

Regional microstructural and electrical variations in large-sized ZnO varistor ceramics processed by cold sintering assistance

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ABSTRACT: The cold sintering process (CSP) is recognized as an emerging low-temperature densification strategy that provides a scalable and energy-efficient route for producing advanced ceramics and composite materials. However, its application has thus far been largely confined to small samples (diameter < 15 mm), leaving the behavior of large-sized electronic ceramics scarcely explored. Here, a multidoped ZnO-based varistor ceramic with a diameter of 40 mm was employed to investigate the regional heterogeneity induced by cold sintering and subsequent annealing. The synergistic effects of radial pressure attenuation, liquid-phase migration, Marangoni convection, and pore evacuation accelerated densification at the edges, leading to an intensified dissolution–precipitation process. Consequently, the edge region exhibited higher densification (relative density (ρ_r) = 94.3%), smaller pore volume (V_p = 0.215 cm³·g⁻¹), and larger grains (average grain size (G_{aver}) = 233 nm) compared with the center part (ρ_r = 91.6%, V_p = 0.385 cm³·g⁻¹, and G_{aver} = 189 nm). Furthermore, the regional heterogeneity originating from the CSP extended into the annealing stage, as reflected by a reduced leakage current (I_L = 0.3 μ A·cm⁻²), enhanced nonlinearity (α = 66), and a high breakdown field (E_b = 1108 V·mm⁻¹) at the edge region. The superior electrical performance is attributed to the larger interface state density (N_s = 2.9×10¹⁵ m⁻²) and higher barrier height (ϕ_b = 1.92 eV). This work elucidates the regional effect of cold sintering and offers theoretical insight for its industrial application.

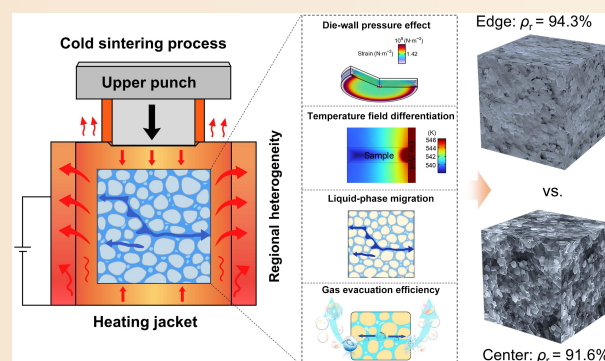
KEYWORDS: cold sintering; ZnO-based varistor ceramics; regional heterogeneity; microstructure; breakdown field

1 Introduction

The advent of low-temperature sintering represents a significant milestone in promoting environmentally responsible manufacturing of advanced electronic ceramics. Distinguished by its mechanistic synergy of “dissolution–precipitation”, the cold sintering process (CSP) enables various ceramic and composite systems to achieve near-theoretical density within a temperature window of ambient to 300 °C [1,2]. Beyond substantially lowering the energy demand during fabrication, this method offers exceptional capability to maintain or further refine microstructural features and functional performance [3,4]. It has therefore been extensively employed in electronic ceramics and multifunctional composites. Despite their promising mechanical and electrical characteristics, cold-sintered ceramics have thus far been explored predominantly as miniature specimens with diameters below 15 mm. This dimensional limitation has become

a major bottleneck for their deployment in industrial electronic ceramic manufacturing.

Accordingly, understanding size-dependent effects in cold-sintered ceramics is essential for advancing the process toward industrial-scale applications. Such insight is needed to clarify how enlarged dimensions reshape microstructural evolution and electrical behavior and to establish a theoretical basis for scalable processing. In other advanced sintering processes, variations in sample dimension have been acknowledged as a crucial factor influencing both the densification pathway and the resulting mechanical and electrical properties. As exemplified by microwave sintering, a nonuniform electromagnetic field distribution frequently induces substantial temperature gradients across large-scale samples, consequently giving rise to insufficient densification or delayed grain growth in their central regions [5–7]. In addition, during spark plasma sintering, the uneven distribution of current pathways and contact resistance within large cross-section samples



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commonly results in higher temperatures at the edges than at the center, thereby producing spatial heterogeneity in both microstructure and hardness [8–10]. In flash sintering, enlargement of sample dimensions can exacerbate core-surface temperature differentials as a result of radiative heat dissipation from the surface, leading to the development of structural heterogeneity [11]. Moreover, as in hot pressing, die-wall friction impedes the inward transmission of the applied pressure, causing strain accumulation near the mold walls and thereby promoting higher densification in the peripheral regions [12,13]. Collectively, these studies demonstrate that sintering involves pronounced macroscopic heterogeneity in heat transfer, mass transport, and strain distribution. Such heterogeneity is amplified with increasing sample size, ultimately affecting microstructural uniformity and performance consistency. However, size effects in the CSP are more intricate but far less explored, particularly with respect to multifunctional electronic ceramics such as ZnO-based varistors.

Motivated by the above analyses, the present work focuses on ZnO-based varistor ceramics with a diameter of 40 mm, providing a systematic characterization of the regional heterogeneity arising in large-sized samples fabricated via the CSP. The results from porosity assessment, phase characterization, and electrical property analysis revealed that the edges of cold-sintered ceramics attain higher densification and superior electrical performance, from which four dominant influencing factors were derived (Fig. 1). (I) Die-wall pressure effect: During uniaxial pressing, frictional constraints between the powder compact and the die wall generate a radial strain gradient, producing elevated local effective strain (σ_{eff}) near the periphery [14,15]. The densification rate ρ' follows an Arrhenius-type relation $\rho' = A \exp(-Q_{\text{eff}}/(RT)) \sigma_{\text{eff}}$, where A is a material constant, Q_{eff} is the effective activation energy for diffusion-controlled densification, T is the temperature, and R is the gas constant [16]. The friction-induced pressure field effectively reduces $Q_{\text{eff}} = Q_0 - \lambda \sigma_{\text{eff}}$ (where Q_0 denotes the intrinsic activation energy and λ is the strain-activation energy coupling coefficient), facilitating particle rearrangement, interparticle neck growth, and pore closure near the edge. (II) Liquid-phase migration: Capillary forces and pressure gradients drive the migration of the transient liquid phase toward the edges [17]. This convective mass transfer enhances the dissolution-precipitation

kinetics of Zn^{2+} , Bi^{3+} , and Cr^{3+} ions, lowering the energy barrier for local densification. The transport regime is characterized by the Péclet number $P_e = UL/D$, where U is the convective velocity, L is the characteristic length, and D is the diffusion coefficient; $P_e > 1$ at the periphery indicates convection-dominated transport [18]. (III) Temperature field differentiation: The temperature gradient induces surface-tension variations along liquid-solid interfaces, giving rise to thermocapillary convection that can be quantified by the local Marangoni number $M_a = -[(\partial\gamma)/\partial T \cdot L \cdot \Delta T]/\mu\alpha_T$, where γ is the surface tension, μ is the viscosity, and α_T is the thermal diffusivity, which quantifies surface-tension-driven convection [19]. At the sample periphery, the combined effects of a larger local temperature difference (ΔT) and reduced liquid viscosity at elevated temperature markedly increase the Marangoni number, shifting the mass-transport regime from diffusion-dominated to convection-dominated. (IV) Gas evacuation efficiency: The shorter degassing path at the periphery allows rapid removal of volatile species (e.g., acetic acid and hydroxyl groups), preventing pore agglomeration and enabling smooth transition from pore to boundary. These mechanisms are intrinsically coupled rather than independent. Pressure gradients drive liquid-phase migration toward the edge, while temperature gradients induce thermocapillary convection, jointly enhancing dissolution-precipitation kinetics. Together with more efficient gas evacuation at the periphery, these effects promote pore elimination and accelerate local densification in large-sized cold-sintered samples.

