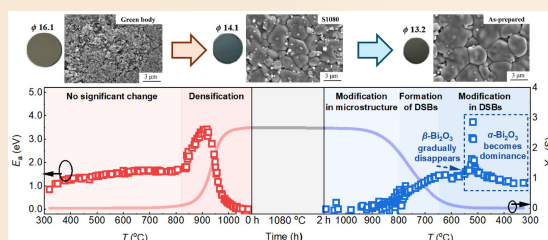


Tracking the formation of double Schottky barriers during sintering of ZnO varistor ceramics using *in-situ* dielectric spectroscopy

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ABSTRACT: Deciphering the dynamic evolution of double Schottky barriers (DSBs) during high-temperature sintering remains a fundamental challenge in establishing structure–function relationships in ZnO varistor ceramics. *In-situ* dielectric spectroscopy is employed to continuously monitor capacitance and conductance throughout the entire sintering process, with measurement fidelity ensured by rigorous decoupling of system impedance. During sintering, a pronounced transition to negative permittivity in ZnO varistor ceramics is directly observed above 700 °C, originating from electron plasma oscillations within the semiconducting bulk. The apparent activation energy (E_a) of direct current (DC) conductance is identified as a robust descriptor for tracking DSB evolution. The results reveal a temporal decoupling between microstructural densification and electrical functionalization: Grain growth is largely completed during the heating and soaking stages, whereas DSB formation predominantly occurs during the cooling stage. Specifically, from 800 to 650 °C, E_a increases from nearly 0 to approximately 1.4 eV, accompanied by an increase in grain boundary resistance (R_{gb}), indicating the progressive formation of DSBs. Scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) line scans of quenched samples further reveal grain boundary enrichment of Bi and Sb, accompanied by the redistribution of Mn and Ni after soaking and during cooling, supporting the concurrent evolution of the grain boundary chemical environment. Upon further cooling, DSB formation suppresses the free-carrier response, R_{gb} increases markedly, and the negative permittivity gradually disappears. Meanwhile, E_a decreases slightly from 650 to 600 °C and exhibits a distinct peak in the 500–600 °C range. *In-situ* X-ray diffraction (XRD) shows that this feature coincides with the gradual disappearance of β - Bi_2O_3 and the increasing dominance of α - Bi_2O_3 , suggesting that the Bi-rich phase transition contributes to the subsequent modification of DSBs. By directly linking *in-situ* electrical behavior to microstructural evolution during sintering, this work provides a deterministic framework for the rational design and performance optimization of functional electroceramics.



KEYWORDS: varistor; sintering; double Schottky barrier; dielectric spectroscopy; negative permittivity

1 Introduction

Unveiling intrinsic structure–function relationships is a longstanding goal for the advanced ceramic community, facilitating the development of high-performance devices such as transistors, sensors, detectors, and actuators [1–6]. Specifically, ZnO-based varistor ceramics are pivotal for overvoltage protection in electronic devices and power systems due to their superior nonlinear current–voltage (I – V) characteristics [7,8]. This

nonlinearity is primarily ascribed to the double Schottky barriers (DSBs) at grain boundaries (GBs) [9–11]. Formed during high-temperature sintering, DSBs render the varistors insulating at operating voltages and semiconducting under surges, thereby protecting parallel-connected equipment across a wide range of voltages from several volts to megavolts. Although the decisive role of DSBs in electrical performance is well established, their dynamic formation and evolution during sintering are still not fully understood [12–15]. Consequently, tracking the formation of

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DSBs throughout the entire sintering process is of great importance for developing advanced varistor ceramics [16–22].

Traditional characterization techniques for DSBs, including *I*–*V* deconvolution, capacitance–voltage (*C*–*V*) testing, and conventional dielectric spectroscopy, are carried out below 300 °C. However, the extremely high sintering temperatures, typically exceeding 1000 °C, present a substantial obstacle to investigating the evolution of DSBs *in situ* [23]. Consequently, current research on the structure–function relationships of ZnO varistor ceramics is largely restricted to the control variable method or rapid quenching. The former approach often involves separately evaluating the effects of elemental doping or sintering parameters, such as soaking temperature, holding time, and cooling rate, on the resulting microstructures and electrical properties [23–27]. The latter method must freeze specific sintering states by quenching to reconstruct a discrete sintering timeline. Nevertheless, these *ex-situ* methods can hardly capture the continuous, real-time evolution of DSB formation and are inherently resource intensive [28–30].

Recent *in-situ* studies of ZnO varistor ceramics during sintering have focused primarily on microstructural evolution and phase transformations [31,32]. For instance, densification was monitored via geometric evolution to construct master sintering curves, while phase transitions were characterized through *in-situ* thermal analysis [33], X-ray diffraction (XRD) spectra [32,34], and Raman spectra [35]. However, these techniques cannot directly reveal the formation of DSBs because DSBs originate from electrically active defect structures localized at GBs [9,14,36]. Consequently, the evolution of electrical properties during sintering remains insufficiently understood, and the intrinsic relationships among electrical response, grain boundary barrier formation, microstructural evolution, and phase transformations have yet to be established.

To address these gaps, *in-situ* electrical characterization is required to directly track the formation and evolution of DSBs during sintering. Building upon our preliminary conference report [39], advanced *in-situ* dielectric spectroscopy is employed to characterize carrier transport and electrical inhomogeneity throughout the sintering process. The high-temperature negative dielectric response is further analyzed to clarify the transition from Drude-like carrier transport to barrier-controlled electrical behavior during cooling. By correlating these electrical responses with microstructural and phase evolution, this study provides direct insight into the formation mechanism of DSBs during sintering.

2 Experimental

Commercial ZnO–Bi₂O₃-based green bodies containing Sb₂O₃, Co₂O₃, Mn₂O₃, and NiO as functional additives were used in this work, and the detailed formulation is summarized in Table 1. To ensure consistent composition and initial microstructure, all green bodies were taken from the same production batch, with an initial diameter of 16.1 mm and a thickness of 3 mm. The sintering curve is shown in Fig. 1(a). The samples were sintered in air at 1080 °C for 2 h using the same heating and cooling rates of 3.33 °C/min.

In-situ dielectric measurements were performed to monitor the electrical response of the samples throughout sintering. The

samples were measured over 10²–10⁶ Hz using an impedance analyzer (Concept 43, Novocontrol, Germany), which automatically recorded the dielectric response and sample temperature during the sintering process. Before the *in-situ* dielectric measurements, Pt electrodes were selected because of their high melting point and thermal stability [37,38]. They were screen-printed onto both surfaces of the ZnO green bodies and pre-fired to improve both adhesion to the samples and electrical contact with the Pt disk electrodes of the high-temperature impedance analyzer. The preparation procedure and pre-firing process are shown in Fig. S1 in the Electronic Supplementary Material (ESM).

