Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electromechanical active pairs dynamics in Gd-doped ceria single crystal

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Supplementary information

Interferometry

Measurements were performed with a single-beam laser interferometer SIOS NA analyzer coupled with an Ametek 7230 DSP Lock-in Amplifier. The resolution was 0.1-0.2 nm depending on the environmental noise. We applied an AC voltage at several frequencies *f* and set the lock-in amplifier to detect oscillation at *2*f* as electrostrictors oscillate as twice of the AC frequency. As bulk samples need high voltage, we coupled a signal generator AIM-TTI TGP 3100 to a voltage amplifier Trek 2220 with maximum output of 2 kV. The contacts are made with tungsten tips. **Figure S1** depict a diagram of the experimental setup.

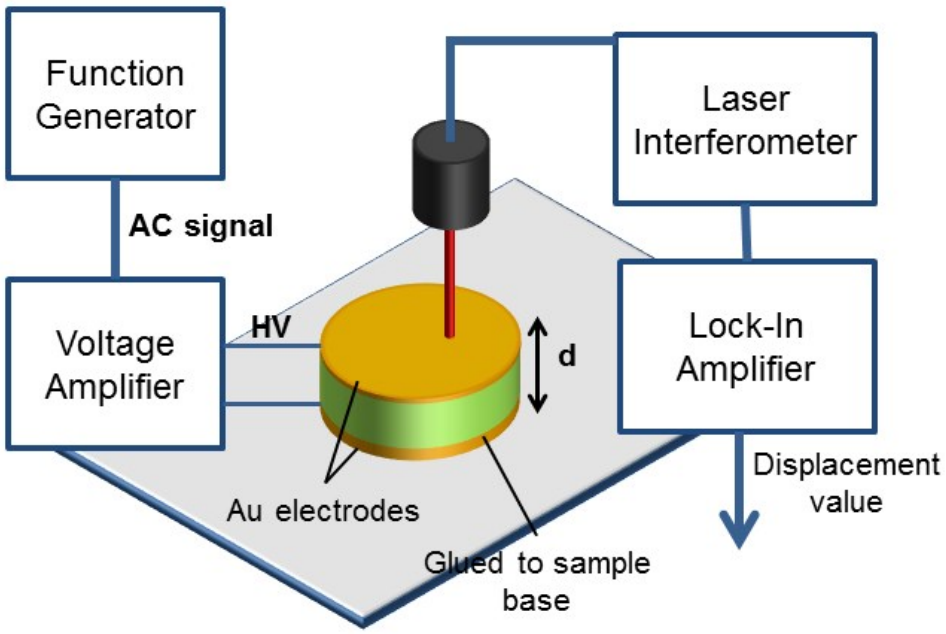

Figure S1: Diagram of the setup used to measure electrostrictive performances of CGO single crystal (green disc).

Structural characterization

Figure S2 depicts representative graphic results of the Rietveld refinement on the X-ray powder diffraction, carried out with the program FullProf. X-ray powder diffraction were carried out using a PANalytical X'Pert MDP Pro diffractometer with Cu-Kα radiation and a θ/θ-arrangement in Bragg-

