

Colossal dielectric response of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles

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We observed a colossal dielectric response of small (5–10 nm) oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles ($x = 1-0.4$), prepared by solid-state organonitrate synthesis. The effective dielectric permittivity of the pressed $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders has a pronounced maximum at 38–88 °C, the shape of which can be fitted by the Curie-Weiss type dependence modified for the diffuse ferroelectric-paraelectric phase transition. The maximal value of the dielectric permittivity increases from 1.5×10^3 (for $x = 1$) to 1.5×10^5 (for $x = 0.4$) at low frequencies (~ 4 Hz), being much smaller, namely, changing from 7 (for $x = 1$) to 20 (for $x = 0.4$) at high frequencies (~ 500 kHz). The frequency dispersion of the dielectric permittivity maximum position is almost absent; meanwhile, the shape and width of the maximum changes in a complex way with increase in frequency. The temperature dependencies of the dielectric permittivity and resistivity are almost mirrorlike turned over with respect to each other, which means that all their features, such as position and shape of maxima, plateau, minima, and inflexions, almost coincide after the mirror reflection with respect to the temperature axis. These correlations of resistivity and dielectric permittivity are well described in the Heywang barrier model applied together with the variable range hopping conduction model in semiconducting ferroelectrics. Ferroelectriclike behavior of the small oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles is expected from the Landau-Ginzburg-Devonshire approach and density functional theory calculations. Obtained results may be useful for developing silicon-compatible functional nanomaterials based on $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles.

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I. INTRODUCTION

Nowadays thin films [1], multilayers [2], and superlattices [3] of hafnia (HfO_2) and zirconia (ZrO_2) and their solid solutions $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($0 < x < 1$) have become indispensable Si-compatible ferroelectric materials [4] used in advanced electronic memories [5] and logic devices, including steep-slope or/and negative capacitance field-effect transistors with hafnia-zirconia gate oxides [6,7]. Cheema *et al.* [8] demonstrated the pronounced ferroelectric properties of ultrathin $\text{Hf}_{0.8}\text{Zr}_{0.2}\text{O}_2$ films synthesized by atomic layer deposition on Si substrate buffered with a SiO_2 layer. Also,

the thickness-induced antiferroelectric-to-ferroelectric phase transition in thin ZrO_2 films on Si substrate was revealed experimentally, and the ferroelectricity in ultrathin (5 Å thick) ZrO_2 film was observed [9]. Later, Cheema *et al.* [10,11] experimentally studied polar properties and charge storage in ferroelectric-antiferroelectric $\text{HfO}_2/\text{ZrO}_2$ multilayers and superlattices deposited on Si substrate and demonstrated the capacitance enhancement via the negative capacitance effect.

However, the underlying physical mechanisms of the ferroelectric, ferroelectric, and/or antiferroelectric property emergence in the nanoscale $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ are still under debate [12–14] and most probably have an extrinsic nature [15] related to size effects. The anomalous size dependence of ferroelectricity in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$, which contradicts the conventional ferroelectric behavior, is conditioned by their fluorite-type structure that enables the surface energy driven phase transition at the nanoscale, unlike, e.g., perovskite ferroelectrics, where the depolarization effects suppress or reduce ferroelectricity with a decrease in their size [1–5].

Due to the size effects, the vast majority of ferroelectric crystalline materials exhibit ferroelectric properties in the bulk and become nonpolar (paraelectric or dielectric) when their

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actual size decreases below the critical size: The so-called size-induced transition to the nonpolar phase happens [16]. Hafnia-zirconia is a very rare exception because bulk HfO_2 and ZrO_2 single crystals are dielectrics from low to high temperatures (up to 1200 K) and pressures (up to 15 GPa) [17,18]. Bistable spontaneous polarization (or antiferroelectric long-range order), domain structure, and ferroelectric (or antiferroelectric) hysteresis can appear in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($0 \leq x \leq 1$) thin films only with a decrease in their thickness to the nanoscale [19,20]. At that, the ferroelectric state stabilizes in a rather narrow thickness range, from 5 to 30 nm [21]. The origin of the thickness-induced ferroelectricity is related to the film transition from the nonpolar monoclinic m phase (space group $P2_1/c$) to the polar orthorhombic o phase (space group $Pca2_1$). The ferroelectric o phase is metastable in comparison with the bulk m phase.

The ferroelectric-antiferroelectric properties of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films are very sensitive to the content x of Hf atoms [22], interface effects [23], synthesis methods, and doping [24,25]. Recent experimental studies [12,13,26,27] and theoretical calculations [28,29] revealed a significant role of the oxygen vacancies [30], surface effects, and grain size [31] in the stabilization of the ferroelectric o phase in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films. Density functional theory (DFT) calculations [32,33] confirmed that the m phase is the ground state in bulk $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$; however, the energy difference between the ferroelectric o phase and nonpolar m phase can be rather small (e.g., ~ 20 meV/f.u. [33]). The latest DFT calculations have revealed that indirect switching paths of the spontaneous polarization are energetically preferable in HfO_2 due to competing m and o phases [34,35]. Phenomenological Landau-Ginzburg-Devonshire (LGD) theory predicted [36] that polydomain or single-domain ferroionic states can be stable in spherical $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles of sizes 5–30 nm covered with surface ions and/or oxygen vacancies, when their concentration exceeds 10^{17} – 10^{19} cm $^{-2}$.

To the best of our knowledge, any direct experimental observation of the ferroelectric (or ferroelectriclike) properties of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles are still absent. A few observations of the o -phase mixture ($Pca2_1$, $Pbca$, and $Pbcm$) in the small size (3–30 nm) $\text{Hf}_x\text{Zr}_{1-x}\text{O}_{2-y}$ nanoparticles were obtained by x-ray diffraction (XRD) analysis [37–39]. However, these experimental observations are not convincing because only the o phase $Pca2_1$ is ferroelectric; the o phases $Pbca$ and $Pbcm$ are neither polar nor ferroelectriclike. Little more convincing (but indirect) evidence is the charge accumulation effect observed in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanopowders, sintered by the autocombustion sol-gel method, which were related to the appearance of the ferroelectriclike polar regions in the nanoparticles.

In this work, we study a dielectric response of small (5–10 nm) oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles ($x = 1, 0.6, 0.5$, and 0.4) prepared by the solid-state organonitrate synthesis, where the domination of the o phase was proved by XRD. We reveal that the effective dielectric permittivity of the pressed $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders has a pronounced maximum at 38–88 °C, the shape of which can be fitted by the Curie-Weiss-type law modified for the diffuse ferroelectric-paraelectric phase transition. The temperature dependencies of the dielectric permittivity and resistivity are almost

mirrorlike turned over with respect to each other, in the case of resistivity being in quite good agreement with the Heywang [40] barrier model applied together with the variable range hopping (VRH) conduction model in semiconducting ferroelectrics. The observed behavior of the dielectric permittivity can be explained by the LGD approach and DFT calculations, which reveal that small $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles can become ferroelectric in the presence of oxygen vacancies.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Preparation of the oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles and their characterization

Using solid-state organonitrate synthesis, we prepared several sample groups of oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 1, 0.4, 0.5$, and 0.6) nanopowders. The preparation details of the samples are listed in Table I. For this purpose, the mixtures of zirconium and hafnium nitrate salts, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Hf}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, were dissolved in distilled water to a concentration of 5%–10% or less. The dextrin, glycine, polyvinyl alcohol, cellulose, etc., were used as organic additives. Based on the combination of properties and synthesis parameters, the fibrous cellulose was selected in the form of ashless filters of various densities and cotton cosmetic discs, which were impregnated with solutions of zirconium and hafnium nitrates and dried at 90 °C to remove water. The compositions obtained in this way were subjected to heat treatment in a $\text{CO} + \text{CO}_2$ atmosphere at 500–600 °C for several hours. The black color of the pyrolysis products is due to the presence of the (20–50) wt. % ultrafine carbon, which was removed by the short-term oxidation at 600 °C for 5 min.

The XRD analysis was performed using the XRD-6000 diffractometer with $\text{Cu-K}\alpha 1$ emission ($2\theta = 15^\circ$ – 70°); and the database of the International Committee for Powder Diffraction Standards (JCPDS PDF-2) was used for identification of the crystallographic phases of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles. In the result, we confirmed the coexistence of the m phase (space group $P2_1/c$, the content varies from 13 to 5 wt. %) and inseparable o phases (space groups $Pbca$, $Pbcm$, and ferroelectric $Pca2_1$, the content varies from 87 to 96 wt. %) inside the nanoparticles (see Table I). Note that the o -phase content is maximal for the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample annealed at 600 °C for 2 h in $\text{CO} + \text{CO}_2$ and minimal for the HfO_2 sample annealed at 500 °C for 6 h in $\text{CO} + \text{CO}_2$. The size of the coherent scattering regions (CSRs) varies from 80 to 100 Å for the o phases and from 120 to 170 Å for the m phase. Corresponding diffractograms are presented in Fig. S1 in the Supplemental Material [41].

The higher content of the monoclinic phase in the $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowders compared with the $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$ nanopowders can be related with the different stability of the m and o phases in the presence of oxygen vacancies, the concentration of which can depend on the Hf content x . As a matter of fact, the concentration of oxygen vacancies, which can stabilize the polar o phase [13,27–29], indeed depends on the content x in the studied samples [42]. This assumption is confirmed by the x dependence of the defect-related luminescence in Raman spectra and in the x dependence of the saturation magnetization, induced by paramagnetic

TABLE I. Characteristics of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders.

Sample name and chemical composition	Characteristics of the samples from XRD				
	Lattice parameters ($\text{\AA}$) ^a		Phase (wt. %), ^b CSR size ($\text{\AA}$)		Preparation details
	<i>o</i> phases	<i>m</i> phase	<i>o</i> phases	<i>m</i> phase	
HZO1	$a = 10.118$ $b = 5.202$	$a = 5.125$ $b = 5.158$	87%	13%	Decomposition of nitrates at 500 °C, 6 h in CO + CO ₂
HfO ₂	$c = 5.122$	$c = 5.305$	80 $\text{\AA}$	120 $\text{\AA}$	
HZO2	$a = 10.108$ $b = 5.128$	$a = 5.148$ $b = 5.167$	95%	5%	Decomposition of nitrates at 600 °C, 2 h in CO + CO ₂
Hf _{0.6} Zr _{0.4} O ₂	$c = 5.160$	$c = 5.331$	85 $\text{\AA}$	150 $\text{\AA}$	
HZO3	$a = 10.062$ $b = 5.128$	$a = 5.146$ $b = 5.163$	96%	4%	Decomposition of nitrates at 600 °C, 2 h in CO + CO ₂
Hf _{0.5} Zr _{0.5} O ₂	$c = 5.160$	$c = 5.328$	100 $\text{\AA}$	140 $\text{\AA}$	
HZO4	$a = 10.109$ $b = 5.128$	$a = 5.130$ $b = 5.208$	89%	11%	Decomposition of nitrates at 600 °C, 2 h in CO + CO ₂
Hf _{0.4} Zr _{0.6} O ₂	$c = 5.160$	$c = 5.307$	90 $\text{\AA}$	170 $\text{\AA}$	

^aThe monoclinic angle $\beta = 99.2^\circ$ for the *m* phase. This angle was fixed for all samples during the refinement process.