To obtain the intrinsic dielectric response of the ZnO sample, a short-circuit reference was used to correct the background impedance arising from the internal resistance of the impedance analyzer and the Pt-electrode configuration. This correction was particularly important before stable DSB formation, when the ZnO ceramic exhibited low bulk resistivity and a high-temperature Drude-like free-carrier response [39]. The separate reference measurement was performed under an identical sintering process by directly shorting the Pt electrodes without the ZnO sample. The resulting temperature- and frequency-dependent short-circuit impedance ($Z_{s,short}'$, $Z_{s,short}''$) is subtracted from the total measured impedance ($Z_{s,total}'$, $Z_{s,total}''$) to obtain the intrinsic series impedance of the ZnO bulk ($Z_{s,ZnO}'$, $Z_{s,ZnO}''$) (Figs. S2–S4 in the ESM for the directly measured dielectric response and short-circuit reference). Accordingly, the intrinsic dielectric response was calculated using Eqs. (1) and (2):

$$C_p' = -\frac{1}{\omega} \cdot \frac{Z_{s,ZnO}''}{(Z_{s,ZnO}')^2 + (Z_{s,ZnO}'')^2} \quad (1)$$

$$Y_p' = \frac{Z_{s,ZnO}'}{(Z_{s,ZnO}')^2 + (Z_{s,ZnO}'')^2} \quad (2)$$

where C_p' is the parallel capacitance; Y_p' is the parallel conductance; ω is the angular frequency. The above series representation was used solely for short-circuit impedance subtraction, whereas all subsequent dielectric analyses were based on the intrinsic parallel parameters of the ZnO sample.

To correlate the *in-situ* electrical response with structural evolution during sintering, densification and Bi-rich phase evolution were monitored by *in-situ* dilatometry and high-temperature XRD, respectively. Densification was measured using a thermal expansion analyzer (L75VS1400C, Linseis, Germany). The evolution of the Bi-rich phases during cooling was tracked using a diffractometer equipped with a high-temperature chamber (D8 Advance, Bruker, Germany). During cooling, XRD patterns were collected in two modes: continuous scans over 26°–33° at 5 (°)/min to track the Bi-rich phase evolution and full-range scans over 10°–75° at 10 (°)/min at selected temperatures.

In addition, quenching experiments were further performed to examine the microstructural morphology and grain/grain boundary elemental redistribution at different sintering stages. Samples were quenched at selected temperatures during the heating (H), soaking (S), and cooling (C) stages. At each target temperature, the sample was rapidly removed from the furnace and placed on a stainless-steel block in air to interrupt sintering.

Table 1 Detailed formulation of commercial ZnO varistor green bodies used in this work

(Unit: mol%)

Component	ZnO	Bi ₂ O ₃	Sb ₂ O ₃	Co ₂ O ₃	Mn ₂ O ₃	NiO
Content	96.5	0.5	1	1	0.5	0.5



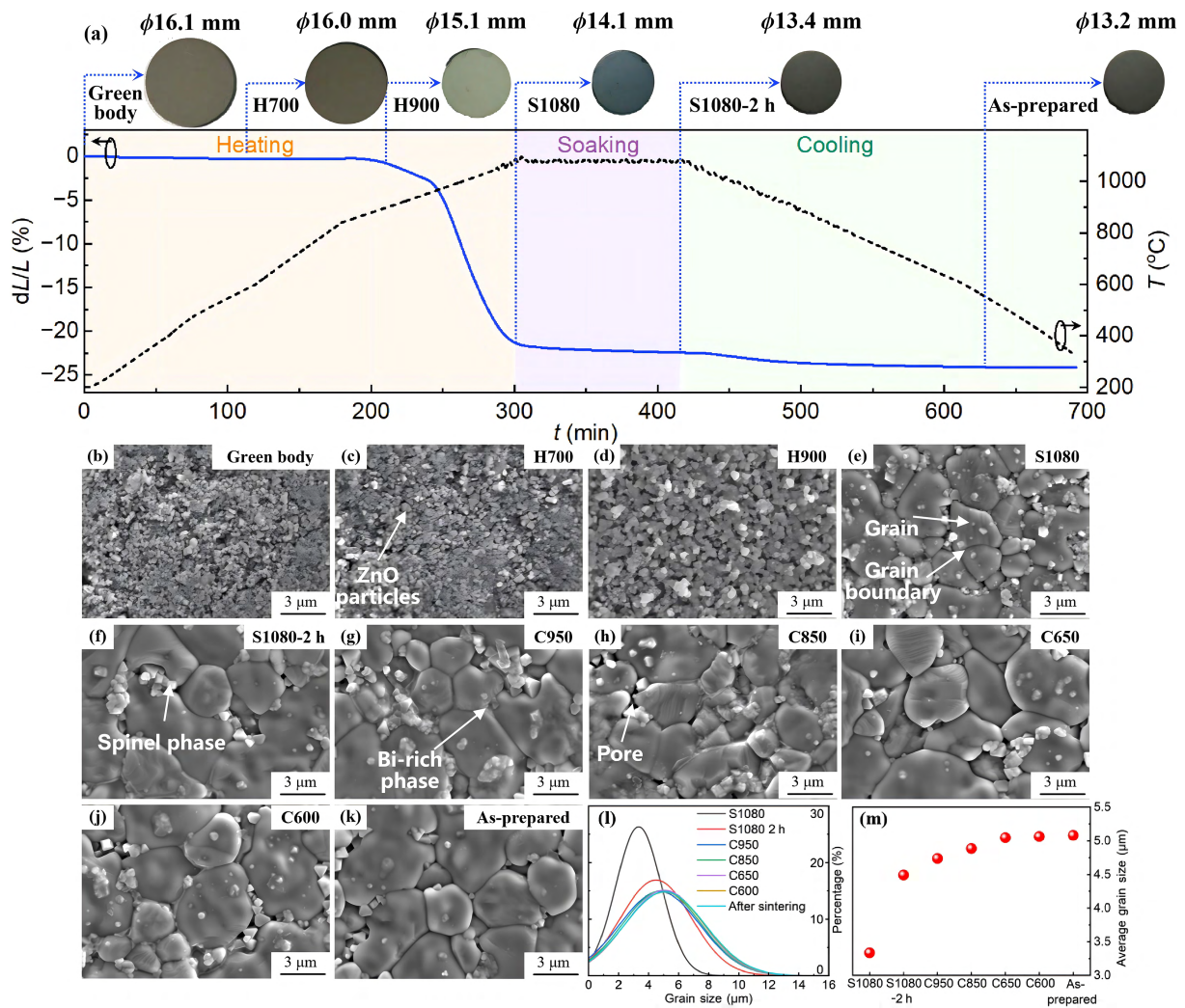


Fig. 1 Linear shrinkage and dimensional evolution of samples during sintering process: (a) sintering curve and linear shrinkage rate; microstructures of (b) green body, (c) H700, (d) H900, (e) S1080, (f) S1080-2 h, (g) C950, (h) C850, (i) C650, (j) C600, (k) as-prepared; (l) log-normal distribution of average grain size; (m) variation of average grain size.

