Volatile-Templated Ceramic Microstructures for Resonant and Dielectric Function

A Process-Structure Review of Burnout-Derived Pore Architecture, Phase Segregation, and Wave-Response Design in Low-Temperature Ceramic Systems

Materials process intelligence analysis and review

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Abstract

Volatile processing phases in ceramic systems are usually treated as sources of defects to be removed by controlled drying, debinding, and burnout. This review evaluates the complementary design premise: transient additives, solvents, salts, binders, and gas-evolving phases can also act as microstructure-forming agents whose removal or segregation leaves functional architecture. Evidence from starch consolidation, polymer debinding, freeze casting, porous acoustic media, dielectric oxide ceramics, carbon-containing refractories, and ZnO-Bi2O3 varistors shows that process history can govern open and closed porosity, pore connectivity, carbonaceous residues, flux-derived glass films, segregated grain boundaries, and rehydratable internal surfaces. These structures are directly relevant to acoustic damping, dielectric constant and loss tangent, RF/microwave absorption, nonlinear current-voltage response, moisture-mediated dielectric behavior, and candidate phononic or photonic filtering. The review proposes a process-structure-property framework for volatile-templated ceramic function, separates established mechanisms from design hypotheses, and defines the characterization stack required to validate wave-response claims. The central conclusion is evidence-bounded: burnout-derived architecture is already a proven route to porous and boundary-controlled ceramic microstructures; its extension to deliberately engineered resonant and dielectric function is credible only when volatile pathway, residual structure, and measured response are linked by controlled experiments.

Keywords: porous ceramics; binder burnout; freeze casting; starch consolidation; dielectric ceramics; acoustic absorption; varistors; microstructure; process-structure-property relationships

1. Introduction

Ceramic processing is not a neutral route from powder to fired solid. Before densification or partial vitrification is complete, the green body undergoes drying, solvent migration, binder decomposition, pore-former burnout, carbonate or hydrate decomposition, flux melting, gas evolution, surface segregation, grain-boundary enrichment, and cooling-driven phase partitioning. In conventional processing, many of these events are managed as defect risks: bloating, delamination, black coring, cracking, residual carbon, uncontrolled porosity, and nonuniform shrinkage. In functional ceramics, however, microstructure is not merely a defect state; it is frequently the carrier of the property of interest. Porosity controls permeability, thermal conductivity, acoustic impedance, and dielectric effective medium behavior. Grain-boundary chemistry controls nonlinear electrical transport in varistors. Carbonaceous phases can convert an insulating body into a lossy microwave absorber or leakage network. Aligned lamellae produced by ice templating can impose anisotropic transport and scattering. These facts motivate a reframing: volatile removal should be treated as a microstructure-forming operation as well as a defect-control operation.

The review develops the term volatile-templated ceramic microstructure for residual pore, boundary, phase, or surface architectures formed by components that leave, transform, migrate, or segregate during thermal processing. The term is deliberately broad enough to include clean sacrificial pore formers, oxygen-limited carbonizing additives, solvent-templated freezing routes, salt and flux migration, binder-burnout defects, and dopant systems in which a liquid or segregated phase controls grain-boundary response. It is not proposed as a new processing technique in isolation. It is a process-intelligence category that links well-established ceramic processing literature to functional design questions that are often discussed separately.

The evidence base is uneven across functions. Pore formation through starch consolidation and sacrificial templating is well established [1,2]. Freeze casting has an extensive processing-structure literature and can generate highly anisotropic porosity [3-6]. Binder burnout and debinding are recognized as major determinants of defect formation, residual mass, and transient mechanical integrity [7-9]. Porous ceramics and mineral foams can exhibit acoustic absorption governed by flow resistivity, tortuosity, pore connectivity, surface roughness, and microcracks [10-13]. ZnO-Bi_2O_3 varistors demonstrate that segregated grain-boundary phases can create nonlinear electrical response through barrier networks [14,15]. The less mature claim is not that these process families exist; it is that a unified volatile-pathway library can be used to deliberately design dielectric, RF/microwave, acoustic, or resonant response in low-temperature ceramic systems. That is the claim evaluated here.