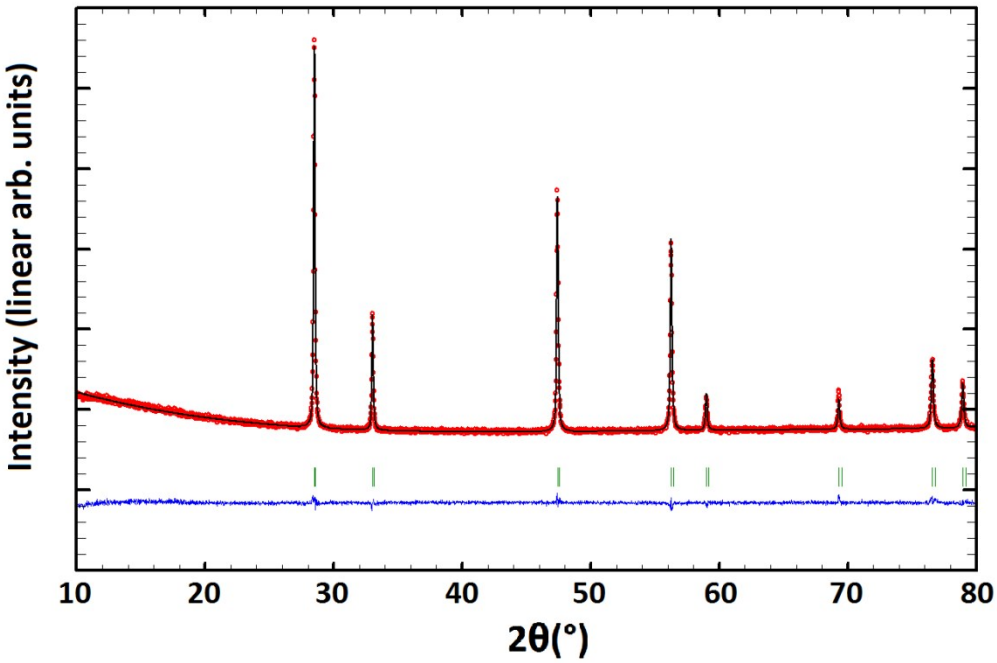

Figure S2: X-ray powder diffraction pattern of the CGO single crystal with results of the Rietveld refinement. Red: experimental pattern. Black: calculated pattern. Green: theoretical Bragg's peak positions. Blue: patterns difference.

Brentano geometry. The diffraction pattern shows phase purity and the Rietveld refinement confirms the crystal structure of the GCO single crystal in fluorite-type structure (space group $Fm\bar{3}m$).

Table S1: Residual values of the Rietveld refinement, including the lattice parameter of the sample.

R_p	R_{wp}	R_{exp}	R_{Bragg}	S	a (Å)
0.0342	0.0436	0.0383	0.0360	1.14	5.4179(4)

The electrochemical impedance spectroscopy (EIS) was performed at 250- 600 °C in air using Solarton 1260, in a frequency range of 0.01 Hz to 1 MHz with a 100 mV alternate signal. The sample

has a bar-like geometry. Gold-silver mixed electrodes pastes were coated on top of the sample and dried at 600 °C for 15 min. Symmetric configuration with platinum wires as current leads were used.

The Electrochemical impedance spectroscopy (EIS) was performed at 250-650 °C in air using Solarton 1260 (UK). **Figure S3** shows the Arrenhius plot of CGO single crystal compared to a polycrystalline Gd doped ceria bulk sample (CGO-10h from *Kabir et al., Acta Mater.*, 2019, **174**, 53–60). The activation energy of the single crystal is measured to be 0.55 eV. This low activation energy can be ascribed to the lack of grain boundaries in the sample.

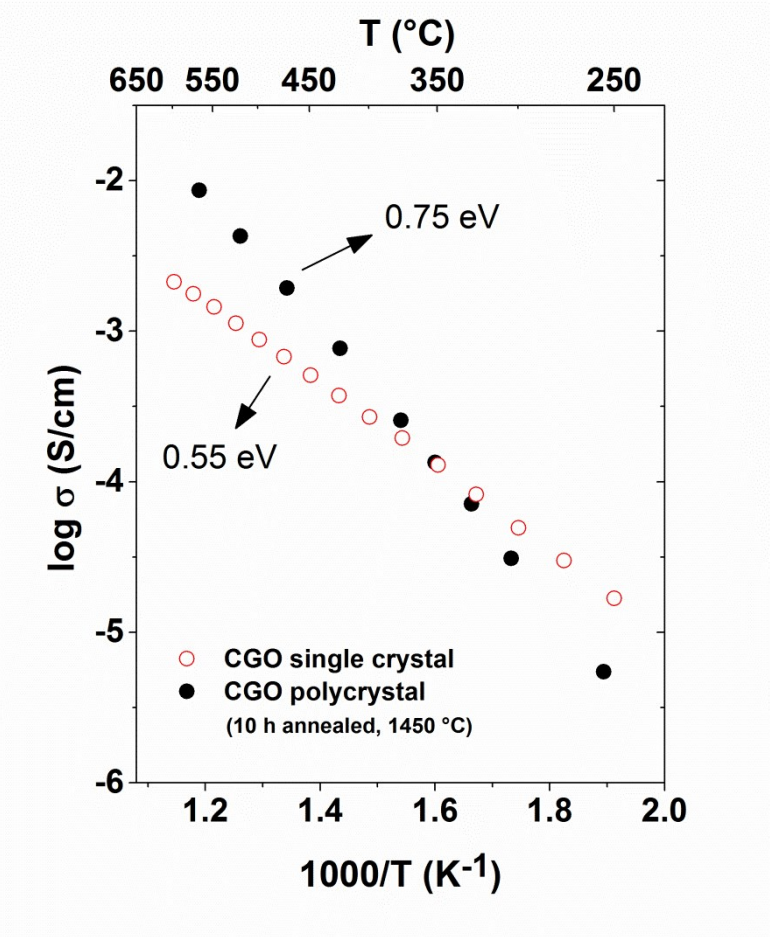

Figure S3: Arrhenius plot of CGO single crystal compared to policrystaline CGO bulk. The activation energy is reported.