As a result, the 40 mm-diameter ZnO varistor sample fabricated solely by CSP exhibited a markedly higher apparent density at the edges (relative density (ρ_r) = 94.3%) compared with the center (ρ_r = 91.6%), accompanied by reduced mesoporosity and smaller mesopore volume. As the edge region of the cold-sintered sample underwent more evident thermal maturation, grain growth was considerably more pronounced than that in the center, yielding an average grain size of 233 vs. 189 nm at the center. Moreover, the regional characteristics established during the CSP persisted through the subsequent thermal treatment, as the postannealed samples exhibited a lower leakage current (J_L = 0.3 $\mu\text{A}\cdot\text{cm}^{-2}$), higher nonlinearity coefficient (α = 66), and comparable breakdown field (E_b = 1108 $\text{V}\cdot\text{mm}^{-1}$) at the edge regions. Defect-state characterization further reveals that regional

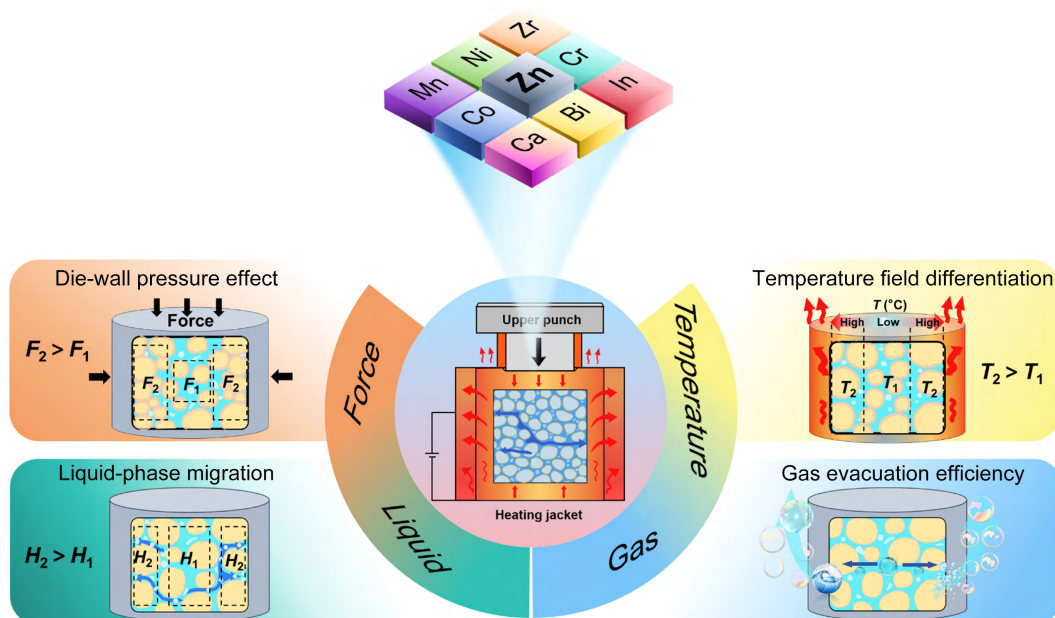


Fig. 1 Mechanistic schematic illustrating regional heterogeneity during CSP.

heterogeneity gives rise to higher grain-boundary barriers ($\phi_b = 1.9$ eV) and greater surface-state density ($N_s = 2.9 \times 10^{15} \text{ m}^{-2}$) at the periphery, whereas the central region exhibits slightly lower values ($\phi_b = 1.87$ eV, $N_s = 2.84 \times 10^{15} \text{ m}^{-2}$). Therefore, this work not only complements the theoretical framework of size effects in existing sintering technologies but also provides critical guidance for process optimization during the scale-up of cold-sintered ceramics toward industrial applications.

2 Experimental

2.1 Material synthesis

The sample preparation involved two distinct stages, cold sintering and subsequent thermal treatment. Initially, precursor powders comprising ZnO (99.5%, particle size of $\sim 0.5 \mu\text{m}$; Acros, USA), Bi_2O_3 (99%, Alfa, USA), Co_2O_3 (95%, Alfa, USA), MnO_2 (98%, Aladdin, China), Cr_2O_3 (98%, Alfa, USA), NiO (99%, Aladdin, China), ZrO_2 (99.99%, Aladdin, China), In_2O_3 (99.99%, Aladdin, China), and CaO (99.6%, Aladdin, China) were precisely weighed according to the chemical formulation below, $94.38\text{ZnO} - 1.5\text{Bi}_2\text{O}_3 - 1.0\text{Co}_2\text{O}_3 - 0.5\text{MnO}_2 - 0.10\text{Cr}_2\text{O}_3 - 1.0\text{NiO} - 1.0\text{CaO} - 0.02\text{In}_2\text{O}_3 - 0.5\text{ZrO}_2$ (mol%). These powders were dispersed in anhydrous ethanol and homogenized via ball milling at 300 r/min for enhanced mixing efficiency. The resulting slurry was subsequently dried and finely milled to achieve a uniform particle size. The prepared powder was then combined with a 3 mol% acetic acid solution at a 5:1 mass ratio and thoroughly mixed in a mortar. The homogenous mixture was poured into a 40 mm diameter steel die under a uniaxial pressure of 200 MPa and sintered at 300 °C with a ramp rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ to produce cold-sintered samples. For annealing, the cold-sintered samples were heated in air using a muffle furnace at a rate of $1^\circ\text{C}\cdot\text{min}^{-1}$ to 850 °C and held for 2 h. For regional analysis, the edge and center portions of the samples were mechanically separated by precision cutting.

2.2 Material characterization

The phase composition of the samples was assessed using an X-ray diffractometer (XRD; PANalytical Empyrean, the Netherlands). Microstructural analysis and elemental mapping of the cross-sections were performed with a scanning electron microscope (SEM; Carl Zeiss Microscopy LLC, Zeiss, Germany) and a transmission electron microscope (TEM; Titan3 G2, FEI, USA) equipped with energy dispersive spectroscopy (EDS). The average grain size of the ceramics was determined via the linear intercept method. Bulk density was measured using the mass-to-geometric volume ratio alongside the Archimedes principle. Microcomputed tomography (micro-CT) was conducted using an X-ray inspection system (V|tome|x M300/180, Germany), and the samples were trimmed to approximately 2 mm in size to ensure high spatial resolution. Mesoporosity and specific surface area were characterized by nitrogen adsorption-desorption measurements based on the Brunauer-Emmett-Teller (BET) method using a surface area and pore-size analyzer (Autosorb-iQ-MP, USA). The thermal decomposition process of cold-sintered samples was recorded by a thermogravimetric analyzer (TG; SDT Q600, TA, USA). Karl Fischer moisture determination was carried out using an oven (Karl Fischer, DO308, Mettler Toledo, Swiss) coupled with coulometric titration (860 Oven Sample Processor with 852 Coulometer, Metrohm, Switzerland). For electrical characterization, gold electrodes were deposited on both surfaces of the samples using a high-resolution sputter coater (Q150TS, Quorum, UK). For both cold-sintered and annealed samples, a

full-area electrode was applied on one side, while the opposite side was coated with a circular electrode of 8 mm in diameter. The current density–electric field strength (J – E) characteristics were measured using a pA meter (HP4140B, Hewlett-Packard, USA) operated in direct current (DC) mode. Capacitance–voltage (C – V) behavior was obtained using a broadband dielectric spectrometer (Novocontrol Concept 40, Novocontrol, Montabaur, Germany) over a voltage range of 0–40 V at 1 kHz.

3 Results and discussion

3.1 Mechanistic analysis of regional heterogeneity

Simplified simulations of the temperature and strain distributions within the green body confined in a steel die were first performed (Figs. 2(a) and 2(b)). The green body was modeled as a continuous medium under die-wall constraints, with the temperature and applied pressure set to 300 °C and 300 MPa, respectively. The ZnO compact was treated as a homogeneous continuum medium to simplify the simulation process. In addition, the applied pressure in the model was moderately increased to 300 MPa to provide clearer visualization of the strain-transfer behavior. Since 200–300 MPa already corresponds to a near-saturated pressure regime for cold-sintered ZnO varistor ceramics, the use of 300 MPa does not substantially deviate from the actual experimental conditions. As heat transfer during cold sintering proceeds from the die toward the compact, a temperature gradient naturally develops from the edge toward the center, as highlighted in the enlarged view of Fig. 2(a). In addition, the simulated strain field reveals a pronounced attenuation of strain in the central region (Fig. 2(b)). To verify the die-wall pressure effect, green bodies with the same composition were prepared, and the true density (ρ_i) of the center and edge regions was measured using the Archimedes method. The theoretical density (ρ_0) of the sample was calculated as Eq. (1):

