the material achieved micrometric grain sizes (>2 μm) with a partially relaxed microstructure after the sintering process (Fig. 1d), with hexagonal and equiaxial grains (dihedral angle ≈120°). In contrast, grain growth is limited in the PCO25-SPS sample (Fig. 1f). Constrained diffusion is generally associated with the fast-heating rates which occur during the field-assisted sintering process and limit the grain growth.\textsuperscript{37}

Residual porosity in SPS samples is around 3-4% of the total volume and is homogeneously distributed in the pellet.

Fig. 1g displays the XRD pattern of the as-sintered pellets. The pattern index refers to the cubic fluorite structure (\textit{Fm\textit{3}m} – ICSD #241840) for pure ceria.\textsuperscript{40} The slight broadening of the diffraction peak of PCO25-SPS material confirms the sample's nanocrystalline nature.\textsuperscript{41} Within the detection limit of the XRD technique, no additional diffraction peaks are visible. Such remarks, together with the EDS maps' results in Fig. 1b-c, indicate that samples are homogeneous after sintering.

Both samples show a slight shift of the diffraction peaks to lower angles, indicating an increase of the cell parameters. This feature could be attributed to the larger ionic radius of Pr\textsuperscript{3+} (1.13 Å) than the host Ce\textsuperscript{4+} (1.01 Å).\textsuperscript{42} However, due to Pr-doping's bivalent nature, which leads to varying ionic radius of the dopant (Pr\textsuperscript{4+} = 0.99 Å), controversial information about Pr-doped ceria compositions are found in the literature.\textsuperscript{43,44}

Fig. 2 reports the EIS results collected on the sintered samples, and literature reference.\textsuperscript{28} Fig. 2a displays the Nyquist plots normalised by the sample's geometry. The plots exemplify the total impedances as a function of the frequency as the sum of the bulk and grain boundary contributions, fitted by the inset's equivalent circuit. The plots show that the grain boundary dominates the electrical behaviour, leading to a high impedance at intermediate frequencies (10–100 kHz). The PCO25-10h shows a lower conductivity than the SPS sample and previously reported values (reference Fig. 2b). Since PCO25-10h was exposed to a high temperature for an extended period in air, we expect most of the Pr-ions to be in the Pr\textsuperscript{4+} oxidation state, limiting the formation of oxygen vacancies and hindering the ionic conduction.

Fig. 2b also shows superior conduction for the SPS sample compared with previously reported results for the PCO25 composition.\textsuperscript{45} At first glance, a higher density of grain boundaries could indicate a higher
blocking effect due to grain boundary. However, this is not true for nanocrystalline ceramics on ceria.\textsuperscript{46}\textsuperscript{47} Nanocrystalline ceria can increase electrical conductivity by forcing space charge regions (SCR) at the near-grain-boundary, introducing electronic species.\textsuperscript{46,47} Such an effect can arise from an inhomogeneous distribution of the 3+ species and dopants within the materials.\textsuperscript{48,49} For PCO, selective segregation of Pr\textsuperscript{4+} and Ce\textsuperscript{3+} at the SCR can balance oxygen defects trapped at the grain boundary.\textsuperscript{50} From a compositional perspective, the high heating rates during the SPS process can induce such conditions. Moreover, the chemical reducing conditions during the SPS can consolidate oxygen vacancies at the nanocrystalline grain boundaries disorder with stable Pr\textsuperscript{4+} and Ce\textsuperscript{3+} ions population.\textsuperscript{30,51}

Such a compositional inhomogeneity can result in a change in the charge transport mechanisms. In Fig. 2b, the activation energy value (0.5 to 0.6 eV) is lower than the typical value for doped ceria 0.9 eV, suggesting another mechanism for conduction than oxygen vacancy transport. Pr-doped ceria compositions show an n-type electronic conduction mechanism at high pO\textsubscript{2}; thus, this low activation energy value can arise from the presence of mixed ionic-electronic conduction.\textsuperscript{5,52} The activation energy reported in the literature (0.49 eV) is similar to the obtained for the PCO25-10h (0.55 eV). However, the PCO25-SPS shows slightly higher activation energy of 0.6 eV. Such a difference suggests a somewhat alternative crystalline environment or possible nanodomains with the coexistence of significant ionic conductivity contributions. Despite such variances, when comparing the PCO25-SPS with other PCO similar compositions reported in the literature, it shows comparable performance (Table I).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Electrical Conductivity [S/cm] at 500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCO25-SPS</td>
<td>1.97 \times 10^{-3}</td>
</tr>
<tr>
<td>PCO25-10h</td>
<td>2.98 \times 10^{-4}</td>
</tr>
<tr>
<td>PCO25\textsuperscript{55}</td>
<td>2.44 \times 10^{-4}</td>
</tr>
<tr>
<td>PCO20\textsuperscript{52}</td>
<td>1.90 \times 10^{-3}</td>
</tr>
<tr>
<td>PCO20\textsuperscript{53}</td>
<td>3.35 \times 10^{-3}</td>
</tr>
<tr>
<td>PCO20\textsuperscript{54}</td>
<td>5.70 \times 10^{-3}</td>
</tr>
</tbody>
</table>