^bAs shown in earlier studies of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanoparticles performed by Fujimoto *et al.* [37], the decomposition of the XRD spectra can be done using the *m* + *o* and *m* + *t* bases, where *t* means the tetragonal phase. It is impossible to distinguish the *t* and *o* phases in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders because corresponding XRD peaks are diffused in small nanoparticles. In agreement with Ref. [37], the decomposition of the XRD spectra using the full *m* + *t* + *o* basis performed in Ref. [39] appeared doubtful due to the proximity of the *o*- and *t*-phase spectral lines. In this work, we start fitting the XRD spectrum using the *m* + *o* basis and reach good convergency with different lattice constants *a*, *b*, and *c*, listed in Table I. The condition $a = b$ should be valid in the *t* phase. When one starts from the *m* + *t* + *o* basis in the considered case of oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders, the axes *a* and *b* do not become equal at the end of the fitting time. We have tested this result for all samples, which confirmed that we have the *o* + *m* case, probably due to the large amount of oxygen vacancies stabilizing the *o* phases.

oxygen vacancies [42]. The increase of the *m*-phase fraction in the $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowders correlates with the decrease in the vacancy concentration in the particles [42]. Namely, the defect-related luminescence and the magnetization is smaller in the $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowder than that of $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$ nanopowder (see Fig. 2(a), Table I, and Fig. 3(a) in Ref. [42]).

A clear distinction between the polar *Pca*2₁ and the centrosymmetric *Pbca*/*Pbcm* phases is very important, but it has fundamental limitations due to the nature of diffraction methods. Both the powder XRD and electron diffraction do not allow us to unambiguously distinguish the *Pca*2₁ phase from the *Pbca*/*Pbcm* phases. It should be noted that the presence of ferroelectricity in thin $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films can be studied in detail using modern STEM methods, such as iDPC-STEM, ddPC, and 4D-STEM (see e.g., Refs. [43–45]). These methods allow determining the exact positions of light atoms (particularly oxygen atoms), which makes it possible to analyze polarization processes and phase transitions. However, such studies for nanopowder samples are very complex and require a separate experimental design and modeling, which is beyond the scope of this work.

The average size (~5–10 nm) of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles was determined by high-resolution transmission electron microscopy (TEM) [see images in Figs. 1(a)–1(d) as typical examples]. Typical differential thermal analysis (DTA) of pyrolysis products is shown in Fig. 1(e).

For comparison with $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders, BaTiO_3 nanoparticles with the average size 24 nm and with the content of the ferroelectric phase 98 wt. % were prepared by the nonisothermal solid-state synthesis. Their preparation details are listed in Appendix S1 in the Supplemental Material [41], and their XRD characterization is given in Ref. [46].

III. RESULTS OF ELECTRICAL MEASUREMENTS AND THEIR ANALYSIS

A. Dielectric response and conductivity of the pressed $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders

To study the transport of electric charge carriers in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders, the tableted powder samples were placed in a Teflon cylinder between two brass plungers, which serve to create uniaxial pressure and are used as electrical contacts. The distance between the plungers was determined by the thickness of the sample. The diameter of the samples is 4 mm, their thickness and the distance between the contacts are $(300 \pm 20) \mu\text{m}$. Measurements of the capacitance and resistance of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders pressed at 5 MPa were carried out by the RLC-meter LCX200 ROHDE & SCHWARZ in the frequency range 4 Hz–500 kHz.

The porosity of the studied samples was estimated as (20–30)% in dependence on the applied pressure. We tried to account for the porosity under theoretical interpretation of the obtained results by using the effective media model. Within the model, the pressed nanopowder is considered a binary mixture of quasispherical core-shell $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles (with volume fraction μ) and air (with volume fraction 1μ). The simplest way to account for the porosity is to regard μ as a fitting parameter that varies in a reasonable range for the fitting of the effective dielectric response, which is measured below and analyzed theoretically in Sec. IV.A.

The temperature dependences of the effective relative dielectric permittivity and resistivity at different frequencies for the pressed $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders are shown Fig. 2. In the frequency range from 4 Hz to 1 kHz, the effective permittivity has a pronounced maximum at 38 °C for the HfO_2 sample, a

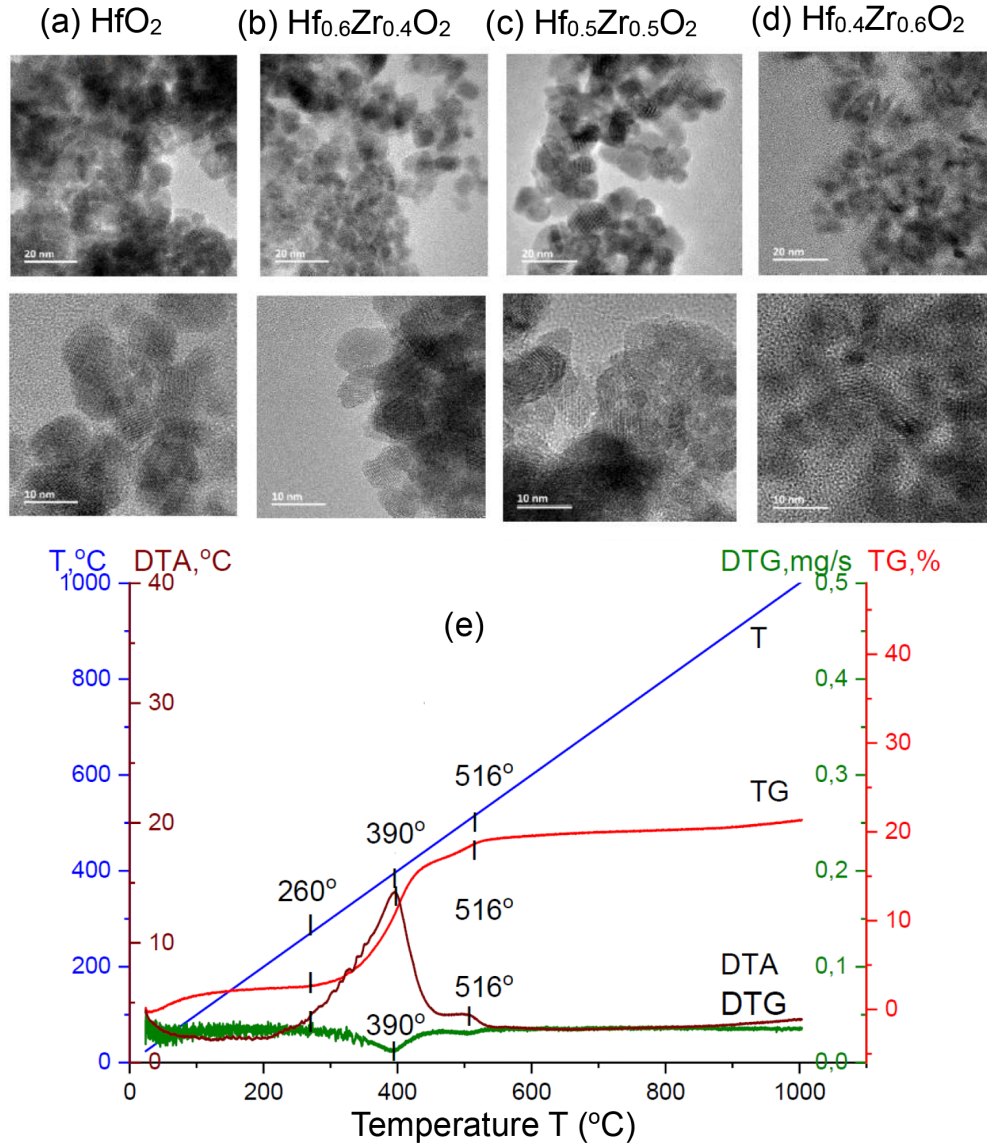


FIG. 1. (a)–(d) Typical high-resolution TEM images of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders. (e) DTA of pyrolysis products of a mixture of zirconium and hafnium nitrates (60:40) with fibrous cellulose at 600 °C, 6 h, in a $\text{CO} + \text{CO}_2$ environment. Heating was performed in the air with a rate of 10 °C/min.

pronounced maximum at 38 °C followed by the quasiplateau up to 88 °C for the $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$ sample, a relatively sharp Λ -shaped maximum at 50 °C for the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample, and a high maximum at 88 °C with a left-side shoulder at 38 °C for the $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ sample. The maximum height decreases strongly and monotonically with an increase in frequency from 4 Hz to 500 kHz. At low frequencies (~ 4 Hz) the maximum height is $\sim 1.5 \times 10^3$ for HfO_2 nanopowder, 2×10^3 for $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$ nanopowder, 1.1×10^4 for $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanopowder, and 1.3×10^5 for $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowder. The increase in the maximum height correlates with a decrease in Hf content from 1 to 0.4. At high frequencies (~ 500 kHz), the maxima height is much smaller; it changes from 7 (for HfO_2 nanopowder) to 20 (for $\text{Hf}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowder). The frequency dispersion of the dielectric permittivity maximum position is almost absent; meanwhile, the shape and width of the maximum change in a complex way with the frequency change. The position of the dielectric permittivity maxi-

um coincides with the pronounced minimum of the electric resistivity for all studied samples.

The temperature and frequency behavior of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowder permittivity and resistivity are qualitatively similar to the behavior of these dependences in the pressed BaTiO_3 nanopowder, shown in Fig. 3. It is seen that the permittivity of BaTiO_3 nanopowders has a pronounced maximum at 73 °C, which corresponds to the ferroelectric-paraelectric phase transition and to related changes from the tetragonal to the cubic symmetry. The transition is shifted to lower temperatures in comparison with a bulk BaTiO_3 (~ 125 °C) due to the size effects in stress-free small nanoparticles [47], while anisotropic strains in the core can lead to the opposite trend [48]. The maximum height decreases strongly and monotonically with an increase in frequency from 4×10^5 (at 4 Hz) to 30 (at 500 kHz). The frequency dispersion of the maximum position is almost absent, but its shape changes with frequency. The position