$$\rho_0 = \left(\sum m_i \% M_i \right) / \sum V_i \quad (1)$$

where M_i is the molar mass of each component, m_i is the molar percentage of each component ($i = 1, 2, \dots$), and ρ_i is the theoretical density of each constituent phase [20]. The ρ_i of each sample was then determined based on the ratio ρ_i/ρ_0 . A comparison of ρ_r across five sample sets reveals a marginally higher average density (ρ_{aver}) in the edge regions, indicative of increased powder compaction at the periphery and an accelerated densification rate (Fig. 2(c)). In addition, TG analysis of the cold-sintered samples reveals a larger mass loss in the edge region (CSP-edge) than in the center (CSP-center) (Fig. 2(d)). As cold sintering assisted by acetic acid solutions promotes the formation of acetate intermediates, such as zinc, cobalt, and calcium acetate, a higher decomposition extent indicates a more complete reaction during cold sintering. Notably, the dominant mass loss occurs above 290 °C, which closely corresponds to the thermal decomposition temperature of these acetate species [21,22]. The more pronounced dissolution-precipitation reactions observed in the CSP-edge sample can be attributed to the enrichment of moisture and a more uniform thermal environment. Capillary forces combined with pressure gradients drive the transient liquid phase toward the sample periphery, while stronger thermal radiation at the edge further intensifies dissolution-precipitation kinetics, thereby accelerating local densification. To elucidate the mechanism of liquid-phase transport, residual moisture in different regions was quantified by Karl Fischer titration. Two independent samples were examined for both the center and edge

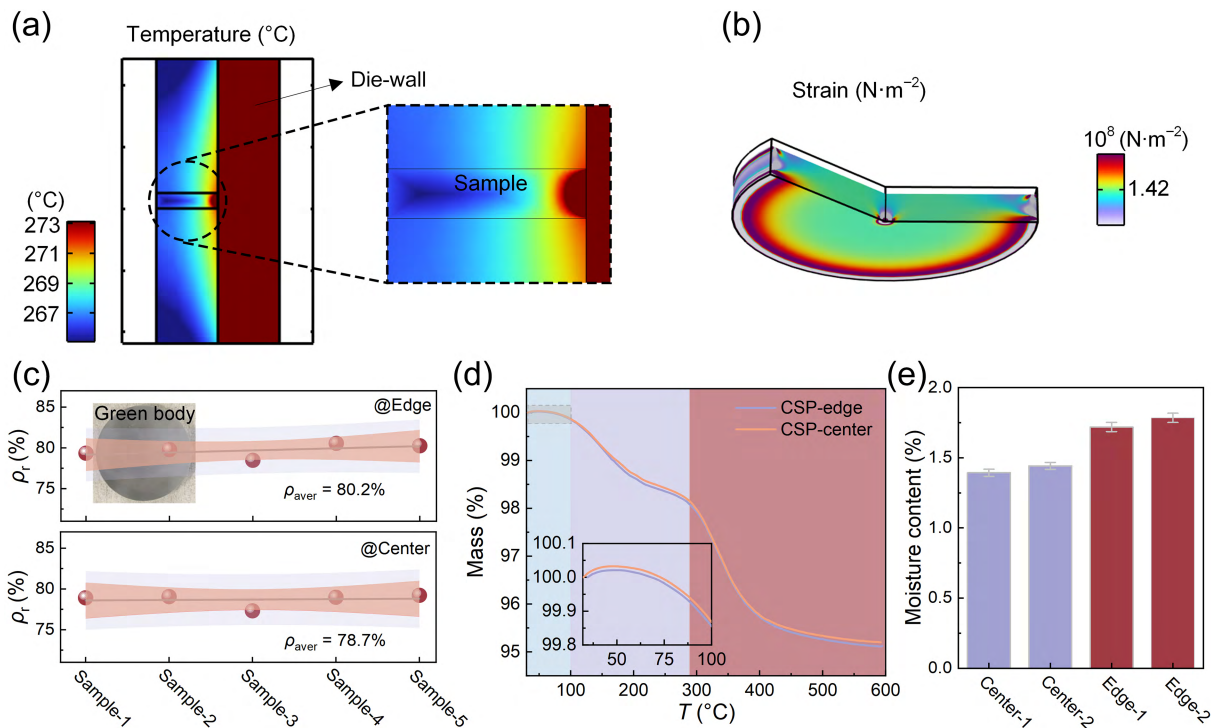


Fig. 2 Simulated (a) temperature distribution and (b) strain distribution of the sample during the CSP. (c) Relative density statistics of the green bodies. (d) TG analysis of the CSP-edge and CSP-center samples. (e) Residual moisture content in the cold-sintered samples; center-1 and center-2 denote two samples taken from the central region of the cold-sintered sample, while edge-1 and edge-2 denote two samples collected from the edge region.

regions. As expected, the edge region exhibits a higher moisture content than the center, as shown in Fig. 2(e).

To further evaluate the plausibility of thermocapillary flow and convective transport during the CSP, order-of-magnitude estimates of the Marangoni number (M_a) and Péclet number (P_e) were performed. The Marangoni number, which characterizes the relative importance of surface-tension-driven convection to thermal diffusion, can be expressed as Eq. (2):

$$M_a = (|\partial\gamma/\partial T|\Delta T \cdot L)/(\mu \cdot \alpha_T) \quad (2)$$

where $\partial\gamma/\partial T$ is the temperature coefficient of surface tension, μ is the viscosity, α_T is the thermal diffusivity, and L is the characteristic length scale [19,23,24]. Based on literature-reported values for transient liquid phases in oxide systems, $|\partial\gamma/\partial T|$ is typically on the order of 10^{-4} – 10^{-3} N·m⁻¹·K⁻¹ [25], while the viscosity of molten or solution-assisted phases at moderate temperatures can range from 10^{-2} to 10^{-1} Pa·s [26]. Thermal diffusivity is generally on the order of 10^{-7} m²·s⁻¹ [27]. Taking $\Delta T \approx 6$ K (from simulation) and $L \approx 40$ mm (sample size), the estimated Marangoni number is 2400–240,000. This suggests that thermocapillary flow is not dominant but can provide a nonnegligible contribution to mass transport during the CSP.

Similarly, the Péclet number, which compares convective transport to diffusive transport, can be expressed as Eq. (3) [28]:

$$P_e = uL/D \quad (3)$$

where u is the characteristic flow velocity, and D is the effective diffusion coefficient. Using the scaling relation for Marangoni-driven flow $u \sim \Delta\gamma/\mu$ and assuming typical diffusion coefficients for ionic species in liquid-assisted sintering systems ($D \approx 10^{-10}$ – 10^{-9} m²·s⁻¹) [29–31], the estimated P_e is on the order of unity or higher at the sample periphery. These results indicate that both convective and diffusive transport mechanisms may coexist, with convection becoming increasingly relevant near the edge region

where liquid accumulation and temperature gradients are more pronounced. Therefore, the proposed mechanisms should be regarded as coupled transport processes rather than strictly independent or dominant contributions.

3.2 Regional variations in microstructural features

A 40 mm-diameter cold-sintered sample was sectioned to evaluate regional variations (Fig. 3(a)) with the corresponding annealed counterparts designated AN-center and AN-edge. XRD analysis was used to characterize the phase composition and solid solubility in each region, thereby assessing the completeness of the CSP (Fig. 3(b)). From the perspective of the cold-sintered samples, all samples exhibit the hexagonal wurtzite structure of ZnO, accompanied by the appearance of a Bi₂O₄ secondary phase. This observation is consistent with our previous findings [32], where metastable β -Bi₂O₃ was shown to exhibit enhanced reactivity under cold sintering conditions, readily undergoing phase transformation and absorbing oxygen released from other metal oxides to produce Bi₂O₄. Despite the presence of multiple metal-oxide dopants, XRD analysis revealed only ZnO and Bi₂O₄ crystalline phases. The lack of detectable other secondary phases may be attributed to dopant contents below the XRD detection threshold (1%–3%) or amorphous incorporation of dopants [33,34]. Upon annealing, the Bi₂O₄ peaks gradually evolved into the δ -Bi₂O₃ phase, a well-known phenomenon in ZnO-based varistor ceramics, indicative of effective thermally driven phase transformation.