To unveil the dominant charge transport mechanisms, we show the variation of total electrical conductivity for the PCO25-SPS sample at 600 °C under different pO\textsubscript{2} (Fig. 3). The results are compared with a previous work reported for a similar composition (PCO20) at 650 °C.\textsuperscript{5} The fitted line represents the conductivity model, as reported by Tuller et al.\textsuperscript{32} An essential feature in Fig. 3 is the decrease in conductivity at high pO\textsubscript{2}, following an approximate -1/6 slope within experimental error. This effect is due to the oxidation of Pr\textsuperscript{3+} into Pr\textsuperscript{4+}, decreasing the V\textsubscript{O} concentration following the equation (1), which states the proportionality $[V_{O}] \propto P_{O}^{-1/6}$. Since the ionic conductivity is directly dependent to the carrier density, being $V_{O}$, it also shows a -1/6 slope.\textsuperscript{32}

A peak in conductivity at around 10\textsuperscript{-2} atm arises when the Pr\textsuperscript{3+} and Pr\textsuperscript{4+} concentrations are approximately equal. Such a peak is only clearly visible for highly doped PCO compositions (>20% at. Pr), enabling a significant concentration of neighbouring Pr ions. Usually, this peak in conductivity appears between 10\textsuperscript{-2} atm to 10\textsuperscript{-5} atm, which agrees with our measurements.\textsuperscript{3,53} Interestingly, the PCO25-SPS shows a much sharper slope than -1/6 and a higher conductivity peak. This effect indicates that the Pr\textsuperscript{3+}--Pr\textsuperscript{4+} carrier hopping mechanisms are enhanced for this sample. This change could be associated with an accumulation of defective species, like V\textsubscript{O} and Pr\textsuperscript{3+}, induced by the high concentration of grain boundaries due to the nanometric grains.\textsuperscript{49} The segregation of these point defects along the grain boundaries could also contribute to this effect, enhancing Pr\textsuperscript{3+}--Pr\textsuperscript{4+} pairs local density, and therefore the carrier hopping.

At sufficiently low pO\textsubscript{2} (< 10\textsuperscript{-15} atm), conductivity increases again, resulting from an intrinsic n-type polaronic conductivity due to the host Ce\textsuperscript{4+} to Ce\textsuperscript{3+} reduction.\textsuperscript{5,32} Yet, the overall properties are comparable with previously reported PCO with a similar dopant content.\textsuperscript{3,52}

For the electromechanical properties, Fig. 4 illustrates the electrostriction of the PCO25 pellets at room temperature. A remarkable saturation feature is visible in Fig 4a for the PCO25-SPS at 10 Hz. Such a behaviour has been previously observed in Gd-doped ceria compositions, and it relates to the Ce\textsuperscript{4+}--V\textsubscript{O} active complexes relaxation.\textsuperscript{3,55} Plots in Fig. 4b clarify that strain response lowers for both samples over an increase in frequency. This effect is also common in gadolinium doped ceria compositions, and it is due to a still unknown relaxation mechanism associated with the V\textsubscript{O} species responsible for the electromechanical behaviour.\textsuperscript{55} The PCO25-10h sample showed a similar response to previously reported for 10% Gd-doped ceria but with a decreased performance at high frequencies (> 80 Hz).\textsuperscript{2}
Remarkably, the PCO25-SPS sample displays close to a linear decrease in $M_{33}$ vs frequency, maintaining a higher electromechanical response in the high-frequency range (Fig. 4b). Overall, the PCO25-SPS sample exhibited a superior electromechanical response at higher frequencies than any material characterised so far, achieving $5.9 \times 10^{-17}$ m$^2$/V$^2$ at 100 Hz. The performance at the low frequency is also impressive, reaching up to $1.4 \times 10^{-16}$ m$^2$/V$^2$ at 1 Hz. Such a value is much higher than what is expected in ceramic electrostrictors.$^{18,56}$ Typically, in PMN-based relaxors, the best performing ceramic electrostrictors, $M_{33}$ values are around $10^{-18}$ m$^2$/V$^2$. For PCO, the value approaches polymeric electrostrictors such as PVDF-based compounds$^{57,58}$, but with much higher elastic moduli ($\sim 200$ GPa for PCO$^{59}$ vs $\sim 2$ GPa for PVDF-based polymers$^{58,60}$). Therefore, these nanostructured materials show outstanding electromechanical features.