2. Evidence standard and scope

This review follows an evidence-first standard. A processing claim is treated as established when the literature directly reports a reproducible relation between formulation, thermal pathway, and microstructure. A functional claim is treated as established only when the relevant property is measured. A design hypothesis is allowed when the literature supports the process and the physical coupling principle, but no direct measurement yet links the specific volatile-templated architecture to the claimed response. This distinction is essential because many plausible wave-response claims fail at scale matching, loss control, repeatability, or measurement specificity.

The scope emphasizes low-temperature and partially sintered ceramic systems because they are the regimes in which volatile effects are often retained rather than erased. High-temperature densification can remove porosity, oxidize residual carbon, homogenize segregated phases, or close the pore network. Low-temperature or partial-sintering routes, by contrast, can preserve open porosity, glass films, carbon-lined pathways, lamellar channels, and chemically distinct surfaces. Low-temperature is therefore not treated as an inferior approximation of dense ceramics; it is treated as a processing domain where transient phases have a higher probability of leaving functionally legible structure.

The term resonant is used conservatively. Acoustic resonance, RF/microwave response, and dielectric dispersion are measurable response classes. Claims of photonic, phononic, THz, or metamaterial behavior require a feature scale, periodicity, contrast, and loss profile appropriate to the target wavelength; in the absence of those measurements, such claims remain hypotheses. The practical review question is therefore not whether volatile templating can create visually interesting ceramics, but whether it can produce repeatable structures whose measured response differs from dense, untemplated, or randomly porous controls.

3. Process-structure-property framework

The central causal chain is straightforward: green-body composition defines possible transient events; drying and firing determine which components migrate, decompose, oxidize, carbonize, melt, volatilize, or segregate; those events generate residual pore and phase architecture; the residual architecture modifies transport, polarization, scattering, damping, conduction, or impedance. Figure 1 summarizes the framework.

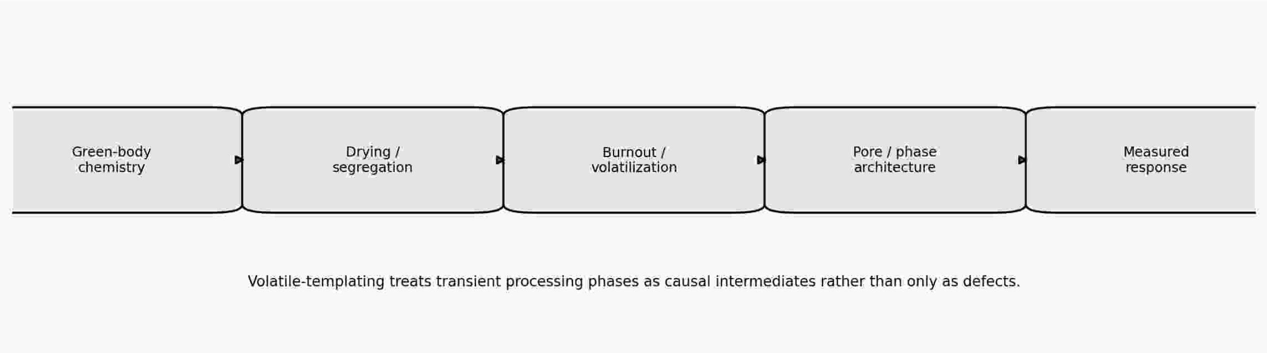

Figure 1. Causal chain for volatile-templated ceramic microstructures. The transient phase is treated as a controlled process intermediate, not merely as material removed from the final body.