More importantly, magnification of the ZnO characteristic diffraction peak ($\sim 32^\circ$) highlights the solid solubility of dopants within the ZnO matrix, providing a key metric for identifying regional heterogeneity. As depicted in Fig. 3(c), the CSP-edge sample shows an evident shift toward lower 2θ values compared with the CSP-center sample, indicating a tendency for lattice expansion in the ZnO matrix. CSP is widely recognized not only

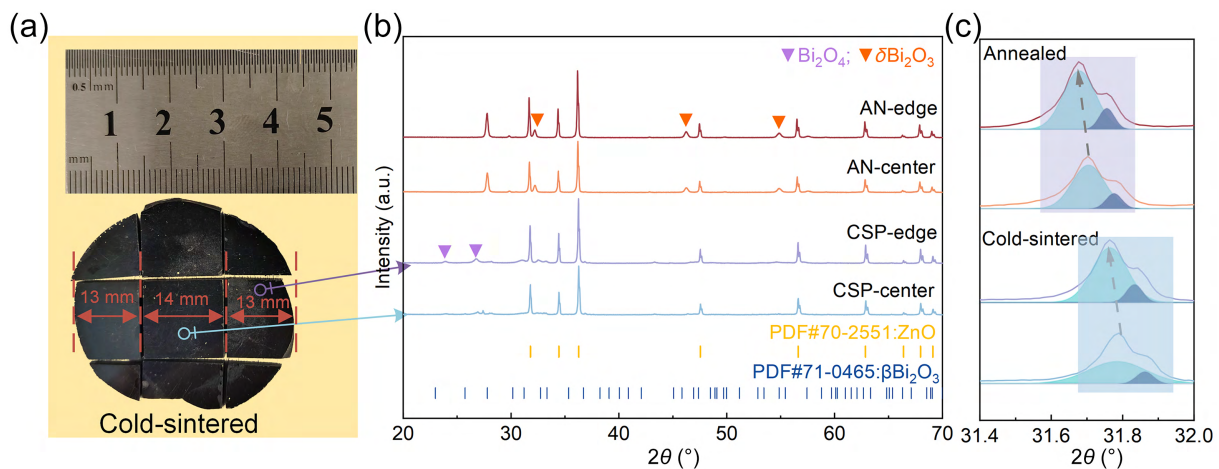


Fig. 3 (a) Photograph of 40 mm diameter cold-sintered ZnO-based varistor ceramic and schematic illustration of regional partitioning strategy. Disk was divided into three approximately equal sections along the diameter direction. (b) XRD patterns of cold-sintered and annealed samples collected from center and edge regions, showing phase evolution before and after annealing. (c) Enlarged view of diffraction region at approximately 31.7° in (b).

as a method of densification but also as a reactive process that facilitates enhanced ionic substitution. According to Bragg's law [33,35], Zn^{2+} ($r = 0.74 \text{ \AA}$) can be partially substituted by smaller cations such as Co^{3+} ($r = 0.55 \text{ \AA}$), Mn^{3+} ($r = 0.58 \text{ \AA}$), and Cr^{3+} ($r = 0.62 \text{ \AA}$), as well as by larger In^{3+} ions ($r = 0.80 \text{ \AA}$) [32]. Considering the elemental distribution and the ionic radii of the dopant species, it can be inferred that In^{3+} plays a dominant role in the lattice expansion of ZnO. The pronounced lattice expansion at the CSP edge indicates that a more active solid solution reaction occurs at the periphery. The Rietveld refinement of the ZnO diffraction peaks (Fig. S1 in the Electronic Supplementary Material (ESM)) provides a direct comparison of the lattice parameter evolution, as summarized in Table S1 in the ESM. Compared with the CSP-center sample, the CSP-edge sample exhibits a noticeable expansion along the a/b axis, increasing from 3.24813 to 3.24829 $\text{\AA}$. A more pronounced lattice expansion is observed after annealing. Although the c -axis shows a slight contraction, the overall unit-cell volume still increases. This regional heterogeneity is further inherited by the annealed state, as the AN edge shows an enhanced level of ionic substitution. Owing to the more developed interparticle necks achieved during cold sintering, the CSP-edge sample allows easier dopant diffusion and substitution under identical annealing conditions.

A comparative microstructure was collected to elucidate the differences between the edge and center regions of the cold-sintered and annealed samples (Figs. 4(a)–4(h)). The CSP-center sample (Figs. 4(a) and 4(b)), although reasonably densified, still exhibits distinct individual grains with visible pores and traces of insufficient sintering. Conversely, the CSP-edge sample (Figs. 4(c) and 4(d)) demonstrates pronounced densification with well-developed grain bonding and neck formation, indicative of a more advanced sintering stage. Quantification of the average grain size (G_{aver}) indicates that the CSP-edge sample possesses a larger G_{aver} (~233 nm), confirming its superior sintering state. Moreover, while no pronounced difference in grain size was observed after annealing, the AN-center sample displayed noticeably larger and more numerous pores, reinforcing the preestablished advantage of the AN-edge region developed during cold sintering. Fig. 4(i) summarizes the corresponding grain size and relative density and further compares the densification levels of ZnO-based varistor ceramics fabricated by various mainstream sintering techniques (Fig. 4(j)) [33,36–55]. Notably, all referenced data, except those from this work, were obtained from samples with diameters below 15 mm. It can be observed that small-sized cold-sintered samples

achieve a densification level ($\rho_r \geq 97\%$) comparable to that of other sintering techniques. However, large-scale cold-sintered samples display a moderately reduced relative density ($\rho_r = 94.3\%$), highlighting the importance of investigating large-format cold-sintered samples for promoting the industrial scalability of ZnO-based ceramics.

Furthermore, elemental mapping corresponding to Figs. 4(b), 4(d), 4(f), and 4(h) provides compelling evidence for the regional heterogeneity induced by cold sintering, as illustrated in Figs. S2–S5 in the ESM. The CSP-center sample displays a homogeneously dispersed elemental distribution and scarce elemental clustering (Fig. S2 in the ESM), implying a low extent of intergranular phase formation. In contrast, the CSP-edge sample exhibits pronounced elemental aggregation, particularly of Bi (Fig. S3 in the ESM). Combined with the XRD results of the cold-sintered samples, this aggregation is inferred to be the Bi_2O_4 -rich phase. By comparing the elemental distributions of the two types of samples, the more pronounced Bi enrichment observed in the CSP-edge region is likely attributable to the more advanced cold-sintering state at the periphery, which facilitates the formation of a more abundant Bi_2O_4 -rich phase. It is evident that the enhanced densification in the edge region of the cold-sintered sample is reflected in grain growth and phase transformation. In the annealed samples, the AN-center sample develops a more distinct Birich phase (Fig. S4 in the ESM), whereas the AN-edge sample exhibits diminished elemental segregation as a consequence of its higher level of ionic incorporation (Fig. S5 in the ESM).

To visualize the microporous structure of the cold-sintered samples, micro-CT was employed to analyze the pore distribution. Bulk samples of approximately $2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$ were extracted from the CSP-center and -edge regions for comparative analysis. It is worth noting that, due to the spatial resolution limit of the micro-CT system ($\sim 1 \text{ }\mu\text{m}$), the comparison of structural heterogeneity between the edge and center regions can only be performed based on the detection of relatively large open pores. The three-dimensional (3D) reconstruction of the CSP-edge sample (Figs. 5(a)–5(c)) reveals a highly compact structure without any observable micron-sized pores. No visible pores were detected along the X, Y, or Z projection planes (Fig. 5(a)). A 3D model with a side length of $1.5 \text{ }\mu\text{m}$, reconstructed from the real sample for magnified observation, yielded consistent results, confirming the absence of detectable porosity. A similar analysis was carried out for the CSP-center sample (Figs. 5(d)–5(f)), where distinct micron-sized pores were detected. The pore distribution