Remarkably, for Gd-doped and Ca-doped ceria, we obtained different results. For those materials, nanostructures by SPS and other conventionally sintered samples have shown similar electromechanical properties with micrometric structures.$^{2,30,34}$

**Fig. 4:** (a) Electromechanical response of PCO25 samples and (b) $M_{33}$ coefficients (the 10% Gd-doped ceria sample is from ref $^{31}$)

To clarify the chemical features leading to such differences in the two samples, we used Raman spectroscopy under ambient conditions.

**Fig. 5** shows the spectra over the 450 and 570 cm$^{-1}$ bands. The band at 450 cm$^{-1}$ is affected by the Raman active vibration of the fluorite type structure ($F_{2g}$), associated with the symmetrical stretching vibration of the oxygen ions near the cerium ions.$^{38}$ The band at 570 cm$^{-1}$ is due to lattice defects, including oxygen vacancy. The intensity ratio of $F_{2g}$ and lattice defects on the PCO25-10h and PCO25-SPS samples are similar, being 1.63 and 1.41, respectively.

To analyse this lattice defect in detail, this band was split into D1, D2, and D3 using the Gaussian method with a boundary condition that the full width at half maximum (FWHM) value of the D2 band corresponding to Pr$^{4+}$ cations is about 52$^{61}$, where D1 is related to Pr$^{3+}$ and oxygen vacancies, and D3 with Ce$^{3+}$ and oxygen vacancies.$^{62,63}$

**Fig. 5:** Raman spectra and Gaussian fitting of (a) PCO25-10h and (b) PCO25-SPS.

The value of $(D1+D3)/D2$ is related to oxygen vacancies concentration compared to the total defects, and the PCO25-10h and the PCO25-SPS samples show ratios of 0.46 and 0.81, respectively. The ratio corresponding to the oxygen vacancy of PCO25-SPS is about twice as large as that of PCO25-10h. This feature suggests that the PCO25-SPS sample has nearly twice as many oxygen vacancies more
than a conventionally sintered pellet. Therefore, the nanostructure in PCO favours such a configuration as well as an increased population of Pr\(^{3+}/\text{Ce}^{3+}\). Fig. 6 show a schematic representation of the microstructural and defect chemistry differences between the PCO25-SPS and PCO25-10h.

![Conventionally Sintered vs. Spark Plasma Sintered (SPS)](image)

**Fig. 6:** Schematic representation of the primary defect features of the PCO samples.

The different defect chemistry and higher oxygen vacancy concentration could explain the different behaviour shown by the PCO25-SPS sample. In summary, PCO nanostructured features boost electro-chemo-mechanical properties, enhancing both ionic conductivity and electromechanical response at high frequency.

**Conclusions**

High purity nanoscale 25 molar % Pr-doped ceria powders (<20 nm) were synthesised using the co-precipitation method. The spark plasma sintering (SPS) process successfully produced dense pellets while hindering grain growth, producing nanocrystalline pellets (<100 nm). The samples' electrical properties were tuned not only by the sintering process, i.e., microstructure but also by its chemistry. Ceramics processed by SPS showed enhanced electrical performance at high temperatures compared to microcrystalline samples of the same materials produced in this experiment and previously reported values for PCO25. The Pr-doped SPS samples produced a superior electromechanical response that is independent of the operational frequency. These results indicate a superior performance when compared with other non-Newnham electrostrictors such as Gd-doped ceria polycrystalline ceramics. Nanostructured ceramic was identified as playing a key role in this effect, inducing oxygen vacancies due to the high concentration of disordered regions. These frozen defects possibly define electromechanically active oxygen vacancies during the SPS process, which are stabilised in the material by a large population of Pr\(^{3+}\) and Ce\(^{3+}\) species.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

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