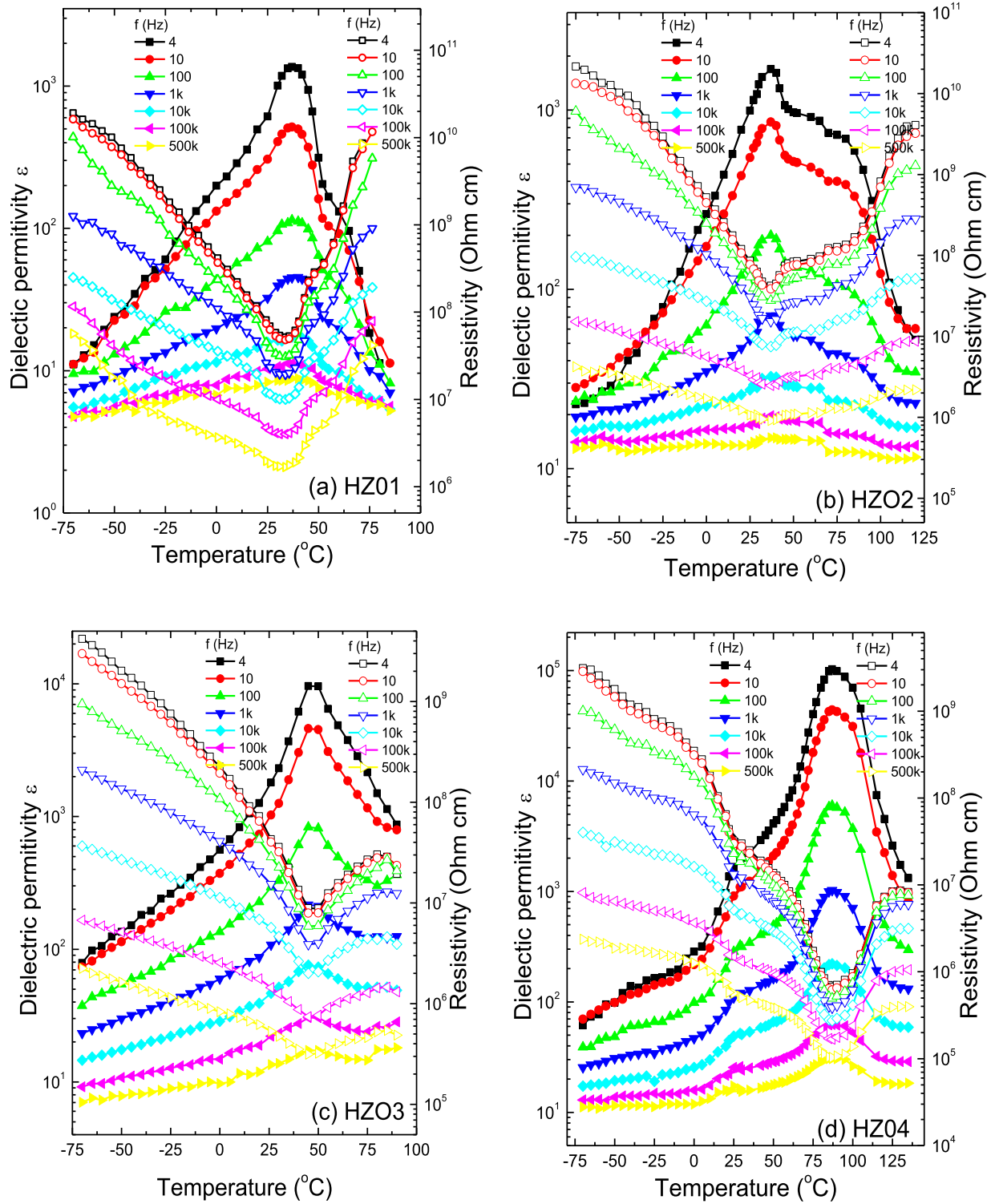


FIG. 2. Temperature dependences of the relative dielectric permittivity (filled symbols) and resistivity (empty symbols) of the pressed (a) HfO₂, (b) Hf_{0.6}Zr_{0.4}O₂, (c) Hf_{0.5}Zr_{0.5}O₂, and (d) Hf_{0.4}Zr_{0.6}O₂ nanopowders at different frequencies from 4 Hz to 500 kHz. The amplitude of the test sinusoidal voltage is 100 mV.

of the dielectric permittivity maximum coincides with the pronounced minimum of the electric resistivity.

Note that nonpolar bulk dielectrics HfO₂ and ZrO₂ have relative dielectric permittivity ~ 25 [49]. The dielectric permittivity of thin Hf_{0.5}Zr_{0.5}O₂ films [50] lies in the range 30–50; it may reach 80 for thin HfO₂ films with La, Bi, or

Nb substitutions [51], being almost temperature independent. At the same time, it is known that, for typical perovskite ferroelectrics like BaTiO₃ and PbTiO₃, the relative dielectric permittivity depends strongly on temperature (reaching a sharp maximum $\sim 10^3$ – 10^4 at Curie temperature). It also depends on the structure and morphology of the ferroelectric

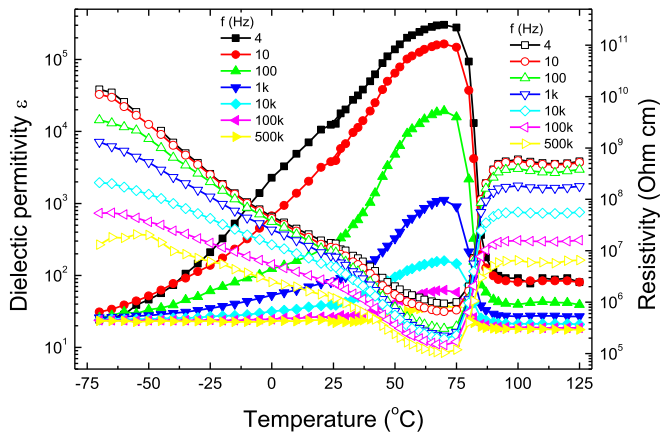


FIG. 3. Temperature dependences of the relative dielectric permittivity (filled symbols) and resistivity (empty symbols) of the pressed BaTiO₃ nanopowder at different frequencies from 4 Hz to 500 kHz.

being different for single crystals, nanopowders, and fine-grained ceramics. The experimentally measured dielectric permittivity of PbTiO₃ powders [52–54] varies from 100 to 1200 at room temperature (being size dependent). The dielectric permittivity of the fine-grained BaTiO₃ ceramics [55,56] and BaTiO₃ nanoparticles [57] varies in the range 1000–7000 at room temperature.

The comparison of permittivity and resistivity behavior in Hf_xZr_{1-x}O₂ and BaTiO₃ nanopowders allows us to suspect a ferroelectriclike phase transition in the Hf_xZr_{1-x}O₂ nanopowders, which occur in the temperature range from 38 °C (for HfO₂ nanopowder) to 88 °C (for Hf_{0.4}Zr_{0.6}O₂ nanopowder). Notably, the temperature of the possible transition increases monotonically with increase in Zr content; meanwhile, the shape and width of the dielectric permittivity maximum change in a more complex way.

However, a colossal dielectric permittivity of ferroelectric nanocomposites and nanograined ceramics is often related to the dipolar relaxation enhanced by interfacial polarization dynamics, leading to the interfacial barrier-layer capacitance (IBLC) effect [58], as well as by the inhomogeneous layers between the electrodes and the sample, known as the surface barrier layer capacitance (SBLC) effect [59]. The origin of colossal dielectric permittivity observed in BaTiO₃ nanopowders may be related to the synergy of IBLC and SBLC effects [58–60], interfacial polarization at the interior of insulating grain boundaries, and/or polaron hopping in semiconducting cores with a large number of induced charge carriers (see, e.g., Refs. [61,62]).

As a rule, the colossal dielectric permittivity related with the IBLC and/or SBLC effects is accompanied by an increase in conduction losses, being a typical manifestation of the Maxwell-Wagner (MW) effect [63]. The colossal values of their dielectric permittivity are accompanied by an increase in the conduction losses. A strong frequency dispersion of the features of dielectric permittivity and losses, namely, the strong frequency shift of the maxima, minima, and/or plateau positions, is inherent to the IBLC, SBLC, and polaronic effects. Since the frequency dispersion of the dielectric

permittivity maximum and resistivity minimum is absent in the studied Hf_xZr_{1-x}O₂ nanopowders, and the temperature of the permittivity maximum coincides with the temperature of the resistivity minimum entire the frequency range (see Fig. 2), it allows us to assume a signification contribution of the expected ferroelectriclike phase transition to the dielectric response.

However, we realize that this argumentation is not fully conclusive. Impedance spectroscopy analysis could help decouple contributions of ferroelectric grains from their IBLC and/or SBLC effects originated from grain boundaries and electrodes. Typical Nyquist plots are analyzed in the Supplemental Material [41] (see Appendix S3 therein). Indeed, we observed the deviations of Nyquist plots from the ideal semicircle, characteristic for the simple RC-circuit connected in parallel. In our case, the semicircle is squashy-shaped and asymmetric. Its pronounced right shoulder can be related to a chaotic network of connected capacitors and resistors. Therefore, the sample volume may be simulated by a chaotic network of capacitors and resistors, the conduction of which obeys, in principle, the percolation theory. Such deviations can be described in the framework of effective medium approximation (EMA), which are considered in detail in Sec. IV A.

Not less important is that we do not observe the frequency dispersion of the relative dielectric permittivity maximum in the Hf_xZr_{1-x}O₂ nanopowders, which is inherent to relaxor ferroelectrics [64,65] and dipolar glasses [66,67]. However, the maxima shape is diffuse or plateaulike, especially for Hf_{0.6}Zr_{0.4}O₂ nanopowders, which may indicate relaxorlike behavior [68]. Following Rivera *et al.* [69], we can suppose a diffuse ferroelectriclike phase transition in Hf_xZr_{1-x}O₂ nanopowders, the classification of which is much wider in comparison with relaxor ferroelectrics.

However, without direct proofs, such as piezoelectric force microscopy (PFM) response or polarization-field (*P-E*) hysteresis loops, the claims about ferroelectricity of oxygen-deficient Hf_xZr_{1-x}O₂ nanoparticles remain speculative.

To the best of our knowledge, the local piezoresponce loops, observed by PFM, are informative for individual nanoflakes with the lateral size much larger than the tip size (5–50 nm). The studied Hf_xZr_{1-x}O₂ nanoparticles, which can be ferroelectriclike according to our claims, have quasispherical shape with the actual size of 5–15 nm. Larger Hf_xZr_{1-x}O₂ particles become nonferroelectric according to theory [36,38] and experiment for films [1]. Therefore, PFM of individual quasispherical Hf_xZr_{1-x}O₂ nanoparticles with sizes 5–15 nm is a very difficult task, which unlikely will give us informative results.

The *P-E* hysteresis loops are not informative to verify the ferroelectricity in pressed nanopowders, if the relative dielectric permittivity of nanoparticles is 10 or larger, as in the considered case. In this case, the electric field is concentrated in the air gaps between the particles and does not penetrate inside them. As a result, one requires application of giant voltages (higher than the air breakdown voltage) to the capacitor with the nanopowder to reverse the polarization of the individual particles.

Pyroelectric-type measurements of the state of the particles can give us direct qualitative evidence of ferroelectricity in

the studied $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders. Imagine a nanopowder with individual ferroelectric nanoparticles. Due to their small size (5–15 nm), the nanoparticles are single domain at temperatures below the Curie temperature T_C . Assuming that the distribution of particle sizes is narrow, and thus, the scattering of their Curie temperature is small, the surface of polarized nanoparticles accumulates screening charges from the ambient medium below T_C . These charges screen the bound charge of the individual particles, whose spontaneous polarization can have different orientation. The charge accumulation can be fast or slow, but the screening charge should disappear above T_C due to the bound charge disappearance. Thus, the maximal values of charge-discharge currents of polarized nanoparticles and the local discharges between the nanoparticles can be expected near $T = T_C$, and the sharp decrease of the charge accumulation ability of the system should happen above T_C [70,71]. To verify the hypothesis, we measured time dependences of the charging current at fixed DC voltage across the sample (2 V) at different temperatures from 20 to 100 °C (see Appendix S3 in the Supplemental Material [41]). The total charge ΔQ accumulated in the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample as a function of temperature is shown in Fig. S1(h) in the Supplemental Material [41]. It appears that the electric charge accumulated by the pressed nanopowders decreases strongly $>70^\circ\text{C}$. We related the observed decrease to the disappearance of the pyroelectric-type charge in the system $>70^\circ\text{C}$. For the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample, the accumulated charge is maximal in the temperature range 55–65 °C, and the current is maximal $\sim 50^\circ\text{C}$. Importantly, the total discharge time (after the voltage removal) is >10 –20 min, which may indicate the pronounced electretlike properties of the samples.