XANES analysis

Table S2: Calculated area of the features calculated by Gaussian fit and plotted in Figure 4. Also, the OFF- OFF difference.

T (°C)	State	Pre-peak area	Δ(On-Off)	Peak *A* Area	Δ(On-Off)	Peak *B* area	Δ(On-Off)

23	ON	0.660(33)	**-0.02(6)**	2.715(33)	**0.242(63)**	3.754(66)	**0.115(100)**
	OFF	0.680(33)		2.473(33)		3.639(34)	
-50	ON	0.590(29)	**-0.02(6)**	2.941(29)	**0.085(59)**	3.918(59)	**0.048(89)**
	OFF	0.607(30)		2.856(30)		3.870(30)	
-125	ON	0.655(32)	**0.00(6)**	2.694(32)	**0.00(6)**	3.740(65)	**0.00(10)**
	OFF	0.653(32)		2.698(32)		3.748(32)	
-194	ON	0.659(33)	**-0.12(7)**	2.695(33)	**0.592(68)**	3.726(65)	**0.196(103)**
	OFF	0.778(35)		2.103(35)		3.530(38)	

EXAFS analysis

Spectra were processed with a standard fitting procedure using IFEFFIT and Artemis softwares. The experimental spectra *χ(k)* were fitted to the model according to the standard EXAFS plane wave expansion:

$$\chi_{theory} = \frac{NS_0^2}{kR^2} e^{-2k^2\sigma^2} e^{-2R/\lambda} f(k)\sin\left(2kR - \frac{4}{3}C_3k^3 + \delta(k)\right) \quad (1)$$

with *N* and *R* are the coordination number and bond length for the Ce nearest neighbors. S_0^2 is the passive electro-reduction factor, that is proportional to the wave amplitude. *k* is the photoelectron mean free path and σ^2 is the Debye-Waller factor, which represents the disorder in Ce-O bond length. *f(k)* is the backscattering amplitude, $\delta(k)$ is a phase shift and C_3 is the anharmonic correction to the pair potential. For the fit, S_0^2 was obtained from previous fit s and kept constant in all the spectra analysis. *N*, *R* and σ^2 were fitted for each spectrum. The Δe correction factor for the absorption energy was kept fixed (1.15 ± 0.66 eV), except for the differential spectra (On-Off) at -125 °C (0.06 ± 2.50 eV). The fits were performed in the *k* range from 2.5 to 7 Å^{-1}. **Figure S4** reports the fit for EXAFS differential *k(χ)* and *FT(χ)(r)* at -50, -125 and -194 °C.

Table S3: χ(k)on and χ(k)off EXAFS fit parameters of CGO single crystal for different temperatures; the Ce-O bond length (R_{Ce-O}) and the bond disorder factor σ^2. The coordination number is the same for all datasets: N= 7.99 ± 0.23.

T (°C)	State	R_{Ce-O} (Å)	σ^2 (Å2)
23	ON	2.300(3)	0.009(1)

	OFF	2.299(3)	0.009(1)
-50	ON	2.300(3)	0.0061(5)
	OFF	2.300(3)	0.0065(5)
-125	ON	2.302(3)	0.0067(5)
	OFF	2.301(3)	0.0068(10)
-194	ON	2.301(3)	0.0067(5)
	OFF	2.304(3)	0.0098(5)

Table S4: Differential Δχ EXAFS spectrum fit parameters of CGO single crystal at different temperatures. ΔN and ΔR are the coordination number and bond length for the nearest neighbours (Ce-O bond). Σ2 is the mean squared disorder factor.