The quenched samples were labeled by stage and temperature (e.g., H700, S1080, and C600) and examined using a scanning electron microscope (SEM; SU3500, Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS; X-MaxN, Oxford Instruments, UK) for line-scan analysis.

3 Results and discussion

3.1 Microstructural evolution and Bi phase transition

The densification behavior during sintering indicates that the major microstructural evolution occurs during the heating and soaking stages, whereas the cooling stage contributes little to dimensional change. The linear shrinkage of the samples (dL/L_0) during sintering is shown in Fig. 1(a), with dL denoting the change in sample length and L_0 the initial sample length before sintering. The majority of the shrinkage occurred during the heating and soaking stages between 700 and 1080 °C, with dL/L_0 exhibiting shrinkage from 0.30% to 22.43%. In the 700–800 °C range, dL/L_0 changed by approximately 3%. An obvious densification stage was observed between ~820 and 1080 °C, characterized by a significant contraction of 21.1% in dL/L_0 . The derivative curve ($d(dL/L_0)/dt$) revealed a distinct shrinkage peak within this interval, with a maximum shrinkage rate of 0.45%/min

(Fig. S5 in the ESM), indicating rapid initial densification. During the soaking stage, dL/L_0 increased from 21.38% to 22.43%, whereas the cooling stage contributed minimally to dimensional change. These observations are in good agreement with the diameters of the quenched samples, which show that after heating and soaking, the sample contracted from $\phi 16.1$ to $\phi 13.2$ mm and remained almost unchanged during cooling.

SEM observations further confirm that grain growth and pore elimination mainly proceed during heating and soaking, while only slight microstructural changes occur during cooling. During the heating stage, from the green body in Fig. 1(b) to H700 in Fig. 1(c), particle contact and slight grain coarsening occur, accompanied by limited bulk diffusion, resulting in a noticeable reduction in interparticle porosity. As the temperature reaches 900 °C, the particles continue to grow, and the initial densification begins, becoming more pronounced at S1080, where well-defined grains are formed, as shown in Fig. 1(e). The densification predominantly occurs during the soaking stage, with rapid closure of intergranular pores and noticeable volumetric shrinkage, while grain growth progresses. During cooling, the grain size changes minimally. Grain size evolution during the soaking and cooling stages was quantified by binarizing and delineating SEM images using ImageJ, and the grain size distribution was fitted to a log-normal function $f(d)$, as given by Eq. (3):

$$f(d) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\ln d - \mu)^2}{2\sigma^2}\right) \quad (3)$$

where d is the grain size, μ is the log-mean, and σ is the log-standard deviation. From the soaking stage to the completion of sintering, the average grain size increased from 3.34 to 5.08 μm , consistent with the observed volumetric shrinkage.

Although only limited morphological changes occur during cooling, the chemical environment near grain boundaries continues to evolve. The ZnO grains are already well defined and closely packed after soaking, with narrow intergranular regions that remain largely unchanged during subsequent cooling. As shown in Fig. 2, SEM-EDS line scans show that the additive elements are relatively uniformly distributed in the green body and H900 samples. After soaking at 1080 °C for 2 h, obvious Bi and Sb enrichment appears at the Zn-depleted grain boundary regions and remains observable in the samples quenched during subsequent cooling, including C850 and C650, as well as in the as-prepared sample. Mn and Ni also show changes in their local distributions near grain boundaries. Bi-rich intergranular phases contribute to the formation of electrically active grain boundaries, while the redistribution of Mn and Ni may modify the local defect chemistry and barrier-related electrical properties [32,40–43]. These compositional changes indicate the continued evolution of the grain boundary chemical environment during cooling, which may influence the formation of DSBs.

To examine the phase evolution during cooling, with particular attention to the Bi-rich phases associated with grain boundary electrical properties, *in-situ* high-temperature XRD was performed. Figure 3(a) presents XRD patterns tested at selected

temperatures during cooling, together with those of the green body and as-prepared sample. ZnO (JCPDS No.79-0206) remains the dominant crystalline phase, while the secondary spinel phases $\text{Zn}(\text{Zn}_{4/3}\text{Sb}_{2/3})\text{O}_4$ (JCPDS No.15-0687) and $\text{Co}(\text{Co}_{4/3}\text{Sb}_{2/3})\text{O}_4$ (JCPDS No.78-0718), as well as temperature-dependent Bi-rich phases, are also identified.

Figure 3(b) presents the continuous evolution of the Bi-rich phases during cooling, revealing three Bi_2O_3 phases: $\alpha\text{-Bi}_2\text{O}_3$ (JCPDS No. 71-2274), $\beta\text{-Bi}_2\text{O}_3$ (JCPDS No. 74-1374), and $\delta\text{-Bi}_2\text{O}_3$ (JCPDS No. 42-0185). The integrated area (A_i) of each selected Bi_2O_3 characteristic peak was normalized to the integrated area (A_{ZnO}) of the ZnO reference peak near 32° to track their relative evolution (see Fig. S6 in the ESM for details of the calculation). At 1080 °C, no distinct Bi_2O_3 diffraction peaks are detected because the Bi-rich phase is predominantly liquid and lacks long-range crystalline order. Under the present cooling conditions, the Bi-rich liquid does not remain amorphous after solidification but progressively crystallizes following the sequence $\text{liquid} \rightarrow \beta + \delta \rightarrow \beta \rightarrow \alpha + \beta \rightarrow \alpha$. From 1080 °C to approximately 800 °C, the β - and $\delta\text{-Bi}_2\text{O}_3$ signals gradually increase. The $\delta\text{-Bi}_2\text{O}_3$ signal then disappears near 800 °C, while metastable $\beta\text{-Bi}_2\text{O}_3$ remains dominant. Below approximately 650 °C, $\alpha\text{-Bi}_2\text{O}_3$ increases as $\beta\text{-Bi}_2\text{O}_3$ decreases, and the β to α transition becomes particularly evident from 600 to 500 °C, where $\alpha\text{-Bi}_2\text{O}_3$ gradually becomes dominant. Because the metastable β and δ phases generally exhibit higher oxygen-ion mobility than stable $\alpha\text{-Bi}_2\text{O}_3$, these phase transformations may alter oxygen transport and local defect chemistry near grain boundaries, thereby influencing the subsequent evolution and stabilization of DSBs [40,41].