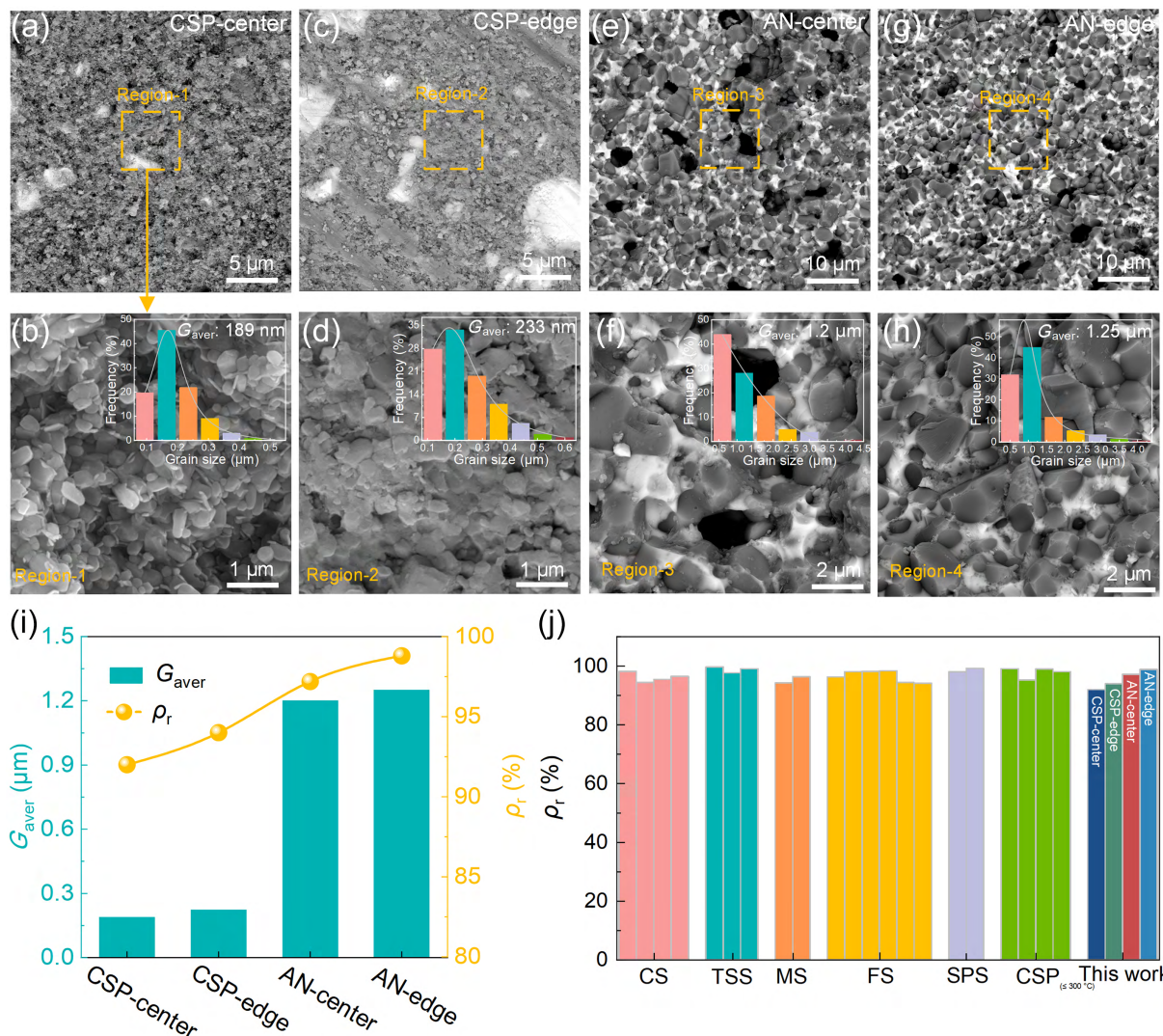


Fig. 4 SEM micrographs of (a) CSP-center and (b) corresponding magnified Region-1; (c) CSP-edge and (d) corresponding magnified Region-2; (e) AN-center and (f) corresponding magnified Region-3; (g) AN-edge and (h) corresponding magnified Region-4. (i) Statistical comparison of ρ_r and G_{aver} . (j) Comparison of ρ_r of ZnO-based varistor ceramics processed by different sintering techniques (CS: conventional sintering; TSS: two-step sintering; MS: microwave sintering; FS: flash sintering; SPS: spark plasma sintering; CSP: cold sintering process).

across the X-, Y-, and Z-projection planes (Fig. 5(d)) shows volumes of approximately 0.0005 mm^3 , while the pore-scale histogram (Fig. 5(e)) indicates that most pores fall below 0.0003 mm^3 , with only a few larger voids. These results align closely with the SEM observations, collectively indicating that the CSP-edge sample achieved superior densification during cold sintering.

3.3 Regional mesoporosity and surface area analysis

The N_2 adsorption-desorption isotherms (Fig. S6 in the ESM) correspond to a type IV profile according to the International Union of Pure and Applied Chemistry (IUPAC) classification, indicating the occurrence of capillary condensation within the mesoporous structure of the ceramic material [56]. The CSP-center sample displays a steep rise in the adsorption branch at high relative pressures ($P/P_0 > 0.8$, where P is the partial pressure of nitrogen and P_0 is its saturation vapor pressure), suggesting the presence of open and connected macropores. Both the CSP-center and CSP-edge exhibit distinct H3-type hysteresis loops with large adsorption capacities. The CSP-center sample shows a significantly higher adsorption capacity than the others, implying a greater abundance of macropores, which can be attributed to

insufficient sintering that leaves residual pores and intergranular voids. In contrast, the annealed samples exhibit smaller hysteresis loops and lower adsorption capacities, characteristic of slit-shaped mesopores (H3 type). This behavior reflects the significant elimination of macropores, leaving only a small fraction of mesopores originating from intergranular gaps. Such evolution results from the enhanced grain growth and densification of grain boundaries during the annealing process. Additionally, the cumulative (Figs. 6(a)–6(d)) and differential pore volume (Fig. 6(e)) data were compiled for all four samples, allowing for direct comparison of their specific surface areas and total pore volumes (Fig. 6(f)). As seen in the pore-size distribution profiles, higher peaks indicate greater pore volumes, whereas narrower peaks suggest a concentrated pore-size range and higher structural uniformity. Conversely, broader peaks correspond to a wider and more disordered pore distribution. In the CSP-center sample, the dimension of the pores is mainly distributed in the range of $40\text{--}120 \text{ Å}$, with a substantial fraction of large pores ($0.385 \text{ cm}^3\text{g}^{-1}$), indicative of numerous unclosed intergranular voids resulting from insufficient sintering. The broad pore-size distribution also points to uneven grain growth. In contrast, both AN-center and AN-edge samples exhibit narrower distributions ($16\text{--}40 \text{ Å}$), where