A quantitative description of the electric conduction mechanisms and dielectric response in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders is given below.

B. Electric conduction mechanisms in the alternate current regime

The frequency dependence of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ sample resistivity at temperatures below the phase transition (shown in Fig. 4 for $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$) demonstrates that the samples manifest a gradual transition to dominating hopping conduction with a decrease in the temperature. It is seen that the frequency dependence at the lowest temperature is well fitted by the power law $\sigma \sim \omega^S$, where $S < 1$, in the whole frequency range, which is characteristic for the hopping conduction at moderate frequencies [72,73].

At the same time, the frequency dependence of resistivity tends to lower its slope and becomes flatter at higher temperatures and lower frequencies. It evidences the gradual change of the hopping conduction to another mechanism caused by the change of crystallographic structure.

Shown in Fig. 5(a) are temperature dependences of resistivity of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample at several higher frequencies in the Arrhenius coordinates. It is seen that, <290 K, the dependences go out onto the activation-type behavior with the activation energy of ~ 67 meV. Frequently, the low-temperature conduction in the alternate current regime in the disordered materials, such as amorphous and doped semiconductors, granule materials, etc., is explained based on the

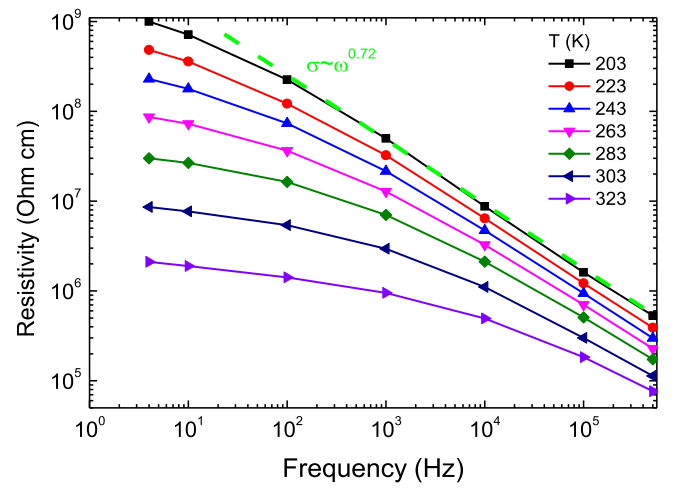


FIG. 4. Frequency dependences of resistivity of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample at different temperatures in the range below the phase transition temperature.

hopping conduction model [72,74]. The hopping conduction in the mixed oxides is considered also within the frames of the small polaron model (see, e.g., Refs. [75,76]), which may give much larger activation energy than the classical hopping model. Thus, one may presume that the high-frequency hopping conduction runs in the regime of small polaron hopping via the nearest neighbors which is characterized by the constant activation energy.

At lower frequencies, the temperature dependences of resistivity do not reach a purely activated behavior, characteristic of any kind of hopping conduction [Fig. 5(b)]. They do not fit by straight lines even in coordinates characteristic of the Mott VRH conduction $\rho \sim \exp[(T_0/T)^{1/4}]$ [77]. Presumably, such behavior may be related to more involvement in conduction of ionic interface conduction aside from the polarization mechanism.

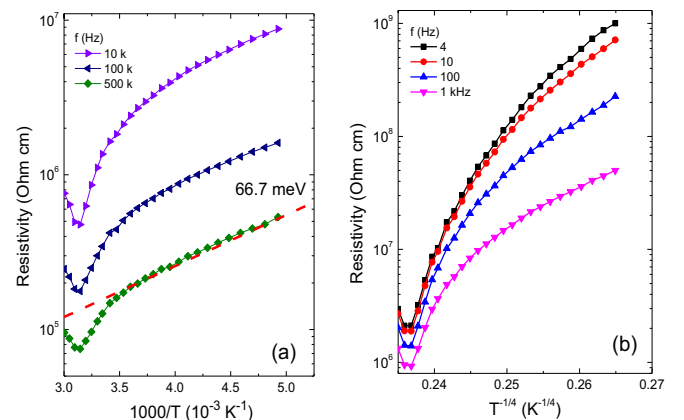


FIG. 5. (a) Temperature dependences of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample resistivity at three higher frequencies in the Arrhenius coordinates. (b) Temperature dependences of resistivity of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample at several lower frequencies in the coordinates of the Mott law $\rho \sim \exp(T_0/T)^{1/4}$.

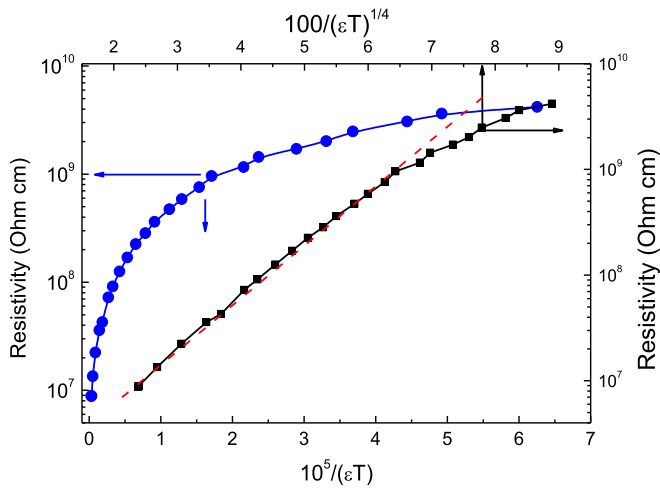


FIG. 6. The temperature dependence of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample resistivity at low frequency in coordinates modified according to the Heywang model [40]. The curve with blue symbols is plotted in the Arrhenius law coordinates $\ln(R)$ vs $\frac{1}{\varepsilon T}$. The curve with black symbols is plotted in the Mott law coordinates $\ln(R)$ vs $(\frac{1}{\varepsilon T})^{1/4}$. The test signal frequency is 4 Hz.

Among the models of electric conduction of ferroelectric oxide compounds not related to the hopping conduction is the model proposed by Heywang [40], which is based on the concept of creation of the interfacial potential Schottky barriers on the grain surfaces. The barrier height φ_s is determined as

$$\varphi_s = \frac{e^2 n_D}{2\varepsilon_0 \varepsilon} d^2, \quad (1)$$

where e is an elementary charge, ε_0 is a universal dielectric constant, ε is a relative dielectric permittivity, d is the width of the barrier layer, and n_D is the electron concentration providing the conduction due to presence of donor centers in the bulk. According to this model, one supposes that the resistance in the bulk is determined by electrons in the conduction band and obeys the law

$$R \sim \exp\left(\frac{\varphi_s}{k_B T}\right) = \exp\left(\frac{e^2 n_D d^2}{2\varepsilon_0 \varepsilon k_B T}\right) \cong \exp\left(\frac{A}{\varepsilon T}\right). \quad (2)$$

Accounting for the strong dependence of effective dielectric permittivity vs temperature, one may suppose this dependence to be fitted by the straight line in coordinates $\ln(R)$ and $\frac{1}{\varepsilon T}$.

However, as is seen in Fig. 6, this is not the case. The curve with blue symbols in Arrhenius coordinates, $\ln(R)$ and $\frac{1}{\varepsilon T}$, strongly decreases its slope. It may be understood supposing nonuniformity in size of nanograins constituting the powder and variation of concentration of centers determining the charge carrier concentration participating in the conductivity along with spread in polarizability among nanograins determining variation the surface barriers parameters. These changes apparently are over the area of a tableted shape powder sample. It is interesting to note that, as shown by the curve with black symbols in Fig. 6, the obtained dependence is quite well fitted by a straight line in coordinates $\ln(R)$ vs $(\frac{1}{\varepsilon T})^{1/4}$, which corresponds to proportionality $R \sim \exp[(\frac{A}{\varepsilon T})^{1/4}]$

similar to the case of the VRH conduction by the Mott law [77]. This may prove the assumption of nonuniformity of the powder sample over its area.

One should also note the impact of the frequency increase on this model. Shown in Fig. S6 in the Supplemental Material [41] is the temperature dependence of resistivity for the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample in Arrhenius coordinates $R \sim \exp(\frac{A}{\varepsilon T})$ at the test signal frequency of 500 kHz. Here, the curve is closer to the Arrhenius behavior. At higher frequency, the areas of the sample with the lower barrier energy, and consequently lower resistivity, dominate in the total resistivity.

Since we observed that the temperature of the pronounced minimum of resistivity coincides with the temperature of the maximal permittivity for both low and high frequencies (see Fig. 7), it allows us to suspect the validity of the Heywang model [40] for the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders. It seems very important that the temperature dependencies of the dielectric permittivity (upper curves in Fig. 7) and resistivity (bottom curves in Fig. 7) are almost mirrorlike reflected with respect to each other, which means that all their features, such as position and shape of maxima, plateau, minima, and inflexions, as well as straight parts, almost coincide after the mirror reflection with respect to the temperature axis. In other words, this means that $\ln(R) \sim (\frac{1}{\varepsilon T})^{1/4}$. A quantitative description of the observed temperature and frequency behavior of the permittivity and resistivity is given in the next section.

Thus, one can conclude that the temperature dependence of resistivity at temperatures both below and above the Curie temperature may be explained in the framework of Heywang model [40], accounting for creations of interfacial barriers on the nanoparticle surface and impact of efficient dielectric permittivity on their height. The temperature dependence of resistivity in this case is well described by the Mott law for the VRH conduction model if we replace the temperature T by the efficient temperature $T_{\text{eff}} = \varepsilon T$. In the case of adopting the hopping conduction model to explain our results, it may mean that the dielectric permittivity also contributes significantly to the modulation of the density of states (DOS) at the Fermi level. The dielectric permittivity decreases strongly and varies slowly at the lowest temperature. In this case, the fingerprints of the hopping conduction appear also, which consist of the characteristic frequency dependence of ω^S . Here, one already does not need an efficient temperature to consider. Meanwhile, this model still demands further development and additional experiments.