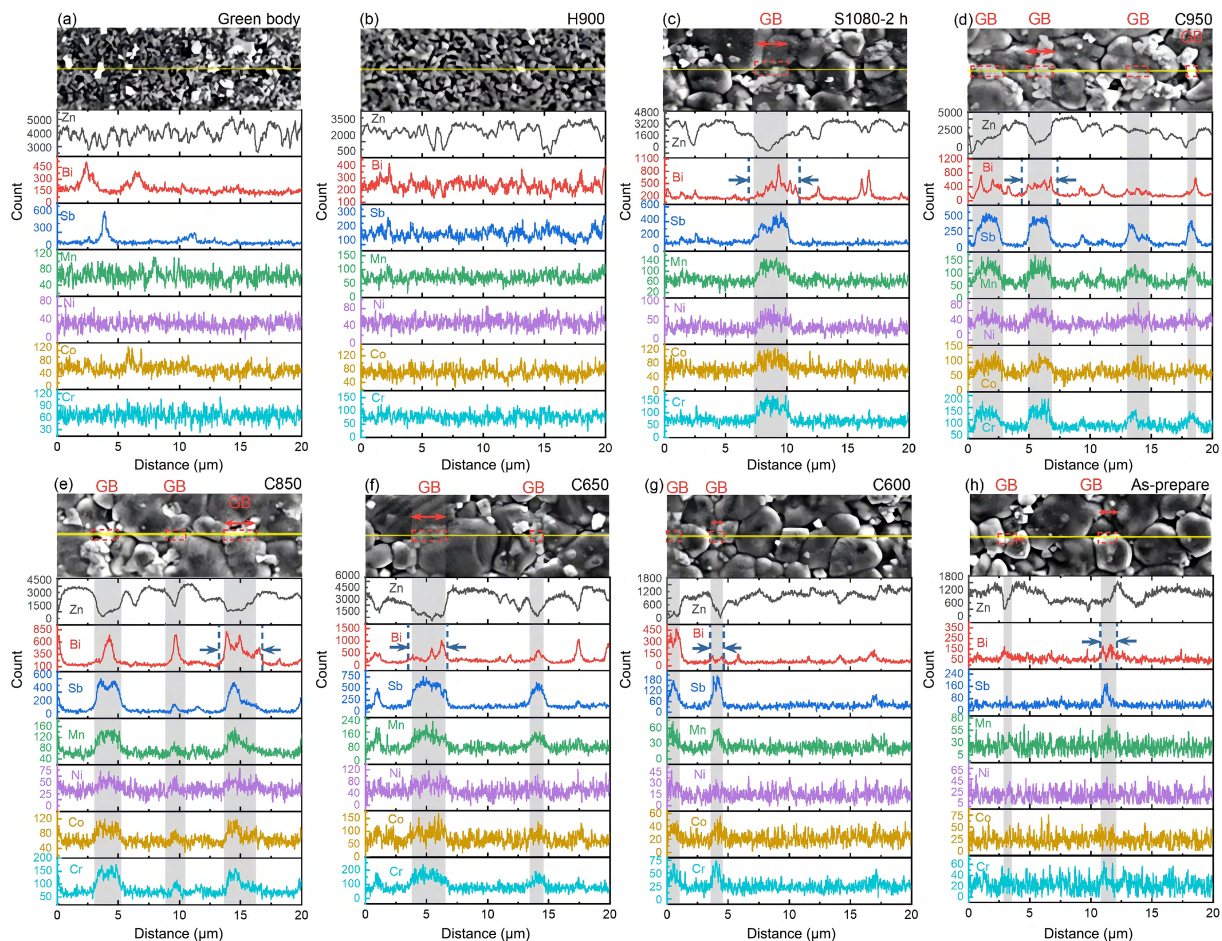


Fig. 2 Evolution of grain boundary elemental segregation during sintering revealed by SEM-EDS line-scan analyses.

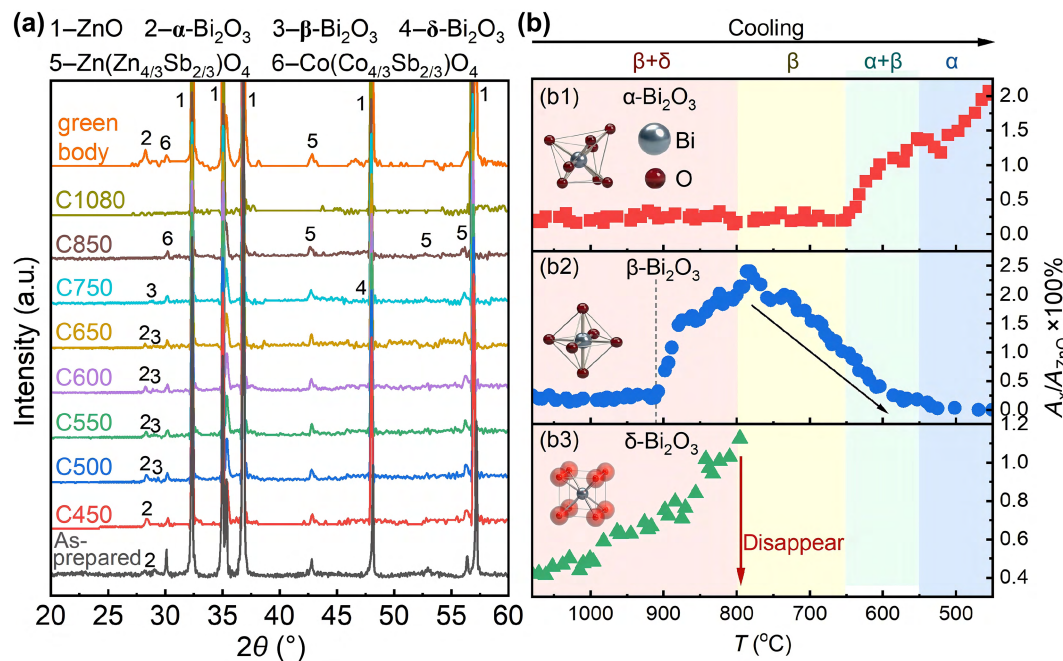


Fig. 3 *In-situ* XRD analysis of Bi-rich phase evolution: (a) XRD patterns of ZnO varistor ceramics at selected temperatures; (b1–b3) relative intensity evolution of α - Bi_2O_3 , β - Bi_2O_3 , and δ - Bi_2O_3 during cooling.