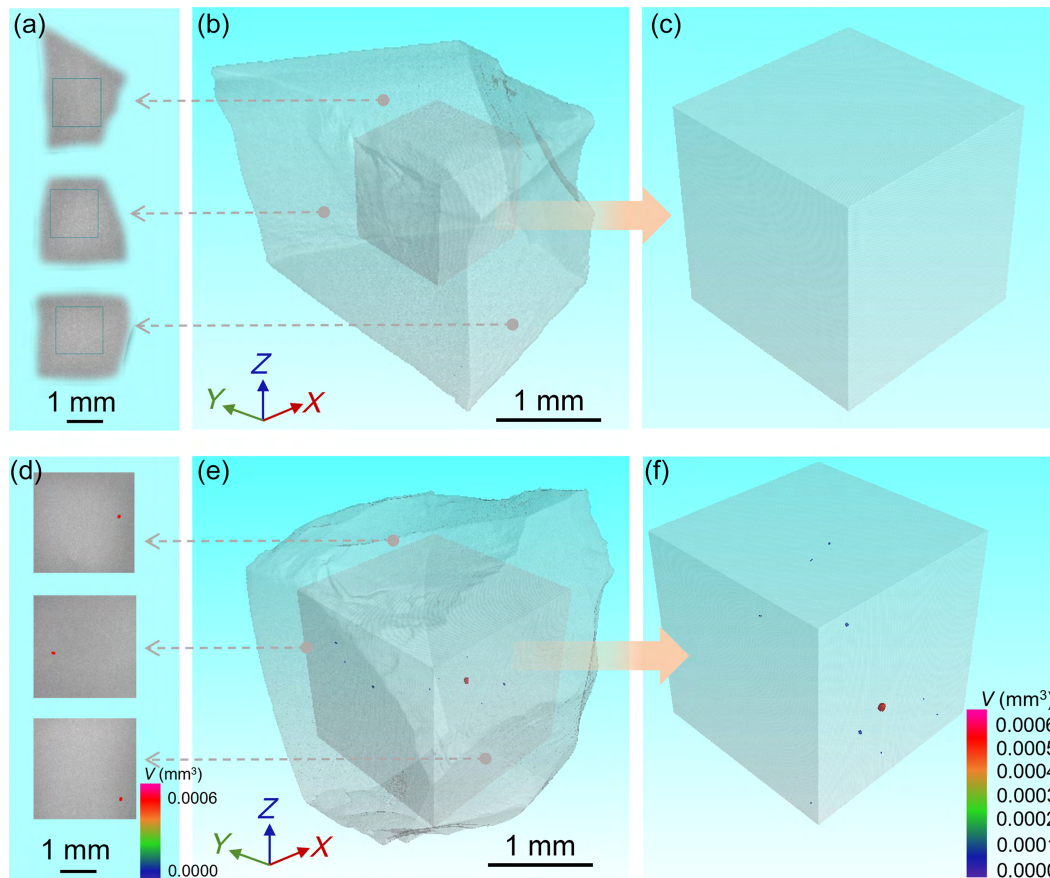


Fig. 5 (a) Orthogonal projections of micro-CT images of CSP-edge sample along three principal axes. (b) Representative micro-CT image of CSP-edge sample. (c) 3D reconstruction extracted from (b). (d) Orthogonal projections of micro-CT images of CSP center sample. (e) Representative micro-CT image of CSP center sample. (f) 3D reconstruction extracted from (e).

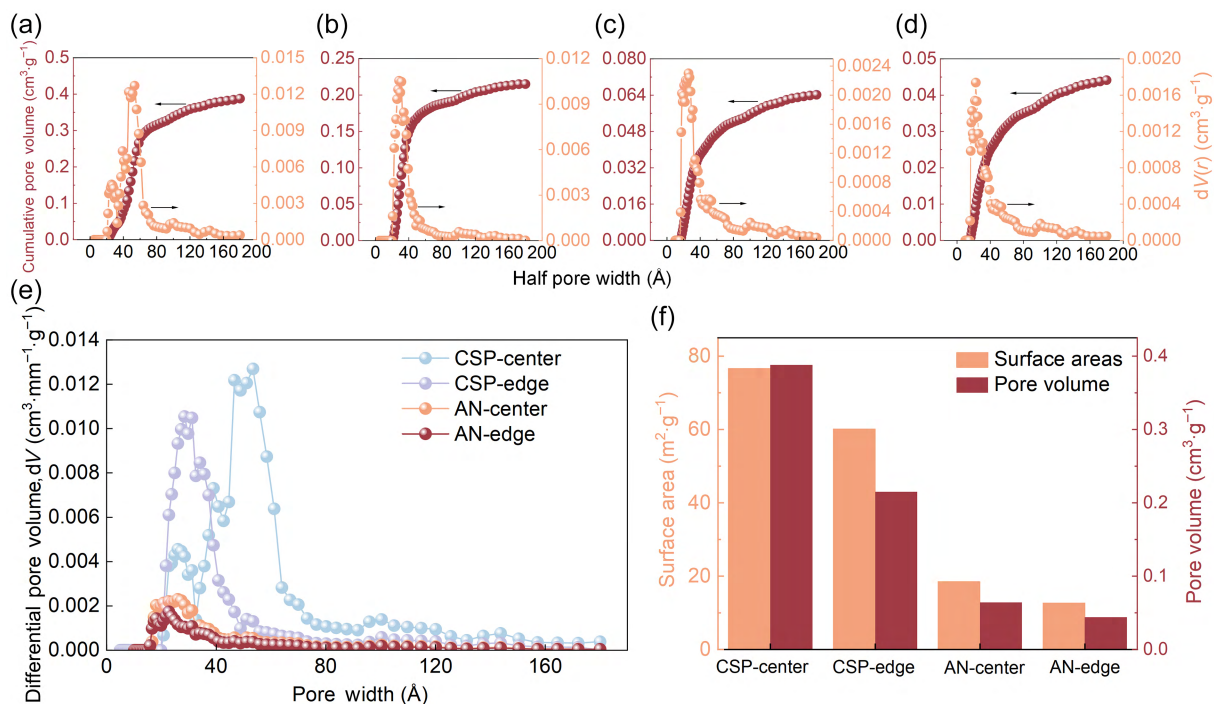


Fig. 6 Cumulative pore volume distributions of (a) CSP-center, (b) CSP-edge, (c) AN-center, and (d) AN-edge samples. (e) Differential pore volume distributions of all four samples. (f) Comparison of specific surface areas and pore volumes for all samples.

the dominance of smaller pores reflects enhanced grain-boundary uniformity and structural refinement. Distinctively, the AN-edge

sample demonstrates the smallest pore size ($\sim 22.7 \text{ \AA}$) and the lowest total pore volume ($\sim 0.045 \text{ cm}^3 \cdot \text{g}^{-1}$), signifying the highest

densification among all samples. Moreover, the specific surface area decreases in the sequence CSP-center > CSP-edge > AN-center > AN-edge, which perfectly correlates with the sintering degree inferred from the grain-size analysis.

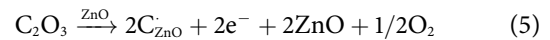
3.4 Electrical performance disparities across regions

Fig. 7(a) presents the J - E responses of both the cold-sintered and annealed samples measured at room temperature. The nonlinearity was quantified using Eq. (4):

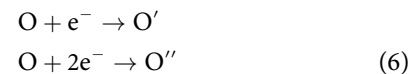
$$\alpha = 1/\log(E_{1\text{mA}}/E_{0.1\text{mA}}) \quad (4)$$

where $E_{1\text{mA}}$ (also referred to as the breakdown field, E_b) and $E_{0.1\text{mA}}$ correspond to the electric field strengths at current densities of 1 and 0.1 mA·cm⁻², respectively [55,57]. A nonlinear coefficient of α close to 1 denotes ohmic conduction, whereas a larger α signifies pronounced varistor behavior [54]. The leakage current density J_L is defined at $E = 0.75E_b$. Figure 7(b) summarizes how regional heterogeneity influences the electrical performance for both cold-sintered and annealed samples. In addition, statistical error analysis of the electrical properties associated with regional heterogeneity was performed based on the data presented in Fig. 7(a) and Fig. S7 in the ESM. Despite exhibiting a comparatively high breakdown field, the CSP samples display only poor nonlinearity ($\alpha = 2$) accompanied by a pronounced leakage current. This suggests that cold sintering promotes initial densification yet does not generate the robust ϕ_b or well-developed intergranular phases required for effective varistor action. The XRD results corroborate this interpretation, revealing only marginal ionic incorporation and the absence of a fully developed grain-boundary phase. Consequently, the high E_b in CSP samples primarily stems from suppressed grain growth, whereas inadequate densification and immature grain-boundary structures are responsible for the increased leakage current and low α . Notably, the CSP-edge sample exhibits higher E_b and α than the CSP-center sample, which can be attributed to the more developed microstructure at the edge during cold sintering. After annealing, the electrical performance of both the AN-center and AN-edge samples is substantially improved. Benefiting from the fine-grained microstructure preserved by low-temperature annealing, samples from all regions demonstrate ultrahigh breakdown fields (> 1000 V·mm⁻¹) together with excellent nonlinearity ($\alpha > 59$). Nevertheless, the regional heterogeneity persists into the annealing stage, resulting in a higher ρ_r for the AN-edge sample (Fig. 4(i)), which in turn effectively suppresses the leakage current. From the perspective of solid solution, ZnO grains in the CSP-edge region exhibit more intimate contact with

the various dopant particles (Figs. 4(b) and 4(d)), which facilitates the formation of interparticle necks between ZnO and dopant species during subsequent annealing. This enhanced interfacial connectivity effectively accelerates the solid-solution reactions of dopants such as Mn₂O₃, Co₂O₃, and Cr₂O₃ into the ZnO lattice, leading to a higher degree of ionic incorporation at the edge. During annealing, C₂O₃-type metal oxides can dissolve into the ZnO lattice, accompanied by defect reactions described as Eq. (5):



where C denotes Mn, Co, Cr, or In. Although annealing at 850 °C is sufficient to effectively suppress dopant volatilization, intimate interparticle contact remains the decisive factor governing efficient ionic incorporation [58]. In ZnO-based varistor ceramics, effective dopant solubility plays a critical role in enhancing oxygen adsorption at grain boundaries and strengthening the associated Schottky barriers. We propose that the reactions described in Eq. (5) proceed more intensively in the CSP-edge region, where a large population of free electrons (e^-) and adsorbed oxygen species (O_{ad}) is generated. The accumulation of O_{ad} at the ZnO grain boundaries will bond with the free electrons distributed along the edges of the N-type ZnO grains [59]. As a result, a significant amount of negatively charged O' and O'' will be produced at the ZnO grain boundaries, leading to higher double Schottky barriers and a wider depletion layer [60]. The defect reactions can be expressed as Eq. (6) [59]:



