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ABSTRACT:

EFFECT OF COMPOSITION ON EXTREME ANHARMONICITY OF CHEMICAL BONDS IN ZR-DOPED CERIA

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Chemical bond anharmonicity underlies many well-known phenomena. These include thermal expansion, Raman scattering, ionic conductivity, nonlinear optics, as well as electrostriction, i.e., a second-order electromechanical response (strain: $u_3 = M_{33} \cdot E_3^2$, where M_{33} is the longitudinal electrostriction strain coefficient (measured in the "direct" mode) and E_3 is the electric field). The Uchino–Cross "small anharmonicity" approximation successfully explains thermal expansion and, importantly, also accounts for Newnham's empirical scaling law, i.e., electrostriction scales as 1/ $(\varepsilon \cdot Y)$, where ε is the relative dielectric permittivity and Y is the elastic modulus.

We studied the evolution of the dielectric, mechanical and electromechanical properties of fluorite-structured $Zr_xCe_{1-x}O_{2-\delta}$, as a function of the Zr concentration, x and oxygen deficiency, δ. For x≤0.1, partial reoxidation of sintered $Zr_xCe_{1-x}O_{2-\delta}$ ceramics brings δ to the range of $200<\delta<500$ ppm. For these samples, the increase in ε and $|M_{33}|$ is exponential with increasing x, from $\varepsilon < 30$ to ≈ 220 and from $|M_{33}|<10^{-18} m^2/V^2$ to $M_{33} \approx -10^{-16} m^2/V^2$, ($M_{33}<0$ indicates contraction parallel to the electric field). The latter (unexpectedly large) value of $|M_{33}|$ identifies $Zr_xCe_{1-x}O_{2-\delta}$ as a non-classical (non-Newnham type) electrostrictor and points to marked changes in local bonding.

Applying "converse" (as distinguished from "direct") electrostriction measurements, M_{33} is defined as $\varepsilon_0\ (d\varepsilon_3/d\sigma_3)$ where σ_3 is the applied uniaxial mechanical stress. Thus, $\varepsilon_3(\sigma)=\varepsilon_3(\sigma=0)+M_{33}\sigma_3/\varepsilon_0$. For $Zr_xCe_{1-x}O_{2-\delta}$, we have observed experimentally that when x=0.08-0.1, $\Delta\varepsilon_3 > \varepsilon_3(\sigma=0)$, where $\Delta\varepsilon_3 = M_{33}\sigma_3/\varepsilon_0$. Within the Uchino-Cross approximation, it is not acceptable that the anharmonic contribution to the bond deformation energy will be larger than the harmonic contribution. Nevertheless, since $M_{33}<0$ for these ceramics, ε_3 decreases under tension and increases under compression. Notably, the anharmonic contribution to the bond energy increases the bond strength,

ensuring that the bond is not broken, which could occur for M_{33}>0. While $Zr_xCe_{1-x}O_{2-\delta}$ ceramics displaying $|u_3|$ > 200 ppm at 100 Hz is attractive for practical applications, they obviously challenge the suitability of the "small anharmonicity" approximation.

The "small anharmonicity" approximation has generally been found to be valid for electrostrictors, both classical and non-classical. The apparent violation by $Zr_xCe_{1-x}O_{2-\delta}$ prompted us to focus on the local structure and dynamics of the Zr and Ce bonding environments. Using X-ray absorption fine structure measurements (EXAFS), these data indicate that, in addition to local disorder, strong anharmonicity is detected in the Zr—O bonds, which is even more striking when the parameters of the [ZrO8] local environment are compared with those of [CeO8]. EXAFS analysis is able to provide explanations based on chemical bonding for the following observations: a) the fact that M_{33} is negative suggests that bond stiffness increases with Zr displacement away from the center of the [ZrO_8]-cube ; b) the absence of detectable transverse electrostriction strain, i.e., $M_{33} < 0$ does not result in expansion perpendicular to the field, $(M_{31} > 0)$, which, if it did occur under compressive stress, could force the relative dielectric permittivity ε_1 to become negative: $\Delta\varepsilon_1 = M_{31}\sigma_3/\varepsilon_0$; c) the fact that a very small concentration of trivalent dopants (0.05 x) , with associated oxygen vacancies, is able to both suppress longitudinal electrostrictive strain and to depress the dielectric permittivity ε_3 supports the suggestion that collective displacement of Zr ions within the [ZrO_8]-cubes is responsible for electrostriction.

Recent experiments have shown that oxidizing $Zr_xCe_{1-x}O_{2-\delta}$, x= 0.1 in 250 atm O_2 at 773 K for 7 days reduces δ to <50 ppm. This stoichiometry change returns the values of ε and M_{33} to approximately those of undoped CeO_2, thereby providing evidence that non-stoichiometry is necessary for bond anharmonicity. DFT-based modelling and ab initio molecular dynamics (AIMD) calculations predict formation of dynamic elastic dipoles arising from distorted [ZrO_8]-cubes and supporting the appearance of collective Zr displacement upon increase in Zr concentration. Thus, modelling and experiment are in agreement. Taken together, our findings suggest that engineering the defect chemistry of Zr-doped ceria can produce ceramics suitable for efficient conversion of electrical energy to mechanical energy (actuation) and vice versa (energy harvesting).