This framework differs from ordinary recipe description because it makes each process stage testable. The additive is not evaluated by name alone. It is evaluated by decomposition temperature, atmosphere dependence, gas species, melt formation, carbon yield, migration pathway, and residual phase. The ceramic matrix is not evaluated by bulk composition alone. It is evaluated by how particle packing, binder distribution, capillarity, wetting, flux chemistry, and sintering kinetics preserve or erase the transient structure. The property is not inferred from a narrative of unusual behavior. It is measured relative to a control.

Input class	Thermal / chemical event	Residual structure	Evidence status
Starch / saccharide pore formers	Gelation, dehydration, oxidative burnout or oxygen-limited char formation	Granule-shaped pores, connected voids, possible carbon residue	Established for porosity; functional tuning requires measurement
Cellulose / sawdust / fibers	Pyrolysis and burnout of fibrous solids	Elongated tunnels, open-pore networks, lower density	Established for porous filters and lightweight ceramics; acoustic design plausible
PVA / PEG / acrylic binders	Debinding, gas evolution, transient loss of green strength	Binder-derived voids, cracking risk, residual carbon if incomplete	Established defect-control domain
Freeze-cast water or camphene slurries	Directional solidification followed by sublimation	Aligned lamellae, anisotropic channels, hierarchical pores	Established microstructure; wave-specific function requires scale-resolved tests
Soluble salts and fluxes	Capillary migration, melting, volatilization, glass formation	Surface enrichment, glassy films, alkali-rich boundaries	Supported; composition mapping required
ZnO-Bi2O3-type systems	Liquid-phase sintering and grain-boundary segregation	Bi-rich intergranular films and barrier networks	Established nonlinear electroceramic case
Carbonizing binders in oxide or refractory matrices	Oxygen-limited pyrolysis and partial oxidation	Carbon-lined pores or percolative carbon networks	Established in carbon-containing refractories; response depends on percolation

The table shows why volatile templating is best treated as a family of process mechanisms rather than one material system. The common feature is not a specific additive. It is a causal dependence of final architecture on a transient phase. The review therefore treats process memory as the central variable: the fired ceramic carries a measurable record of what left, what moved, what reacted, and what remained at boundaries.

4. Burnout and outgassing pathways

4.1 Clean burnout and sacrificial pore formation

Clean burnout occurs when an organic additive decomposes and oxidizes without leaving significant carbonaceous residue. In starch consolidation, starch granules can serve both as consolidation agents and pore formers; after burnout, the fired body can preserve granule-scale pores and connecting porosity controlled by starch content, solids loading, and firing history [1]. General macroporous ceramic processing reviews classify sacrificial templating as one of the major routes to controlled porosity, alongside direct foaming and replica methods [2,16]. The process is mature, but its functional interpretation depends on measurement. A pore former can reduce dielectric constant simply by introducing air, increase acoustic damping by adding flow resistivity and tortuosity, or degrade mechanical strength and Q factor through scattering and crack initiation. The same structural operation can therefore be beneficial or harmful depending on the target response.

The key control variables are additive size distribution, volume fraction, packing, wetting, burnout rate, and sintering temperature. A narrow additive size distribution can yield a narrow pore population, while mixed pore formers can produce hierarchical porosity. Rapid burnout can create internal pressure and cracking, whereas slow debinding can preserve geometry but reduce throughput. A meaningful process map must therefore pair TGA/DSC mass-loss stages with microscopy of residual pore geometry and property measurements of the fired body.

4.2 Oxygen-limited pyrolysis and residual carbon

When oxygen access is limited or organic loading is high, pyrolysis can produce char or persistent carbonaceous residue. In conventional ceramic bodies this is often a defect: black coring, bloating, reduced strength, or uncontrolled conductivity. In carbon-containing refractories and carbon-bonded systems, however, carbon is a functional phase that can improve thermal shock resistance, alter wettability, and introduce electrical or microwave loss pathways [17,18]. The process distinction matters. A clean pore and a carbon-lined pore can have similar morphology under optical microscopy but very different RF, dielectric, and thermal behavior.