This Bi_2O_3 phase evolution path also agrees well with previous reports on ZnO varistor ceramics [28,31]. This phase-evolution trend is mainly evaluated from the continuous narrow-range XRD results in Fig. 3(b), whereas the full-range XRD patterns in Fig. 3(a) are used primarily for reference phase identification. The slight difference between these two datasets, including the very weak δ - Bi_2O_3 peak observed in the C750 full-range pattern, is mainly attributed to their different acquisition modes, scanning rates, and acquisition windows. Therefore, the weak δ - Bi_2O_3 signal in the C750 full-range pattern does not affect the overall Bi-rich phase evolution trend discussed above.

3.2 *In-situ* monitoring of dielectric spectroscopy during the sintering process

Although the above dilatometry, SEM-EDS, and XRD analyses reveal the microstructural and phase evolution during sintering, they cannot directly track the formation of electrically active DSBs. *In-situ* dielectric spectroscopy was therefore employed to continuously monitor the capacitance and conductance spectra of Pt-coated ZnO green bodies throughout the sintering process. The sample obtained after the *in-situ* measurement exhibited excellent nonlinear I - V characteristics, with a breakdown field (E_b), nonlinear coefficient (α), and leakage current density (J_l) of 247.2 V/mm, 46.3, and 0.065 $\mu\text{A}/\text{cm}^2$, respectively (Fig. S7 in the ESM). These results indicate that the *in-situ* dielectric measurement did not measurably affect the electrical properties of the sample.

Figure 4 presents the temperature-dependent evolution of the corrected bulk capacitance (C_p') during sintering. At the initial stage shown in Fig. 4(a), C_p' remained positive over the entire frequency range, exhibiting distinct low-frequency plateaus associated with dielectric relaxation. Such behavior can be attributed to the intrinsic electrical heterogeneity of the green body, arising from ZnO grains and interparticle pores. Upon further heating, negative capacitance first emerged at the high-frequency end in Fig. 4(b) when the temperature exceeded $\sim 700^\circ\text{C}$, marking the onset of this anomalous dielectric phenomenon in the ZnO varistor ceramics. With increasing

temperature, the negative capacitance progressively intensified and eventually dominated the full frequency range above $\sim 850^\circ\text{C}$, as shown in Fig. 4(c). At a given temperature, the magnitude of the negative capacitance increased toward lower frequencies and approached a frequency-independent minimum value.

During the cooling stage, the dielectric response exhibited an opposite temperature trend to that observed during heating. As shown in Fig. 4(d), negative capacitance remains detectable down to approximately 750°C , particularly at high frequencies. Upon cooling, its magnitude gradually diminished, with the entire spectrum shifting toward higher capacitance values. At intermediate temperatures of approximately 550 – 700°C in Fig. 4(e), dielectric relaxation processes re-emerged at low frequencies, restoring positive capacitance in this regime. Further temperature reduction led to the complete suppression of negative capacitance below $\sim 550^\circ\text{C}$, beyond which only positive capacitance was observed throughout the frequency range in Fig. 4(f). In this low-temperature range, the spectra were dominated by capacitance plateaus, which can be reasonably attributed to electrode polarization or electronic relaxation associated with interface states (Fig. S8 in the ESM) [22].

Figure 5 exhibits the evolution of conductance (Y_p') spectra during sintering of the ZnO sample. Generally, the conductance increases with increasing frequency, which has been widely reported to follow Jonscher's universal power law, as given by Eq. (4) [22,44]:

$$\sigma_{ac} = \sigma_{dc} + B\omega^n \quad (4)$$

where σ_{ac} is the alternating current (AC) conductivity; σ_{dc} is the DC conductivity; B is the pre-exponential factor; $0 < n < 1$ is an exponent. As shown in Fig. 5(a), Y_p' followed Eq. (4) at the beginning of heating. When the sample was heated to $\sim 600^\circ\text{C}$, the low-frequency conductance originating from DC conductivity prevailed, which gradually masked the dielectric relaxation-related conductance. As a result, the conductance curves were almost straight lines parallel to the frequency axis in Fig. 5(b). At sufficiently high temperatures, the high-frequency conductance shown in Fig. 5(c) decreased with increasing frequency, which