Furthermore, a small sample with a diameter of 12.7 mm was fabricated using the same composition and CSP to further highlight the engineering implications of regional heterogeneity in cold sintering (Fig. S8 in the ESM). The small-sized sample exhibits a higher breakdown field ($E_b = 1292 \text{ V}\cdot\text{mm}^{-1}$) and a higher nonlinear coefficient ($\alpha = 88$), both exceeding those of the edge and center regions in the large-sized samples. This phenomenon is likely associated with the four coupled mechanisms discussed above. Specifically, the small-sized sample experiences more uniform and concentrated temperature/strain fields, while the liquid-phase migration pathways become shorter and more efficient during the CSP.

3.5 Mechanistic interpretation

To gain deeper insight into the influence of regional heterogeneity on defect states, the capacitance of the ceramics under various bias

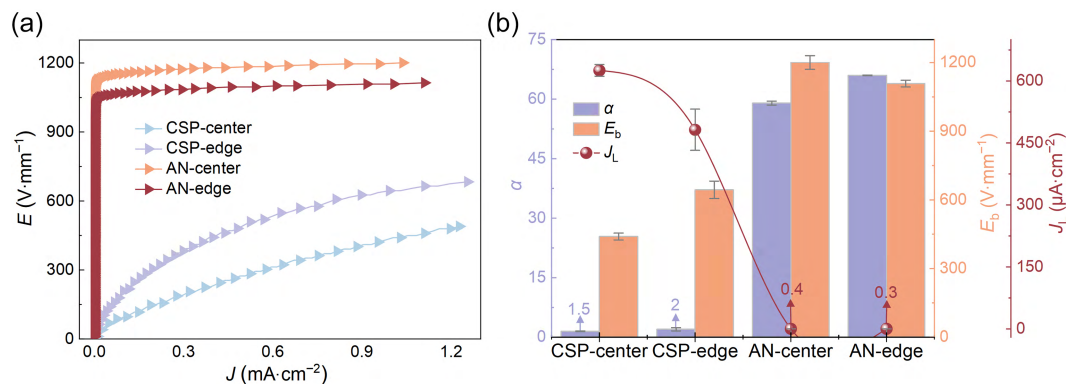


Fig. 7 (a) J - E characteristics of the cold-sintered and annealed samples collected from the center and edge regions, including the CSP center, CSP edge, AN center, and AN edge. (b) Comparison of the extracted electrical parameters for the four samples, highlighting the regional differences in varistor performance induced by cold sintering and subsequent annealing.

voltages was measured, as shown in Fig. 8(a). Based on the capacitance–voltage (C – V) characteristics, the donor density (N_D), interface N_S , and ϕ_b of the ZnO ceramics were calculated using Eq. (7) [61]:

$$(1/C - 1/2C_0)^2 = 2n^2(\phi_b + V_{gb})/(s^2 q N_D \epsilon_0 \epsilon_r) \quad (7)$$

where C_0 denotes the initial capacitance measured at zero bias, while C represents the capacitance measured under an applied bias voltage. q is the elementary charge, n is the number of grain boundaries involved in conduction, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of ZnO, and s is the electrode area. The voltage drop across an individual grain boundary (V_{gb}) is defined as $V_{gb} = V_h/d$, where V_h is the applied voltage and d is the average grain size of the ZnO ceramics. According to these relationships, ϕ_b and N_D were extracted from the intercept and slope of the linear fit with respect to V_{gb} . In addition, N_S can be pledged according to $N_S = (2N_D \epsilon_0 \epsilon_r \phi_b / q)^{1/2}$ [61,62]. However, the CSP sample fails to yield a meaningful linear slope ($k = 2n^2/(s^2 q N_D \epsilon_0 \epsilon_r)$) in the $(1/C - 1/2C_0)^2 - V_{gb}$ analysis, indicating that the measured capacitance is not governed by a well-defined depletion capacitance at the grain boundaries. This behavior implies that a stable depletion-type double-Schottky barrier is not effectively established in the as-cold-sintered sample, and thus, the conventional C – V barrier-extraction model becomes inapplicable within the tested bias and frequency window. This is because their grain boundaries are not yet electrically mature and are partially covered by dissolution–precipitation-derived amorphous/interfacial layers. As a result, the C – V fitting shows segmented behavior rather than a single linear depletion–capacitance relationship. The J – E analysis further confirms that the cold-sintered samples exhibit essentially ohmic behavior with negligible nonlinearity ($\alpha \leq 2$). This behavior can be fundamentally attributed to the absence of a continuous, enriched, and stable intergranular phase derived from low-melting constituents such as Bi_2O_3 . Moreover, instead of forming a well-defined grain-boundary layer, the cold-sintered samples are enveloped by a relatively thick interfacial layer, a feature that is subsequently corroborated by the TEM analysis. In contrast, the annealed samples overcome the aforementioned limitations upon thermal activation at 850 °C, thereby exhibiting markedly improved electrical performance. The edge region attains higher densification and a more continuous intergranular phase, which effectively increases and homogenizes the grain-boundary interface state density ($N_S = 2.9 \times 10^{15} \text{ m}^{-2}$) (Fig. 8(b)). This promotes the formation of stronger and more uniform depletion-type double Schottky barrier networks, resulting in a substantially

enhanced nonlinear coefficient ($\alpha = 66$). By comparison, the center region retains residual porosity and discontinuous grain-boundary phases, leading to insufficient or spatially dispersed N_S ($2.84 \times 10^{15} \text{ m}^{-2}$) together with inhomogeneous N_D ($1.7 \times 10^{22} \text{ m}^{-3}$). It should be noted that the simultaneously increased N_S and N_D ($1.76 \times 10^{22} \text{ m}^{-3}$) values in the AN-edge sample are reasonably consistent with the defect characteristics of ZnO-based varistor ceramics. The intensified dissolution–precipitation and interfacial evolution near the edge region may simultaneously enhance donor incorporation and interface-state formation, thereby contributing to the increased ϕ_b . Although the difference in N_S appears relatively modest and does not reach an order-of-magnitude variation, its amplification effect on the electrical performance of the varistor ceramics is nevertheless quite pronounced [61,63]. These factors weaken the grain-boundary barriers and create preferential leakage pathways, thereby yielding a comparatively lower nonlinearity.

As discussed above, the electrical performance of ZnO-based varistor ceramics primarily depends on grain-boundary characteristics, making it essential to investigate the grain boundaries before and after annealing. Given the resolution limitations of SEM, TEM was utilized to conduct an in-depth analysis of the crystalline structure and grain-boundary features of the CSP-edge and AN-edge samples. Figure 9(a) presents the morphological features of the CSP-edge sample. Figure 9(b) shows a magnified view of an individual grain, where the selected-area electron diffraction (SAED) pattern along the $[001]$ zone axis confirms the hexagonal features of the ZnO matrix (inset). In addition, a thick interfacial layer was observed surrounding the ZnO grains (marked as Zone-1), which is inferred to be the product of the dissolution–precipitation process that occurred during cold sintering [32,52]. The interfacial morphology is distinctly shown in Fig. 9(c), and the corresponding elemental distribution reveals pronounced Bi enrichment (the inset and Fig. S9 in the ESM). High-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) analysis further quantifies the interfacial layer thickness to be approximately 7 nm (Fig. 9(d)). The low-resistance interfacial layer hindered the formation of a high grain-boundary potential barrier, while the considerable porosity in the cold-sintered samples further degraded their nonlinear behavior. Nevertheless, the small grain size of the cold-sintered ceramics contributed to a relatively high resistivity, resulting in an exceptionally high E_b .