IV. THEORETICAL MODELING OF THE DIELECTRIC RESPONSE

A. Effective medium approximation

There are many EMAs [78], among which the most known are the Landau approximation of linear mixture [79], Maxwell-Garnett [80] and Bruggeman [81] approximations for spherical inclusions, and Lichtenecker-Rother approximation of the logarithmic mixture [82]. Most of these approximations are applicable for quasispherical randomly distributed dielectric (or semiconducting) particles in the insulating environment. These EMA models lead to analytical expressions for the effective permittivity $\varepsilon_{\text{eff}}^*$ [83]. However,

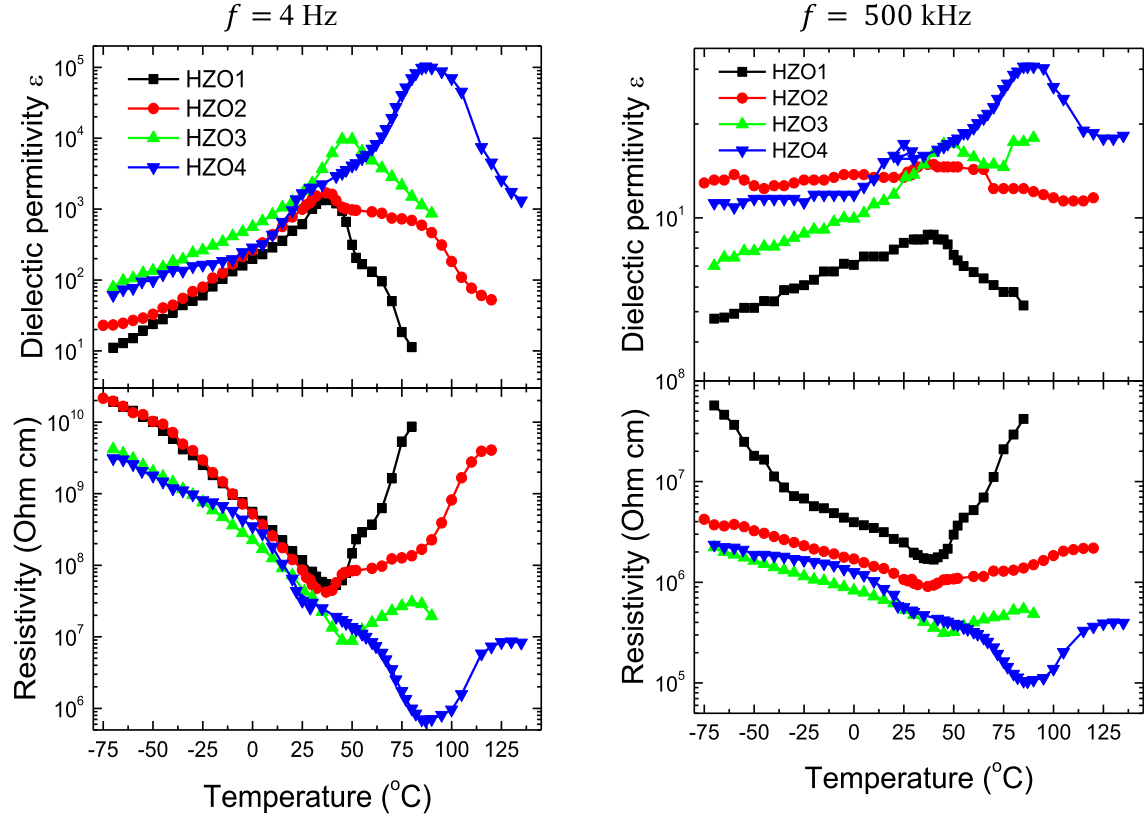


FIG. 7. Temperature dependences of the dielectric permittivity (filled symbols) and resistivity (empty symbols) of the samples HZO1–4 at frequencies of 4 Hz (left) and 500 kHz (right).

their applicability ranges are very sensitive to the cross-interaction effects of the polarized ferroelectric particles, and therefore, most of them are invalid for ferroelectric mixtures and/or colloids, where the content of the particles is $>(20\text{--}30)$ vol. % [84].

EMA models for arbitrary content of the nanoparticles were developed by Petzelt *et al.* [85] and Rychetský *et al.* [86]. As a rule, EMA considers the algebraic equation for the effective permittivity of the binary mixture

$$(1 - \mu) \frac{\varepsilon_{\text{eff}}^* - \varepsilon_b^*}{(1 - n_a)\varepsilon_{\text{eff}}^* + n_a\varepsilon_b^*} + \mu \frac{\varepsilon_{\text{eff}}^* - \varepsilon_a^*}{(1 - n_a)\varepsilon_{\text{eff}}^* + n_a\varepsilon_a^*} = 0. \quad (3)$$

Here, ε_a^* , ε_b^* are complex functions of the relative permittivity of the components a and b , respectively; μ and $1 - \mu$ are relative volume fractions of the components a and b , respectively; and n_a is the depolarization field factor for the inclusions of the type a . In the case $\mu = 0$ or 1 , the solution of Eq. (3) is $\varepsilon_{\text{eff}}^* = \varepsilon_b^*$ or $\varepsilon_{\text{eff}}^* = \varepsilon_a^*$, respectively.

For $n_a = 1$ (i.e., for the system consisting of the layers, perpendicular to the external field), one reduces Eq. (3) to the expression for the Maxwell layered dielectric model $\varepsilon_{\text{eff}}^* = (\frac{1-\mu}{\varepsilon_b^*} + \frac{\mu}{\varepsilon_a^*})^{-1}$. For $n_a = \frac{1}{3}$ (i.e., for the system consisting of the spherical nanoparticles), one rewrites Eq. (3) as $\varepsilon_{\text{eff}}^* = \varepsilon_b^* [1 + \frac{3\mu(\varepsilon_a^* - \varepsilon_b^*)}{\varepsilon_a^* + 2\varepsilon_b^* - \mu(\varepsilon_a^* - \varepsilon_b^*)}]$, which is the Wagner expression.

For $n_a = 0$ (i.e., for the system of the columns, parallel to the external field), Eq. (3) yields $\varepsilon_{\text{eff}}^* = (1 - \mu)\varepsilon_b^* + \mu\varepsilon_a^*$, which is equivalent to the system with parallel connected

capacitors with the complex permittivity ε_b^* and ε_a^* . The columnar model allows the separate fitting of the real (ε_{eff}) and imaginary (σ_{eff}) parts of $\varepsilon_{\text{eff}}^*$, which is the simplest case considered hereinafter among others.

Following EMA, we assume that the cores of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles (abbreviated as C) and their nonferroelectric shells (abbreviated as S) have a complex dielectric permittivity

$$\begin{aligned} \varepsilon_C^*(T, \omega) &= \varepsilon_C(T, \omega) - i \frac{\sigma_C(T, \omega)}{\varepsilon_0 \omega}, \\ \varepsilon_S^*(T, \omega) &= \varepsilon_S(T, \omega) - i \frac{\sigma_S(T, \omega)}{\varepsilon_0 \omega}. \end{aligned} \quad (4a)$$

The effective dielectric permittivity is

$$\varepsilon_{\text{eff}}^*(T, \omega) = \varepsilon_{\text{eff}}(T, \omega) - i \frac{\sigma_{\text{eff}}(T, \omega)}{\varepsilon_0 \omega}. \quad (4b)$$

Following the Heywang model [40] and considering experimental results shown in Fig. 7, the expected Arrhenius- and/or Mott-type temperature dependences (as well as a general stretched-exponential law) for the effective conductivity of the nanopowders could be modified by introduction of the effective dielectric permittivity. Thus, we use the following fitting function for effective conductivity:

$$\sigma_{\text{eff}}(T, \omega) = \sigma_A^0(\omega) \exp \left\{ - \left[\frac{E_A}{k_B T \varepsilon_{\text{eff}}(T)} \right]^\lambda \right\}. \quad (5)$$

Here, E_A is an activation energy of the space charges in the cores/shells ($A = C$ or S). The positive fitting parameter

TABLE II. The values of the fitting parameters R_0 and A used to describe experimentally measured resistivity.

Sample	x	Frequency $f = 4$ Hz		Frequency $f = 500$ kHz	
		$\lambda = \frac{1}{4}$	$\lambda = \frac{1}{9}$	$\lambda = \frac{1}{4}$	$\lambda = \frac{1}{9}$
HZO1 (HfO ₂)	1	$A = 2.230 \times 10^7$ $R_0 = 5.355 \times 10^6$	$A = 1.529 \times 10^{14}$ $R_0 = 6.220 \times 10^3$	$A = 1.123 \times 10^6$ $R_0 = 4.920 \times 10^5$	$A = 7.662 \times 10^9$ $R_0 = 9.326 \times 10^4$
HZO2 (Hf _{0.6} Zr _{0.4} O ₂)	0.6	$A = 6.845 \times 10^7$ $R_0 = 2050 \times 10^6$	$A = 4.517 \times 10^{14}$ $R_0 = 2.756 \times 10^3$	$A = 1.086 \times 10^5$ $R_0 = 5.326 \times 10^5$	$A = 2.491 \times 10^8$ $R_0 = 1.394 \times 10^5$
HZO3 (Hf _{0.5} Zr _{0.5} O ₂)	0.5	$A = 1.854 \times 10^8$ $R_0 = 5.810 \times 10^5$	$A = 9.196 \times 10^{14}$ $R_0 = 1.121 \times 10^3$	$A = 1.354 \times 10^6$ $R_0 = 1.496 \times 10^5$	$A = 9.692 \times 10^9$ $R_0 = 2.701 \times 10^4$
HZO4 (Hf _{0.4} Zr _{0.6} O ₂)	0.4	$A = 7.870 \times 10^8$ $R_0 = 1.014 \times 10^5$	$A = 5.808 \times 10^{14}$ $R_0 = 1.267 \times 10^3$	$A = 0.859 \times 10^7$ $R_0 = 7.387 \times 10^4$	$A = 1.007 \times 10^{11}$ $R_0 = 1.167 \times 10^4$

^aParameter A in Kelvin, R_0 in Ohm cm.

λ varies in the range $0 < \lambda \leq 1$ for a general stretched-exponential law, which includes the Mott law with $\lambda = \frac{1}{4}$ and the Arrhenius law with $\lambda = 1$. Varying λ , one can simulate a possible crossover from the Arrhenius-type dependence to the Mott-type dependence of the effective conductivity.

Hereinafter, we assume that $\varepsilon_{\text{eff}}(T)$ is a real positive value corresponding to the static (i.e., low-frequency) effective dielectric permittivity of the mixture, which should be determined in a self-consistent way or taken from the experiment. It is important that we use the effective value $\varepsilon_{\text{eff}}(T)$ in Eq. (5), which can be determined from experiment, instead of unknown local values of the dielectric permittivity. The assumption explains the minimum of resistivity near the temperature maximum of $\varepsilon_{\text{eff}}(T)$.

Fitting of the effective resistivity based on Eq. (5) is shown in Fig. 8. It appeared that the Heywang model [40] can describe the experimental results quantitatively for the power $\lambda_C \approx \lambda_S \approx \lambda = \frac{1}{4}$ for both low and high frequencies (see dashed curves in Fig. 8 and Table II), which corresponds the Mott-type VRH conduction in the Hf_xZr_{1-x}O₂ nanopowders. At the same time, the best fitting corresponds to $\lambda = \frac{1}{9}$ (see solid curves in Fig. 8 and Table II), but the difference between the fitting curves for $\lambda = \frac{1}{9}$ and $\frac{1}{4}$ is significant at temperatures well below the temperature maximum of $\varepsilon_{\text{eff}}(T)$. At low frequencies, the core contribution dominates, and the shell contribution increases with an increase in frequency (or vice versa).