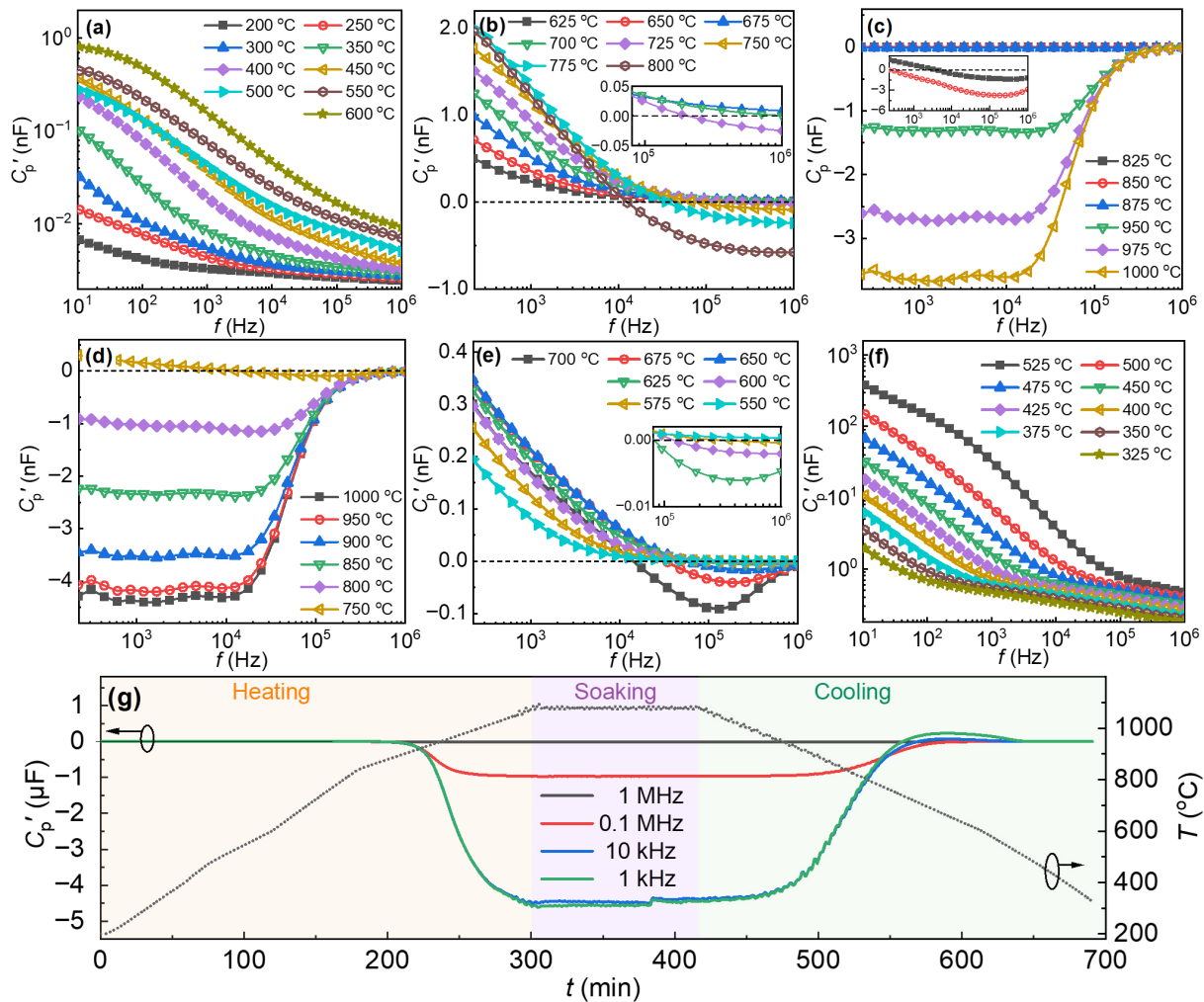


Fig. 4 C_p' spectra during (a-c) heating and (d-f) cooling. (g) Evolution of C_p' during entire sintering process.

apparently differed from Jonscher's universal power law. Although the conductance still followed Eq. (4) in form, the exponent n obtained by fitting was approximately -2 . It was far beyond the range $(0, 1)$. This abnormal decrease in high-frequency conductance could only be ascribed to the negative capacitance behaviors shown in Fig. 4(c).

The conductance behavior during cooling was also the reverse of that during heating to some extent. As shown in Figs. 5(d)–5(f), the conductance as a whole declined with the decrease in temperature. First, the abnormal decrease in high-frequency conductance correlating with the negative capacitance behaviors disappeared. The masking effect of the prevailing DC conductance also became increasingly weaker. Finally, dielectric relaxation-related conductance following Jonscher's power law was observed when the sample was cooled below ~ 500 °C.

An overall evolution of Y_p' at different frequencies during sintering is exhibited in Fig. 5(g). At low frequencies below 0.1 MHz, Y_p' increased during heating, remained constant during holding, and decreased during cooling. In contrast, Y_p' at 1 MHz decreased from 850 to 950 °C during heating and increased from 900 to 600 °C during cooling, reflecting the negative capacitance behaviors observed in Fig. 4(g).

3.3 Equivalent-circuit fitting of dielectric responses during cooling

To clarify the relationship between the dielectric response and

DSB evolution during cooling, the dielectric spectra were analyzed using the Drude model and equivalent-circuit fitting. Negative capacitance is generally attributed to either a Drude-like free-carrier response or Lorentz-type dielectric resonance [45]. In the present work, the magnitude of the negative capacitance shown in Figs. 4(d) and 4(e) increases toward lower frequencies and approaches a nearly frequency-independent limiting value, consistent with the Drude model (Eqs. (5) and (6)) [46]:

$$\varepsilon_d^* = \varepsilon' - j\varepsilon'' = 1 - \frac{\omega_p^2}{\omega^2 - j\omega\omega_\tau} \quad (5)$$

$$\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2 + \omega_\tau^2} \quad (6)$$

where ε_d^* is the complex permittivity from plasma oscillation; ω_p is the plasma frequency; ω_τ is the collisional frequency.

The temperature-dependent dielectric response suggests a gradual transition from free-carrier-dominated transport to barrier-controlled electrical behavior. Above approximately 700 °C, the frequency dependence of the negative capacitance is consistent with the Drude model, indicating a response dominated by thermally activated carriers released through the ionization of trap states in the ZnO grains and grain boundary regions. With decreasing temperature, the Drude-like contribution is progressively suppressed, while positive dielectric relaxation associated with grains and grain boundaries/interfaces re-emerges.