T (°C)	**ΔN**	**ΔR (Å)**	**σ2 (Å2)**
23	-0.19 ± 0.11	2.246 ± 0.024	0.000 ± 0.030
-50	-0.16 ± 0.21	2.250 ± 0.030	0.001 ± 0.024
-125	-0.33 ± 0.89	2.04 ± 0.17	0.026 ± 0.072
-194	-0.99 ± 0.18	2.219 ± 0.003	0.000 ± 0.031

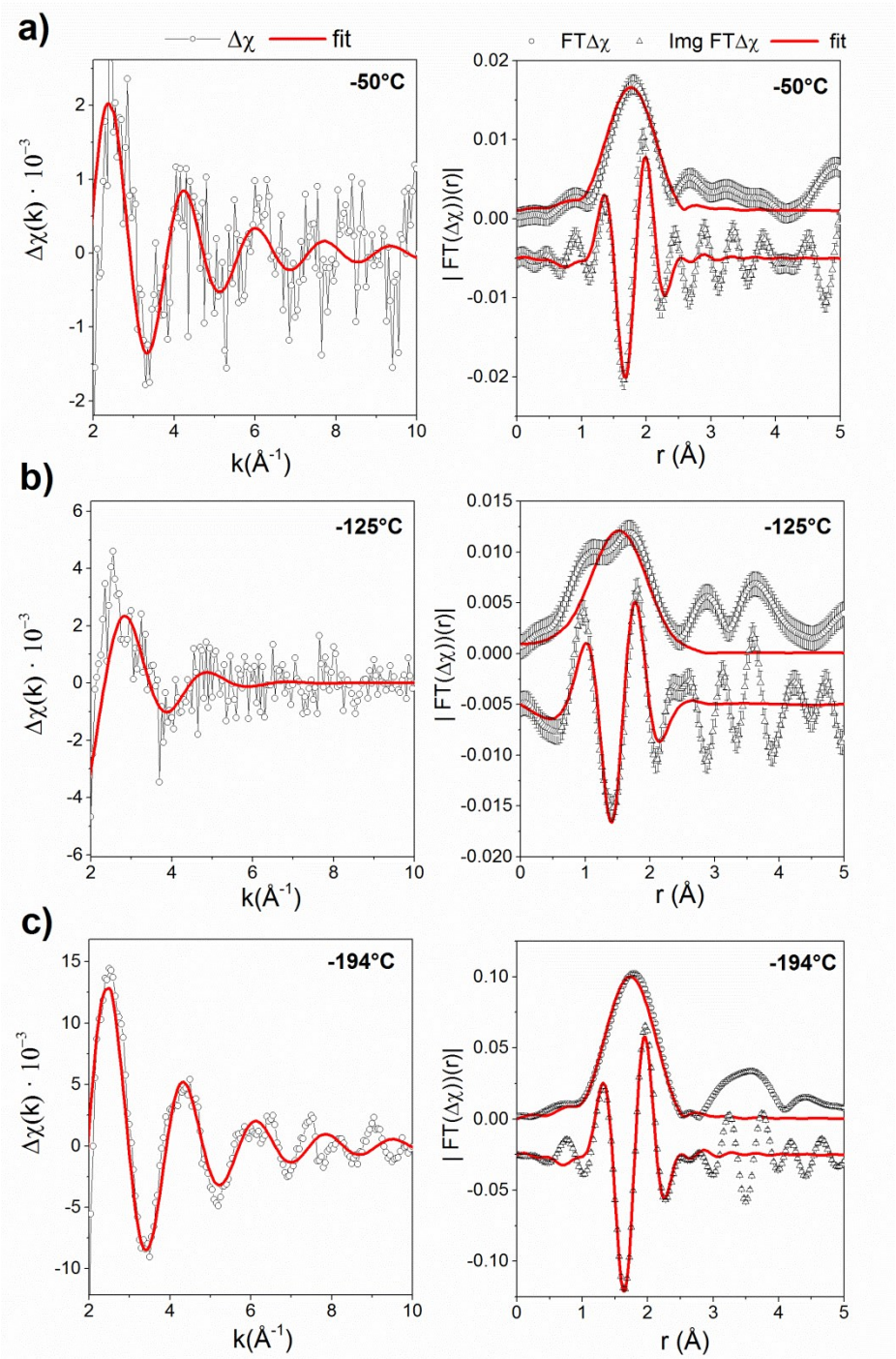

Figure S4: EXAFS fit of *k(χ)* (left) and *FT(χ)(r) (right)* at a) -50 °C; b) -125 °C; and c) -194 °C. All data are reported with error bars.