Hereinafter, we assume that the shell dielectric permittivity ε_S monotonically and relatively weakly depends on temperature but can be frequency dependent

$$\varepsilon_S(T, \omega) \approx \varepsilon_b^0(\omega). \quad (6a)$$

Next, we assume that the dielectric permittivity of the cores consists of the dielectriclike (or paraelectriclike) contribution, originating from the nonferroelectric modes and the ferroelectriclike contribution, which can obey the Curie-Weiss-type law. For the displacive-type ferroelectric mode, the dielectric susceptibility χ obeys the following phenomenological equation: $\chi = \frac{1}{\alpha(T) + 3\beta P_3^2 + 5\gamma P_3^4 + 7\delta P_3^6}$, where α , β , γ , and δ are the Landau expansion coefficients of the free energy over the even powers of the order parameter—polarization P_3 [38,48]. According to the LGD approach, the following fitting function for the permittivity $\varepsilon_C(T, \omega)$ of the core with a diffuse phase

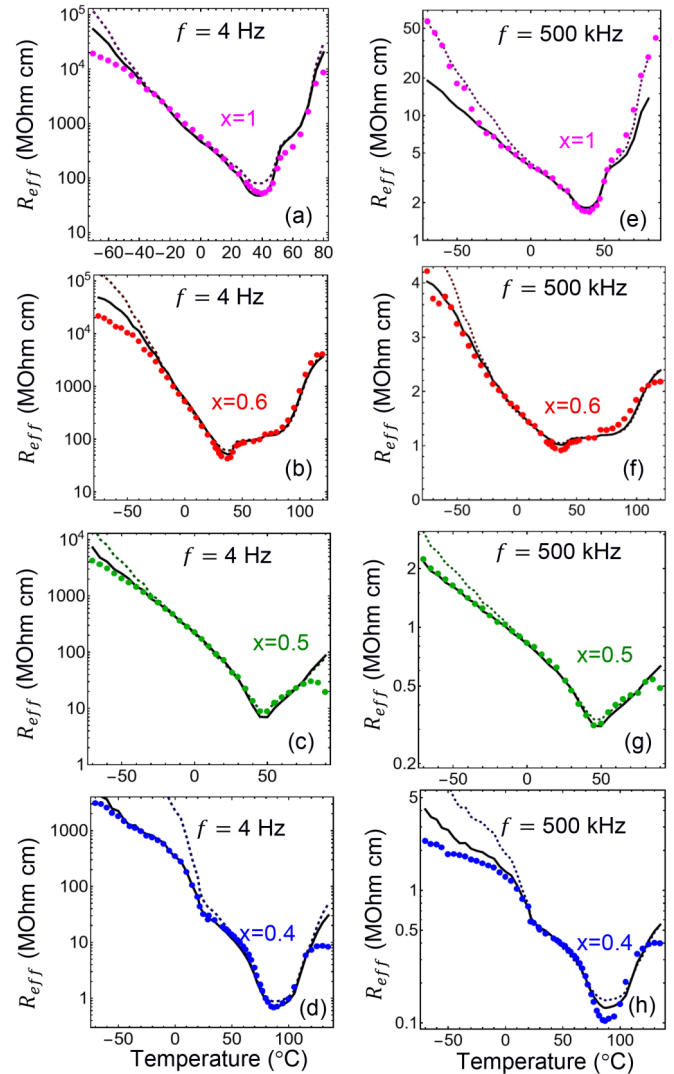


FIG. 8. Temperature dependences of the effective resistivity of the Hf_xZr_{1-x}O₂ nanopowders with different Hf content (a) and (e) $x = 1$, (b) and (f) $x = 0.6$, (c) and (g) $x = 0.5$, and (d) and (h) $x = 0.4$. Symbols are experimentally measured values with the test signal frequency (a)–(d) 4 Hz and (e)–(h) 500 kHz. Curves are the fitting by expression $R \cong R_0 \exp[(A/\varepsilon_{\text{eff}} T)^\lambda]$, for $\lambda = \frac{1}{9}$ (solid curves) and $\lambda = \frac{1}{4}$ (dashed curves). The values of ε_{eff} are taken from experimental data at 4 Hz. The fitting parameters R_0 and A are listed in Table II.

TABLE III. The values of the fitting parameters in Eqs. (6a) and (6b) used to describe the effective dielectric permittivity.

Sample	x	Frequency $f = 4$ Hz	Frequency $f = 500$ kHz
HZO1 (HfO ₂)	1	$\varepsilon_b^0 = 4$, $\Delta_d = 4.5$ K $C_W = 6080.6$ K $\Delta_c = 67.3$ K, $v = 1.50$ $T_C = 42.0$ °C	$\varepsilon_b^0 = 4$, $\Delta_d = 15.2$ K $C_W = 72.1$ K $\Delta_c = 0.3$ K, $v = 0.50$ $T_C = 37.7$ °C
HZO2 (Hf _{0.6} Zr _{0.4} O ₂)	0.6	$\varepsilon_b^0 = 5$, $\Delta_d = 14.8$ K $C_W = 23\,021.4$ K $\Delta_c = 15.2$ K, $v = 1.57$ $T_C = 37.9$ °C	$\varepsilon_b^0 = 5$, $\Delta_d = 61.3$ K $C_W = 558.3$ K $\Delta_c = 2.8$ K, $v = 0.45$ $T_C = 44.3$ °C
HZO3 (Hf _{0.5} Zr _{0.5} O ₂)	0.5	$\varepsilon_b^0 = 5$, $\Delta_d = 5.77$ K $C_W = 55\,626.5$ K $\Delta_c = 8.5$ K, $v = 0.89$ $T_C = 50.6$ °C	$\varepsilon_b^0 = 5$, $\Delta_d = 30.03$ K $C_W = 350.7$ K $\Delta_c = 3.9$ K, $v = 0.74$ $T_C = 50.5$ °C
HZO4 (Hf _{0.4} Zr _{0.6} O ₂)	0.4	$\varepsilon_b^0 = 8$, $\Delta_d = 2.8$ K $C_W = 277\,270.2$ K $\Delta_c = 29.7$ K, $v = 0.91$ $T_C = 98.4$ °C	$\varepsilon_b^0 = 8$, $\Delta_d = 16.8$ K $C_W = 373.4$ K $\Delta_c = 3.7$ K, $v = 0.61$ $T_C = 90.8$ °C

transition can be used:

$$\varepsilon_C(T, \omega) = \varepsilon_b^0(T, \omega) + \frac{C_W}{\sqrt{[T - T_C + 3\vartheta|T - T_C|L^2(T)]^2 + \Delta_d^2(\omega)}}. \quad (6b)$$

Here, $\varepsilon_b^0(T, \omega)$ is the nonferroelectric background permittivity, which can be constant or linear function of temperature. The positive constant C_W is the analog of the Curie-Weiss constant, T_C is the Curie temperature of the ferroelectriclike transition, Δ_d^2 is the permittivity dispersion, and ξ is the power of the permittivity decay. The fitting parameter ϑ can vary in the range $\frac{1}{3} < \vartheta \leq 3$. The dimensionless polarization parameter $L(T) = \frac{P_3(T)}{P_3(0)}$ is approximated as $L(T) \approx \frac{1}{1 + \exp[\frac{T - T_C}{\Delta_c(\omega)}]}$, where the dispersion $\Delta_c(\omega)$ models the diffuseness of the phase transition. The condition $\Delta_c(\omega) \ll T_C$ corresponds to a relatively sharp transition at $T = T_C$. Note that $\vartheta = 1$, and $\Delta_d^2 \rightarrow 0$ for the classical Curie-Weiss law in displacive ferroelectrics with the second-order phase transition.

For the case of the order-disorder-type ferroelectric core, where the order parameter satisfies the equation $L(T) = \tanh[\frac{T_C}{T}L(T)]$, the following fitting function for the core permittivity $\varepsilon_C(T, \omega)$ can be used:

$$\varepsilon_C(T, \omega) = \varepsilon_b^0(\omega) + \frac{C_W}{T \cosh^2[\frac{T_C}{T}L(T)] - T_C}. \quad (6c)$$

The temperature dependence of the dimensionless order parameter $L(T)$ can be approximated as in the previous case $L(T) \approx \frac{1}{1 + \exp[\frac{T - T_C}{\Delta_c(\omega)}]}$, where the dispersion $\Delta_c(\omega) \ll T_C$ for the sharp transition. Here, the background constant $\varepsilon_b^0(\omega)$, the Curie-Weiss constant C_W , and the dispersion $\Delta(\omega)$ are fitting parameters.

The fitting of the low- and high-frequency dielectric permittivity using the hypotheses in Eqs. (6b) and (6c) is shown

in Figs. S7–S8 and S9 in the Supplemental Material [41], respectively. Using the Bayesian optimization with these hypotheses (see, e.g., details in Refs. [87,88]), we can estimate the probabilities of the displacement- and order-disorder-type ferroelectriclike transitions in the Hf_xZr_{1-x}O₂ nanopowders.

Temperature dependences of the effective dielectric permittivity $\varepsilon_{\text{eff}}(T, \omega)$ of the Hf_xZr_{1-x}O₂ nanopowders with different Hf content are shown in Fig. 9. Solid curves are the fitting using Eq. 6(b) and Bayesian optimization. Fitting parameters are listed in Table III. It appeared that the best fitting corresponds to significant deviation from the classical Curie-Weiss law (with $\vartheta = 1$ and $\Delta_d \rightarrow 0$), at which all fitting parameters, except ε_b^0 , depend significantly on the frequency f . The most significant are the frequency dependences of the Curie-Weiss constant C_W , dispersion Δ_d , and parameter ϑ (see Table III). The parameters C_W and Δ_d mostly increase strongly with an increase in frequency. The parameter ϑ decreases (from 30% to 3 times) with an increase in frequency from 4 Hz to 500 kHz. The frequency dispersion of T_C is relatively weak (from 0.1 to 8 K) and may be ascribed to the fitting accuracy for the scattered data.

At the same time, the main maximum of the dielectric permittivity is very large in comparison with other features for all compositions x (see Fig. 9), and its width is much larger than the ordered crystalline ferroelectrics. These trends agree with our assumption that the studied Hf_xZr_{1-x}O₂ nanopowders undergo a diffuse ferroelectriclike phase transition in the temperature range 38–98 °C.