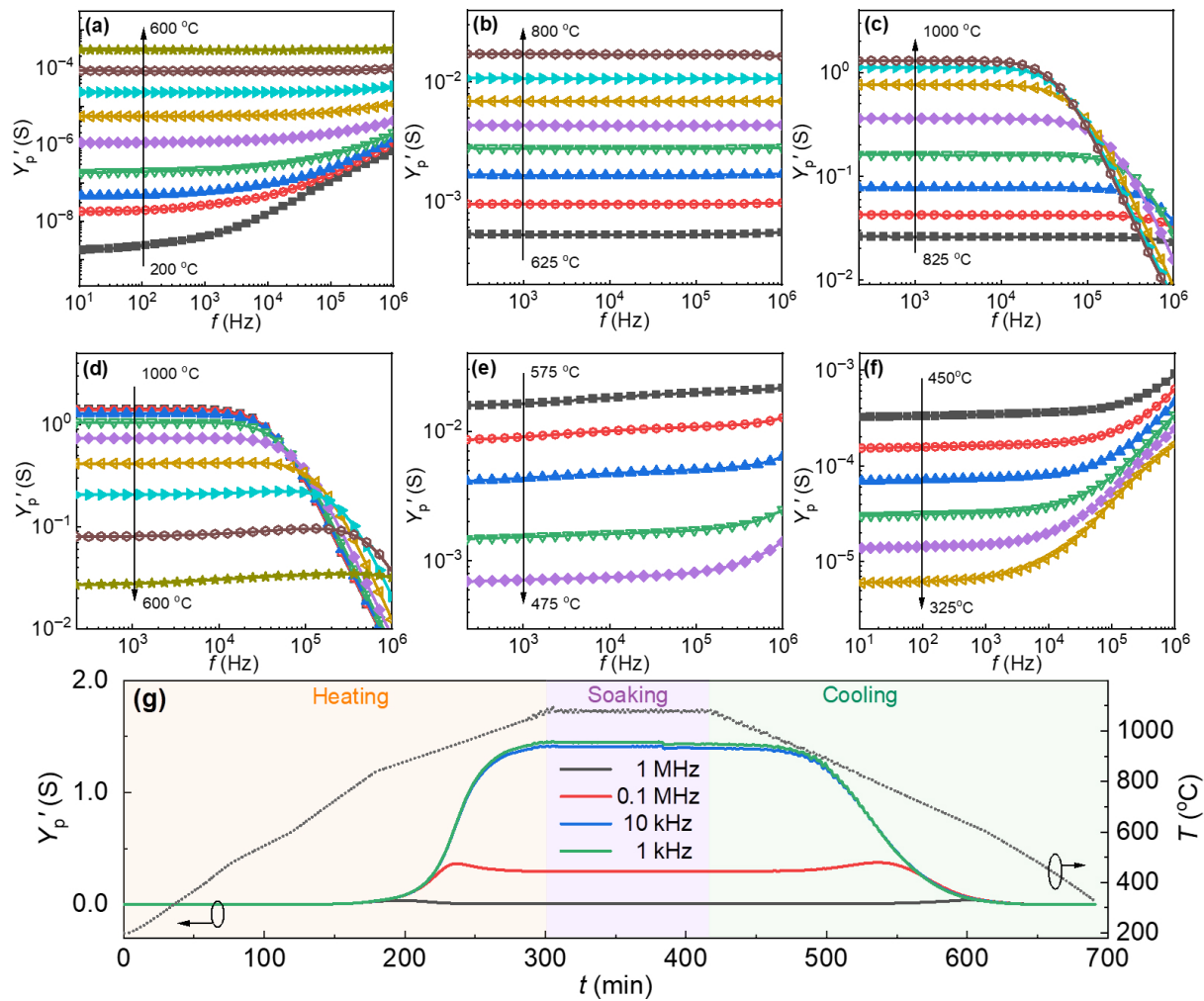


Fig. 5 Y_p' spectra during (a–c) heating and (d–f) cooling. (g) Evolution of Y_p' during entire sintering process.

At lower temperatures, the low-frequency capacitance plateaus may also include contributions from electrode polarization or electronic relaxation associated with interface states (Fig. S8 in the ESM). Thus, the dielectric response evolves from a Drude-like free-carrier-dominated response at high temperatures to a relaxation-dominated response at lower temperatures, with both contributions coexisting at intermediate temperatures. An equivalent-circuit model was therefore constructed to separate these contributions and characterize their evolution during cooling.

As shown in Fig. 6, an equivalent-circuit model combining a Drude-like branch, $C_D || (R_D + L_D)$, with grain and grain boundary/interfacial resistance-capacitance (RC) branches was constructed to fit the dielectric spectra at different cooling temperatures. Constant phase elements (CPEs) were used instead of ideal capacitors to describe nonideal capacitive behavior associated with distributed relaxation times. Here, L_D is not a geometric inductance but an equivalent element describing carrier inertia in the Drude-like response. The model reproduces the experimental spectra well and reveals the evolution of the dominant electrical response during cooling. At 800 °C, the spectra are dominated by the Drude-like branch, indicating that free-carrier transport remains the major contribution, while the fitted R_{gb} is zero, indicating that the grain boundary resistance cannot yet be resolved from the dominant Drude-like response. However, the negative C_p' at this temperature does not exclude the

initial development of DSBs because the strong Drude-like response may mask the positive capacitance contribution from developing depletion layers. As shown in Fig. 6(f), below 800 °C, a finite R_{gb} is obtained and increases continuously with decreasing temperature. From 750 to 600 °C, both the Drude-like branch and the grain boundary/interfacial relaxation branches are required to reproduce the spectra, indicating the coexistence of free-carrier transport and the developing barrier-related response.

With further cooling, the Drude-like contribution weakens, while R_{gb} continues to increase. Because R_{gb} is closely related to the effective grain boundary barrier height [47], its emergence and continuous increase below 800 °C indicate the progressive establishment of grain boundary barriers during cooling. At 500 °C, the spectra are mainly described by the grain and grain boundary RC branches, while the Drude-like contribution is no longer dominant. These results demonstrate the gradual transition from free-carrier-dominated transport to barrier-controlled carrier transport during cooling.

3.4 Tracking DSB evolution during sintering using E_a

The continuous increase in R_{gb} indicates that carrier transport is progressively hindered by developing grain boundary barriers. To quantify this evolution, the DC conductance (Y_{dc}) was approximated by the conductance at 0.1 Hz, and its temperature dependence was analyzed using the Arrhenius relation (Eq. (7)) [22]:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (7)$$

where σ_0 is the pre-coefficient; k is the Boltzmann constant; T is the temperature. Accordingly, the apparent activation energy (E_a) of DC conductance was determined from the $\ln Y_{dc}-1000/T$ relationship shown in Fig. S9 in the ESM. Once grain boundary barriers are established, E_a reflects the effective energy required for thermally activated carriers to overcome the DSB, although its specific physical meaning depends on the microstructural stage of sintering [28,47].

As shown in Fig. 7(a), the evolution of E_a divides the sintering process into five successive stages: no significant change, densification, slight modification in microstructure, formation of DSBs, and modification in DSBs. During initial heating below 800 °C, E_a remains nearly constant at ~1.5 eV, mainly reflecting the effective contact barriers between ZnO particles in the porous

green body. This interpretation is consistent with the limited microstructural changes observed in Figs. 1(b) and 1(c). Above approximately 825 °C, liquid-phase sintering promotes rapid densification and an overall decrease in E_a . A local peak near 900 °C coincides with the maximum linear shrinkage rate and may reflect enhanced carrier scattering and transient changes in particle-contact transport during densification. As heating proceeds toward 1080 °C and during the subsequent soaking stage, E_a decreases to nearly zero, indicating that carrier transport is dominated by a free-carrier response under these high-temperature conditions.

During cooling from 1080 °C to approximately 800 °C, E_a remains close to zero, consistent with the Drude-like free-carrier response reflected by the negative capacitance. As the temperature decreases from 800 to 650 °C, E_a increases markedly from nearly zero to ~1.4 eV, accompanied by the emergence and continuous increase of R_{gb} , suggesting the progressive formation of DSBs. This