In the AN-edge sample, a well-defined intergranular phase is clearly visible (Fig. S10 in the ESM), as marked in Zone-2 of Fig. 9(e). A higher-magnification image of this region (Fig. 9(f))

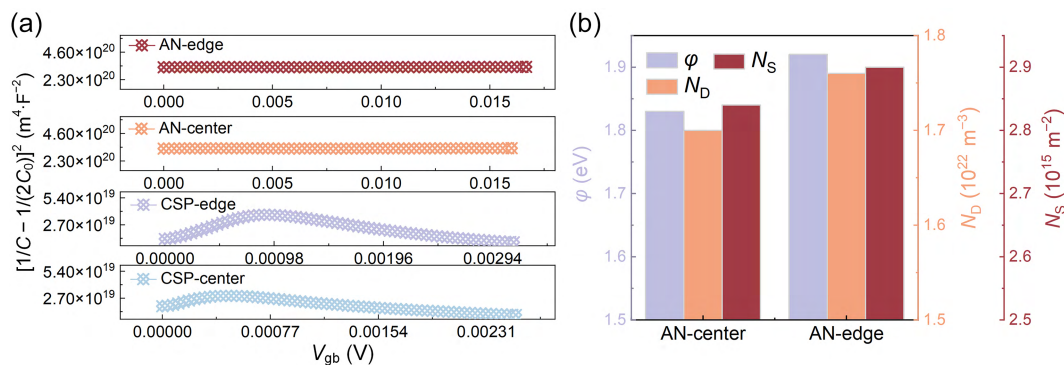


Fig. 8 (a) C – V characteristics of cold-sintered and annealed samples collected from center and edge regions, including CSP center, CSP edge, AN center, and AN edge. (b) Defect-state parameters extracted from C – V analysis, including N_D , N_S , and ϕ_b , illustrating the regional differences in grain-boundary electrical characteristics after annealing.

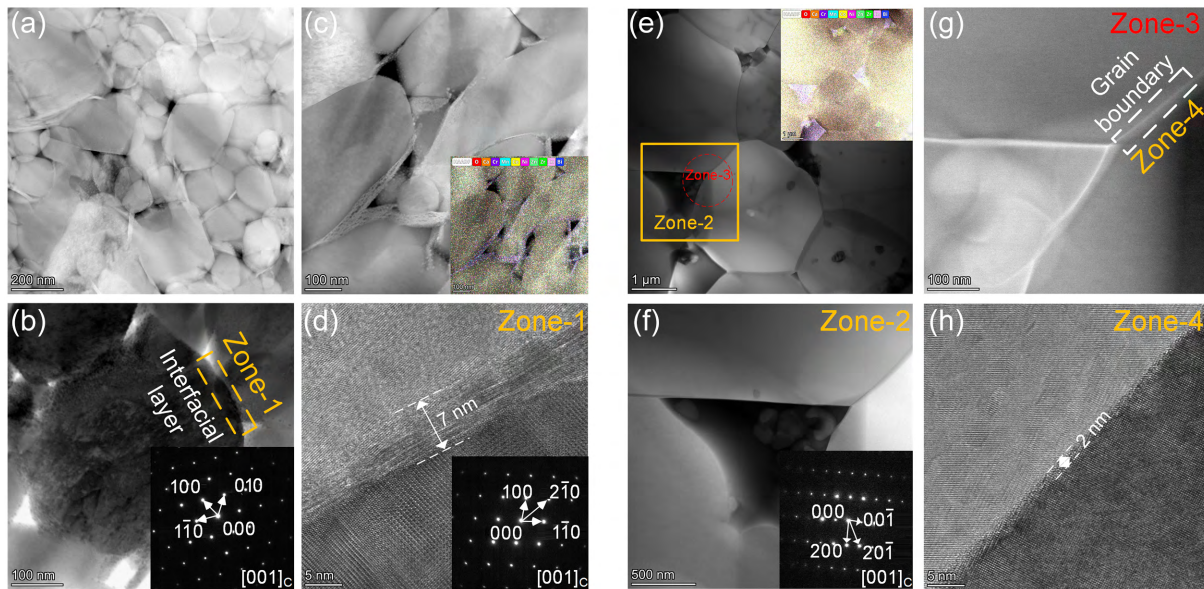


Fig. 9 HAADF-STEM image of (a) CSP-edge sample and (b) an individual grain, with corresponding SAED pattern shown as an inset, confirming ZnO matrix. (c) HAADF-STEM image of interfacial morphology with corresponding elemental distribution maps (inset). (d) Interfacial-layer morphology in Zone-1 with corresponding SAED pattern (inset). (e) HAADF-STEM image of AN-edge sample with corresponding elemental maps (inset). (f) Enlarged view of Zone-2 with SAED pattern of intergranular phase (inset). (g) Grain-boundary morphology in Zone-3. (h) High-magnification image of grain boundary corresponding to Zone-4.

reveals that the intergranular phase is well crystallized and aligns with a cubic structure ($Fm\bar{3}m$), verified by the SAED pattern obtained along the $[010]$ zone axis. Apart from this, a thin and well-defined grain-boundary layer formed after annealing can be observed in Zone-3 (Fig. 9(g)). Furthermore, a detailed examination of the grain boundary in Zone-4 determined a boundary thickness of approximately 2 nm (Fig. 9(h)). This observation provides a reasonable explanation for the fundamental role of the annealing process in enabling the superior nonlinearity of ZnO-based varistor ceramics. On the one hand, the transformation of the amorphous phase into a Birich phase effectively bridges adjacent grains while filling residual pores. On the other hand, the previously loose interfacial layer evolves into a high-resistive grain boundary under sufficient thermal activation, thereby significantly increasing the potential barrier height. Despite the pronounced grain growth induced by annealing, the initial consolidation and interparticle necks established during cold sintering enable the development of excellent varistor characteristics in ZnO ceramics at temperatures as low as ~ 850 °C. By comparison, such phase and interface reactions conventionally demand temperatures near 1100 °C in solid-state sintering routes. Accordingly, the superior varistor performance of the AN-edge sample over the AN-center can be ascribed to the more complete presintering and well-developed neck structures established in the CSP-edge region during the CSP.

In summary, due to the combined effects of higher σ_{eff} enhanced convection and Marangoni flow, and an elevated thermal gradient at the periphery, the edge region completes the CSP more rapidly and thoroughly. Consequently, the CSP-edge sample develops more pronounced interparticle necks and exhibits lower residual porosity. During the annealing stage, earlier chemical maturation of grain boundaries at the edge, coupled with preestablished interparticle necks, promotes their transformation into high-resistive boundaries and enhances solid-solution reactions. This results in a higher N_s and ϕ in the CSP-edge sample, accounting for its superior nonlinear varistor property.

4 Conclusions

This study systematically reveals the regional heterogeneity in large-sized ZnO-based varistor ceramics fabricated via cold sintering. The synergistic effects of radial pressure decay, liquid-phase migration, Marangoni convection, and pore evacuation lead to accelerated densification and intensified dissolution-precipitation at the sample edges. Semiquantitative analysis further suggests that the estimated Marangoni number ($M_a \approx 2.4 \times 10^3 - 2.4 \times 10^6$) and Péclet number ($Pe \gg 1$) render convection-assisted mass transport physically plausible during the CSP. As a consequence, the edge region exhibits lower residual porosity, more developed grain-boundary structures, and moderately improved grain-boundary electrical characteristics after annealing, including increased N_s and ϕ_b . Although the variation in N_s is not on an order-of-magnitude scale, its amplification effect on the electrical response is still pronounced, resulting in an improved nonlinearity coefficient ($\alpha = 66$) and breakdown field ($E_b = 1108 \text{ V}\cdot\text{mm}^{-1}$) at the sample edge. Furthermore, the superior α and E_b of the smaller-sized samples ($\sim 12.7 \text{ mm}$) further highlight the engineering importance of controlling regional heterogeneity during large-scale cold sintering. These findings not only elucidate the intrinsic regional effects of cold sintering but also provide essential theoretical guidance for optimizing large-scale processing and advancing the industrial application of cold-sintered electronic ceramics.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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