However, we are aware that the colossal dielectric permittivity, observed at low frequencies in the Hf_xZr_{1-x}O₂ nanopowders, can originate from the IBLC and/or SBLC effects [58,59] accompanied by an increase in conduction losses [60]. Equation (3), as the EMA model equation, describes the IBLC and/or SBLC effects and, at the same time, includes the limiting cases of the Maxwell layered dielectric model ($n_a = 1$), the Wagner model of spherical nanoparticles ($n_a = \frac{1}{3}$), and the columnar model ($n_a = 0$). According to the fitting results

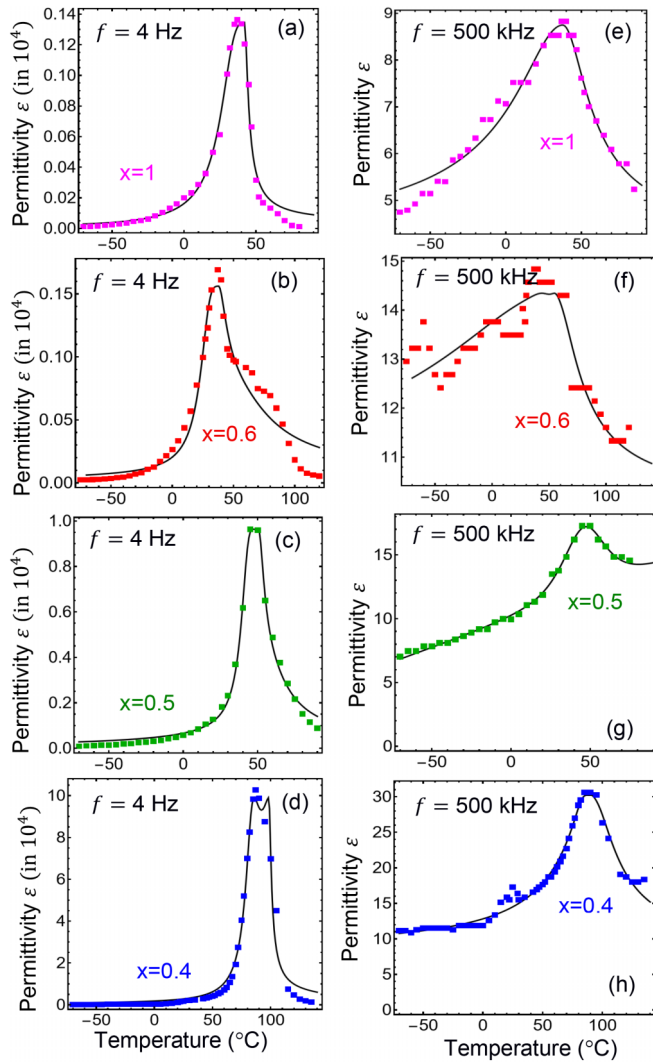


FIG. 9. Temperature dependences of the effective dielectric permittivity of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders with different Hf content (a) and (e) $x = 1$, (b) and (f) $x = 0.6$, (c) and (g) $x = 0.5$, and (d) and (h) $x = 0.4$. Symbols are experimentally measured values with the test signal frequency (a)–(c) 4 Hz and (d) and (e) 500 kHz. Black curves are calculated using the expressions in Eqs. (6a), (6b) and Bayesian optimization. The fitting parameters are listed in Table III.

of the measured dielectric response and conductivity, based on the Bayesian optimization with the working hypotheses in Eqs. (5) and (6), the columnar model is the most probable. This result allows the separate fitting of the real and imaginary parts of ϵ_{eff}^* from Eqs. (5) and (6) and predicts that the ferroelectriclike phase transition may take place in the semiconducting cores of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles.

B. Landau-type phenomenological approach and DFT calculations

Analysis of the spatial-temporal evolution of polarization in the oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles can be performed in the framework of the effective LGD model [36,38]. This approach incorporates the elements of the Kittel-type model [89] with polar and antipolar modes [90–92]

to the Landau-type free energy with effective parameters [93] extracted either from the experiment [19] or from the first-principles calculations. It was shown earlier that the Landau-Devonshire expansion of the Gibbs energy G in even (second, fourth, and sixth) powers of the polar order parameter (P_3) and the antipolar order parameter (A_3) after partial minimization $\frac{\partial G}{\partial A_3} = 0$ can be transformed to the expansion in even powers (second, fourth, sixth, and eighth) of the polarization P_3 [94]. The bulk density of the LGD potential g_{LGD} , which includes the Landau-Devonshire expansion in even powers of the polarization P_3 and the Ginsburg gradient energy has the form

$$g_{\text{LGD}} = \frac{\alpha(T)}{2}P_3^2 + \frac{\beta}{4}P_3^4 + \frac{\gamma}{6}P_3^6 + \frac{\delta}{8}P_3^8 + g_{33ij}\frac{\partial P_3}{\partial x_i}\frac{\partial P_3}{\partial x_j}. \quad (7)$$

The temperature dependence of the coefficient $\alpha(T)$ obeys the Barrett-type law [95] $\alpha(T) = \alpha_T T_q (\coth \frac{T_q}{T} - \coth \frac{T_q}{T_C})$, where T_C is the Curie temperature, and T_q is the quantum vibration temperature. At low temperatures, $\alpha \rightarrow \alpha_T T_q (1 - \coth \frac{T_q}{T_C})$. The coefficients β , γ , and δ are regarded as temperature independent. Tensor g_{ijkl} is the tensor of the polarization gradient energy.

To determine the coefficients α , β , γ , and δ in Eq. (7) from first principles, we performed the DFT calculations of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ structures using the full-potential all-electron local-orbital (FPLO) code [96]. We have used the default FPLO basis. The structural parameters of 12 atom cells are optimized using local density approximation (LDA), a $6 \times 6 \times 6$ k -point mesh for Brillouin zone sampling, an energy convergence threshold of 10^{-8} Ry, and a force convergence threshold of 10^{-6} Ry/Bohr. Both lattice constants and ionic positions are fully relaxed.

The calculated equilibrium lattice parameters a , b , and c were compared with experimental results [97–99] (see Ref. [39] for details and Table S3 in the Supplemental Material [41]). In agreement with earlier works, the crystal structure with a monoclinic symmetry has the lowest ground-state energy in the bulk HfO_2 , $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO), and ZrO_2 . However, the difference ΔU between the energy G_f of the ferroelectric o phase $Pca2_1$ (f phase) and the energy G_m of the m phase $P2_1/c$, calculated using the FPLO basis in Ref. [39], turned out to be smaller than those calculated by other DFT methods. From Table S3 in the Supplemental Material [41], the difference between the m -HZO and f -HZO (~ 7.8 meV/f.u.) is significantly smaller than the difference between the m - HfO_2 and f - HfO_2 (~ 11.6 meV/f.u.). Thus, the addition of Zr may stabilize the f phase. The dependence of the f -HZO total energy on the displacements of the four oxygen atoms (O1) in the z direction from their equilibrium positions in the f phase with the minimal energy are listed in Table S4 in the Supplemental Material [41] and shown in Fig. 10.

The parameters of the classical LGD approach, such as the Curie temperature T_C ; the Curie-Weiss constant C_W ; expansion coefficients $\alpha(T)$, β , γ and δ ; listed in Table IV, are considered to characterize a bulk ferroelectric material, being material parameters per se. These parameters are typically determined from the fitting of experimentally measured

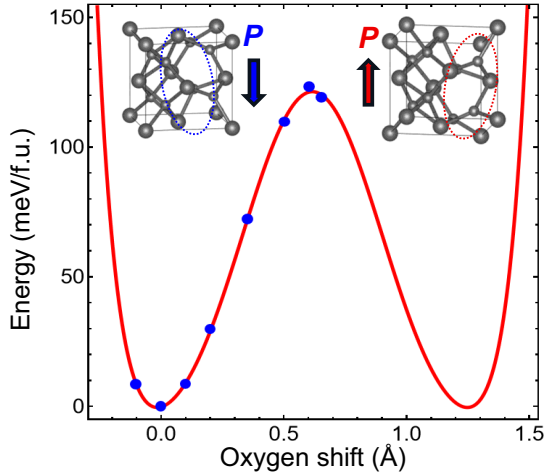


FIG. 10. The dependence of the f - $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ total energy on the displacements of the four oxygen atoms (O1) in the z direction from their equilibrium positions in the f phase with the minimal energy. Symbols are data from Table S4 in the Supplemental Material [41], and the solid curve is the reconstructed Landau-Devonshire potential with α , β , γ , and δ (see Table IV).

temperature dependences of spontaneous polarization and dielectric permittivity by the dependences calculated from the LGD free energy [e.g., from Eq. (7)]. The LGD parameters could vary slightly from sample to sample due to the deviations from stoichiometry, uncontrollable impurities, and/or defects, but a total reproducibility of the results is an established fact for ordered ferroelectrics. For solid solutions (e.g., for the lead zirconate-titanate $\text{Pb}_x\text{Zr}_{1-x}\text{TiO}_3$), the LGD parameters are continuous and often monotonic functions of the solid solution composition x .

For nanoscale ferroelectrics (e.g., thin films and nanoparticles) and layered and/or for disordered ferroelectric systems (e.g., relaxor ferroelectrics, sliding ferroelectrics, and ferroelectrics with diffuse phase transitions), the situation is completely different. As a matter of fact, the applicability of the classical LGD approach to such systems is under debate and requires significant modification because it is impossible to separate the influence of extrinsic factors and size effects (e.g., surfaces, interfaces, substrates, shells, and environment) and intrinsic inhomogeneity (e.g., layered structure, flexoelectric effect, compositional disorder, and induced flexochemical strains) on their physical properties. For several important cases, including $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles [36,38] and thin films [93], the applicability of the LGD approach is based on the renormalized free energy, in which the effective LGD

parameters—which depend on the size, surface characteristics, and environment—are introduced.

In accordance with Refs. [36,38], the effective coefficient $\alpha(T, x)$ of spherical $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles covered with the shell enriched by oxygen vacancies is renormalized by the chemical pressure (analog of surface tension) induced by the vacancies [100,101], depolarization field contribution, and polarization gradient energy

$$\alpha_R(T, R, x) = \alpha(T, x) - Q \frac{\mu_s}{R} + \frac{\varepsilon_0^{-1}}{\varepsilon_b + 2\varepsilon_e + (R/\Lambda_s)} + \frac{2g}{R\Lambda_p + R^2/4}. \quad (8)$$

Here, $Q = Q_{11} + 2Q_{12}$ is the combination of electrostriction coefficients Q_{ij} , μ_s is the coefficient of intrinsic surface stress [102], R is the particle radius, ε_0 is a universal dielectric constant, ε_b is the static background permittivity of the nanoparticles, ε_e is the relative permittivity of the media surrounding the particles, Λ_s is the effective screening length produced by the ions and/or oxygen vacancies adsorbed by the surface of the nanoparticle, $g = \frac{1}{2}(g_{3311} + g_{3311})$ is the combination of the polarization gradient energy tensor g_{ijkl} , and Λ_p is the polarization extrapolation length [36].