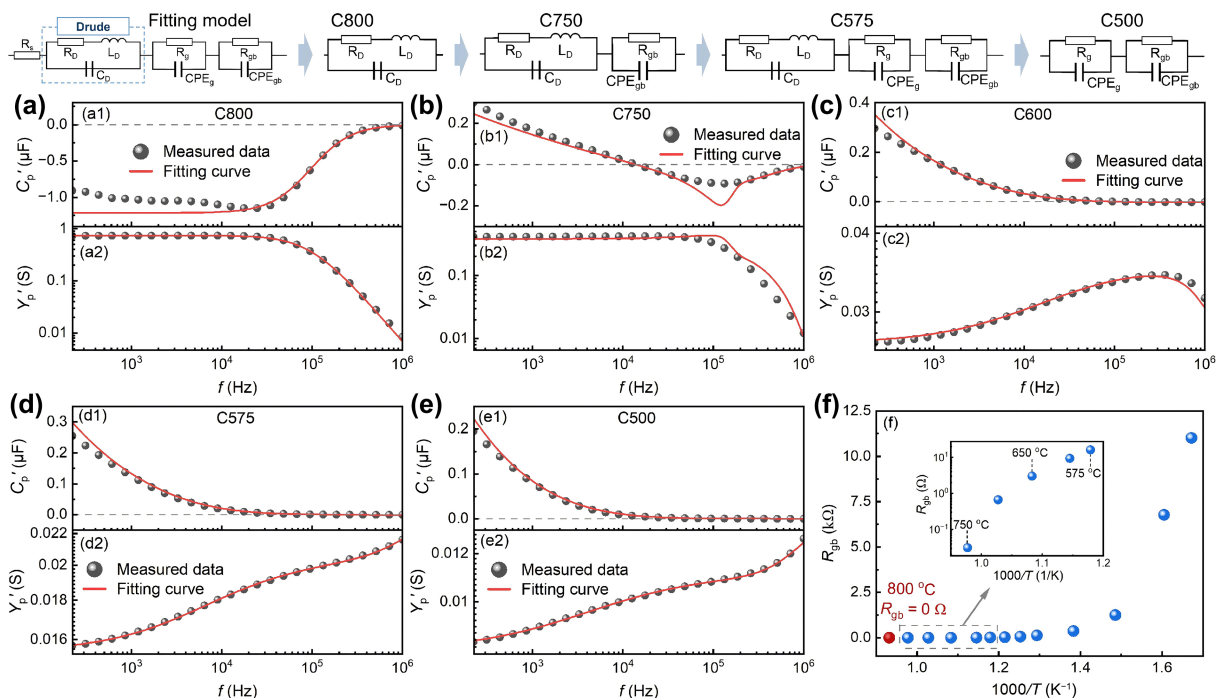


Fig. 6 Equivalent-circuit fitting of dielectric spectra during cooling: (a–g) fitting results of C_p and Y_p spectra from 800 to 500 °C; (h) evolution of R_{gb} during cooling.

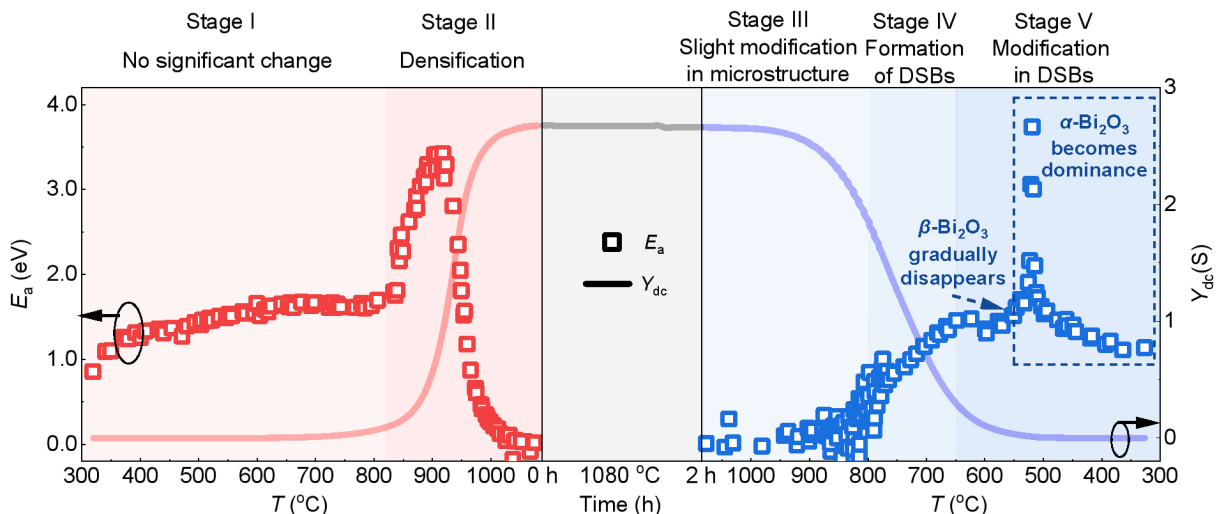


Fig. 7 Evolution of apparent activation energy (E_a) of DC conductance during whole sintering process.

temperature range also coincides with the disappearance of $\delta\text{-Bi}_2\text{O}_3$, the persistence of metastable $\beta\text{-Bi}_2\text{O}_3$ as the dominant Bi-rich phase, and the initial increase in $\alpha\text{-Bi}_2\text{O}_3$ near 650 °C. Upon further cooling, E_a decreases slightly from 650 to 600 °C, exhibits a distinct peak in the 500–600 °C range, and then stabilizes at ~ 1.2 eV, corresponding to the subsequent modification of DSBs. These variations coincide with the progressive β to α transformation, during which $\alpha\text{-Bi}_2\text{O}_3$ becomes dominant and $\beta\text{-Bi}_2\text{O}_3$ nearly disappears. Together with the SEM-EDS evidence of obvious Bi and Sb enrichment and the redistribution of Mn and Ni near grain boundaries, these results suggest that the formation and subsequent modification of DSBs are accompanied by continuous changes in the grain boundary chemical environment [29,33,40,41].

The *in-situ* evolution of E_a agrees well with our previous quenching results [28]. In particular, the activation energies obtained from samples quenched at different cooling temperatures show comparable values and similar evolution trends over the 600–800 °C range (Figs. S10 and S11 in the ESM), supporting the interpretation that the increase in E_a reflects the gradual development of barrier-controlled carrier transport. Although the exact temperature range of DSB formation may vary with material composition and cooling conditions, which affect oxygen adsorption, interface-state formation, and point-defect redistribution near grain boundaries, the present results demonstrate that *in-situ* dielectric spectroscopy provides an effective approach for identifying the key stage of grain boundary barrier development.

4 Conclusions

In summary, *in-situ* high-temperature dielectric spectroscopy, combined with system-impedance correction, equivalent-circuit fitting, and activation-energy analysis, was used to resolve the formation and evolution of DSBs throughout the sintering of ZnO varistor ceramics. The negative-permittivity response observed above ~ 700 °C is attributed to a Drude-like free-carrier response, which is gradually replaced by grain boundary-related dielectric relaxation during cooling. The evolution of R_{gb} and E_a reveals a clear separation between structural densification and electrical functionalization: Densification and grain growth occur mainly during heating and soaking, whereas grain boundary barriers are progressively formed during cooling, particularly from 800 to 650 °C. SEM-EDS and *in-situ* XRD further show that this electrical evolution is accompanied by additive redistribution near grain boundaries and continuous transformation of the Bi-rich phases. In particular, the β to α Bi_2O_3 transition in the 500–600 °C range coincides with the later modification of the established barriers, suggesting that changes in oxygen transport and local defect chemistry contribute to DSB stabilization. These findings provide a mechanistic basis for distinguishing microstructural development from electrical functionalization and for optimizing the sintering process of grain boundary barrier-controlled functional 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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