The ferroelectriclike state may be stable in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticle when its Gibbs free energy G_f is smaller than the bulk energy of the monoclinic phase G_m . In accordance with the DFT results listed in Table S3 in the Supplemental Material [41], the energy difference $\Delta U = G_f - G_m$ is equal to 7.8 meV/f.u. for the bulk $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. From Eqs. (7) and (8), the condition of the f -phase stability is

$$\left[\frac{\varepsilon_0^{-1}}{\varepsilon_b + 2\varepsilon_e + (R/\Lambda_s)} + \frac{2g}{R\Lambda_p + R^2/4} - Q \frac{\mu_s}{R} \right] \frac{P_s^2}{2} < -\Delta U. \quad (9)$$

Here, $P_s \approx 75 \mu\text{C}/\text{cm}^2$ is the hypothetical spontaneous polarization of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ calculated from the DFT using parameters listed in Table IV. The condition in Eq. (9) determines the range of the nanoparticle radii for which the f phase could be stable. Assuming that the contribution of the polarization gradient energy is much smaller than the contribution of the depolarization field energy, namely, $\frac{2g}{R\Lambda_p + R^2/4} \ll \frac{\varepsilon_0^{-1}}{\varepsilon_b + 2\varepsilon_e + (R/\Lambda_s)}$, that is a good approximation for a large Λ_p and a small g , it is easy to derive an approximate algebraic equation for the critical radius determination

$$\frac{\varepsilon_0^{-1}}{\varepsilon_b + 2\varepsilon_e + (R_{cr}/\Lambda_s)} - Q \frac{\mu_s}{R_{cr}} + \frac{2\Delta U}{P_s^2} = 0. \quad (10)$$

Assuming that $(R_{cr}/\Lambda_s) \gg \varepsilon_b + 2\varepsilon_e$, which corresponds to the case of high ionic screening by larger nanoparticles, we obtain that

$$R_{cr} \approx \frac{P_s^2}{2\Delta U} \left(\mu_s Q - \frac{\Lambda_s}{\varepsilon_0} \right). \quad (11a)$$

The nanoparticles may become ferroelectric for $R < R_{cr}$, and the critical radius exists at $\mu_s Q > \frac{\Lambda_s}{\varepsilon_0}$. For estimates, we use the parameters $P_s \approx 75 \mu\text{C}/\text{cm}^2$, $\Delta U = 7.8 \text{ meV}/(5 \text{ Å})^3$, $Q \approx 0.2 \text{ m}^4/\text{C}^2$, $\mu_s \approx 2.5 \text{ N/m}$ [103,104], and $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$, which gives that the condition $\Lambda_s < \varepsilon_0 \mu_s Q$ is

TABLE IV. The values of LGD expansion coefficients.

Parameter	Atomic units	SI units
α	1712.8 meV/(f.u. $\text{\AA}^2$)	$-1.407 \times 10^9 \text{ J m}/\text{C}^2$
β	9667.8 meV/(f.u. $\text{\AA}^4$)	$5.358 \times 10^9 \text{ J m}^5/\text{C}^4$
γ	$-21\,879 \text{ meV}/(\text{f.u. } \text{\AA}^6)$	$-8.181 \times 10^9 \text{ J m}^9/\text{C}^4$
δ	21\,079 meV/(f.u. $\text{\AA}^8$)	$5.318 \times 10^9 \text{ J m}^{13}/\text{C}^4$

valid for $\Lambda_s \leq 0.045 \text{ \AA}$. Despite that the effective screening length is much smaller than the lattice constant ($5 \text{ \AA}$), its value may be quite realistic [105] because the effective screening length Λ_s is related with the real charge-surface separation h as $\Lambda_s \cong h/\epsilon_{\text{eff}}$ [36]. Since the static dielectric permittivity ϵ_{eff} is higher than 10^2 – 10^3 and reaches 10^4 in maximum (see the green curve in Fig. 7, left), the separation h is higher than $(4.5\text{--}45) \text{ \AA}$, being ~ 1 – 10 lattice constants. The upper estimate of R_{cr} is $R_{cr} < \frac{p_s^2}{2\Delta U} \mu_s Q$, which gives $\sim 15 \text{ nm}$.

Assuming that $(R_{cr}/\Lambda_s) \ll \epsilon_b + 2\epsilon_e$, which corresponds to the case of weak ionic screening by smaller nanoparticles, we obtain that

$$R_{cr} \approx \mu_s Q \left(\frac{\epsilon_0^{-1}}{\epsilon_b + 2\epsilon_e} + \frac{2\Delta U}{P_s^2} \right)^{-1}. \quad (11b)$$

From Eq. 11(b), the critical radius is $\sim 0.1 \text{ \AA}$, which is much smaller than the lattice constant and thus has no physical sense.

Thus, we can conclude that, if the concentration of oxygen vacancies is relatively small ($\Lambda_s > 0.1 \text{ \AA}$), the long-range ferroelectric order cannot exist in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles due to the insufficient screening of the emerging spontaneous polarization. At large concentrations of the surface ions and/or charged vacancies, the synergy of high screening ($\Lambda_s \leq 0.05 \text{ \AA}$) and chemical pressure (large term $-Q\frac{\mu_s}{R}$) supports and stabilizes the long-range ferroelectric order in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles. Due to the weakening of size effects with increase in R , the imbalance of the negative surface tension ($-Q\frac{\mu_s}{R}$) and positive depolarization field energy $[\frac{\epsilon_0^{-1}}{\epsilon_b + 2\epsilon_e + (R/\Lambda_s)}]$ contributions arises. As a result, the ferroelectric $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles become paraelectric with an increase in their size above $2R_{cr} \cong 30 \text{ nm}$ and then dielectric with its further increase [36]. A possible stability of the f phase for $R < R_{cr}$ is the synergy of ferroionic coupling and size effects.

We should also underline that the observed maximum of dielectric permittivity, which may be related to the diffuse ferroelectriclike phase transition, is possibly complicated by the significant contribution of IBLC effects. Due to these reasons, the fitting parameters listed in Table III, which describe the dielectric response of the oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders, do not have a direct relation with the LGD parameters of hypothetical bulk crystalline ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ listed in Table IV, which are determined by DFT calculations. Since the bulk ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ does not exist in nature and the nonpolar monoclinic bulk $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ exists instead, the parameters from Tables III and IV cannot be directly linked, as they serve completely different purposes.

The link between the DFT results and effective LGD parameters is given by Eq. (8), which shows how the surface and size effects renormalizes the parameter $\alpha(T)$ calculated by DFT. Using the renormalized parameter $\alpha_R(T, R, x)$ given by Eq. (8) and the energy difference $\Delta U = G_f - G_m$ (calculated from DFT), we formulate the conditions in Eqs. (9) and (10), which allow us to estimate the critical radius R_{cr} of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, below which they may become ferroelectric. The value of R_{cr} given by Eq. 11 agrees well

with the experimental observation of colossal dielectric response and o phases in small (size $< 30 \text{ nm}$) $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles and their absence in larger particles.

V. DISCUSSION AND CONCLUSIONS

We analyze the dielectric response and conductivity of small (5 – 10 nm) oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 1$ – 0.4) nanoparticles prepared by solid-state organonitrate synthesis, where the dominance of the o phases was proved by XRD. We reveal that the temperature dependencies of the dielectric permittivity and resistivity of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders pressed at 5 MPa are almost mirrorlike reflected with respect to each other, which means that all their features, such as position and shape of maxima, plateau, minima, and inflexions, almost coincide after the mirror reflection with respect to the temperature axis. The correlations in behavior of the resistivity and dielectric permittivity are well described in the Heywang model [40] for semiconductor ferroelectrics applied in combination with the VRH conduction model.

The effective dielectric permittivity of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders has a pronounced maximum at 311 – 361 K (38 – 88°C) for Hf content $x = 1$ – 0.4 , the height of which decreases strongly and monotonically with an increase in frequency. The maximal dielectric permittivity increases from 1.5×10^3 for $x = 1$ to 1.3×10^5 for $x = 0.4$ at low frequencies ($\sim 4 \text{ Hz}$); being much smaller at high frequencies, namely, changing from 7 (for $x = 1$) to 20 (for $x = 0.4$) at 500 kHz .

As a rule, the colossal effective dielectric permittivity ($\sim 10^4$ – 10^6) of ceramics and composites with ferroelectric nanograins is related to the IBLC and/or SBLC effects and/or polaron activation and hopping [58–62]. The colossal values of their dielectric permittivity can be accompanied by an increase in the conduction losses [60]. A significant frequency dispersion of the features of dielectric permittivity and losses is inherent to the IBLC, SBLC, and polaronic effects. Since the frequency dispersion of the dielectric permittivity maximum and resistivity minimum is absent in the studied $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders, it allows us to assume a significant contribution of the expected ferroelectriclike phase transition to the dielectric response. Notably, the temperature of the possible transition increases monotonically with increase in Zr content; meanwhile, the shape and width of the dielectric permittivity maximum change in a more complex way.

Notably, we do not observe any frequency dispersion of the dielectric permittivity maximum position in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanopowders inherent to relaxor ferroelectrics and dipolar glasses, but the shape and width of the maximum change strongly with increase in frequency. At the same time, the permittivity maximum is wide or plateaulike, especially for $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{O}_2$ nanopowders in the entire frequency range, which may indicate that we observe a diffuse ferroelectriclike phase transition, the classification of which is much wider in comparison with relaxor ferroelectrics.

The ferroelectriclike behavior of the small (radius $< 15 \text{ nm}$) oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles is expected from DFT calculations and LGD approach, which reveal that the oxygen vacancies create chemical pressure inside the particle and provide effective ionic screening at its surface.

The problem of direct evidence of ferroelectricity in small $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles may be solved by preparation of dense ceramics, where the fraction of nanoparticles exceeds 90%. However, conventional hot-pressed ceramics are not suitable for this purpose because the sintering temperature of hafnia-zirconia is rather high ($>900^\circ\text{C}$), which inevitably leads to the agglomeration of ultra-small nanoparticles to the larger grains with the average size $>30\text{--}50\text{ nm}$. Such grains cannot be ferroelectric according to theoretical calculations of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticle polar properties [36] and experimental results showing the ferroelectricity disappearance in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films of thickness $>30\text{ nm}$ [1].

Obtained results may be useful for developing the next generation of silicon-compatible ferroelectric nanomaterials. Indeed, the ferroelectrics of the next generation, such as $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$, $\text{Al}_x\text{Sc}_{1-x}\text{N}$, and $\text{Zn}_x\text{Mg}_{1-x}\text{O}$, are regarded as Si compatible because they either demonstrate a significant resistance to oxygen loss or have no oxygen at all, and they do not require crystallization at high temperatures (see, e.g., Refs. [1–5] and refs. therein). However, the coercive fields of these ferroelectrics are relatively high [1–5]. The coercive field reduction can be achieved due to the appropriate doping [106–108], proximity effects [109,110], and/or finite size effects [36,93]. It is important to maintain the Si compatibility together with the reduction of coercive field. For instance, Jiang *et al.* [111] achieved an ultra-low-voltage switching of ferroelectric polarization in ultrathin BaTiO_3 films, the direct integration of which with Si substrate requires a SrTiO_3 buffer layer. The Si compatibility of the studied $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles can be reached by their cold sputtering on the appropriate silicon or silicon-oxide substrate; at that, a low deposition temperature ($<300^\circ\text{C}$) is required to prevent their agglomeration. Not less important seems to explore the possibility of their coercive field reduction by size effects. In this sense, small sizes of the nanoparticles can reduce the coercive field significantly due to the depolarization field emerging in the small particles under incomplete screening conditions.

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DATA AVAILABILITY

Some of the data that support the findings of this article are openly available [112]. Data to support Figs. 1–10 are not publicly available. The data are available from the authors upon reasonable request.

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