Residual carbon is not inherently useful. It must be characterized by Raman spectroscopy, elemental analysis, conductivity, microwave loss, and oxidation stability. A percolating carbon network can short a dielectric body; a sub-percolating carbon distribution can increase loss tangent; a localized carbon film can function as an internal heater or absorber; incomplete oxidation can also compromise reproducibility. Thus, oxygen-limited burnout should be treated as a high-leverage but high-risk process branch.

4.3 Solvent templating and freeze casting

Freeze casting or ice templating uses directional solidification to segregate particles into walls between growing solvent crystals. Subsequent sublimation leaves aligned macropores, and sintering consolidates the ceramic walls. Deville and co-workers showed that porous alumina architectures can be obtained by controlling slurry freezing and ice sublimation [5], and later reviews summarize the large body of work relating freezing conditions, solids loading, additives, and solvent selection to microstructure [3,4,6]. Freeze-cast pores are not just voids; they are anisotropic channels whose spacing, wall thickness, roughness, and connectivity depend on front velocity, temperature gradient, particle size, dispersant chemistry, and solvent crystallography.

For wave-response design, freeze casting is important because it can produce length-scale order and anisotropy. The mature claim is that aligned microstructures can be made. The less mature claim is that a given freeze-cast geometry will act as a dielectric waveguide, phononic element, or THz filter. That requires direct measurement of periodicity, effective permittivity, loss tangent, scattering, and band structure. In low-frequency acoustic systems, the relevant lengths are much larger than typical freeze-cast pores; the effect may be damping and flow resistivity rather than Bragg reflection. At microwave or THz frequencies, the scale matching becomes more plausible, but only if pore spacing, contrast, and losses are properly measured.

4.4 Salt, flux, and mobile ionic phases

Soluble salts and low-melting fluxes can migrate during drying, concentrate at surfaces through capillary transport, melt during firing, volatilize, or form glassy boundary films. These pathways are well known in ceramic practice as sources of efflorescence, glaze defects, surface enrichment, alkali transport, and phase segregation. Their relevance to functional microstructure comes from the fact that thin glassy films, alkali-rich regions, and surface-segregated phases can modify dielectric loss, moisture uptake, ionic conduction, and impedance contrast. However, these effects are highly composition-specific. A salt-derived surface sheen is not evidence of RF function; it is evidence that a mobile phase redistributed. The functional step requires XRD, SEM/EDS, XPS or Raman mapping, impedance spectroscopy, and humidity cycling.

4.5 Liquid-phase sintering and boundary segregation

The clearest electroceramic example of functional boundary segregation is the ZnO varistor. ZnO-Bi2O3-based varistors derive their nonlinear current-voltage behavior from grain-boundary barrier networks, with Bi-rich intergranular phases and other dopants contributing to double-Schottky barriers and breakdown behavior [14,15,19]. This case is important not because every ceramic can be made into a varistor, but because it demonstrates a general principle: the decisive electrical structure can be the boundary phase, not the bulk grain. For volatile-templated systems, the analogy is bounded. Salt or flux segregation can create boundary films, but nonlinear response cannot be assumed unless the required electronic barriers, grain chemistry, and I-V behavior are demonstrated.

5. Microstructural outcomes

5.1 Open and closed porosity

Open porosity connects to the surface and governs permeability, capillary uptake, fluid flow, acoustic absorption, and rehydration. Closed porosity lowers density and effective permittivity but may not contribute strongly to flow resistivity or adsorption. The same porosity fraction can have different functional consequences depending on pore size distribution, connectivity, tortuosity, throat size, and wall roughness. Standard density and porosity measurements are therefore insufficient; process-property work requires image analysis, micro-CT or serial sectioning, and transport metrics where relevant.

5.2 Aligned channels and lamellae

Aligned pores produced by freeze casting create anisotropic microstructures. In mechanical testing, anisotropy can dominate strength and modulus. In transport, aligned channels can decouple through-thickness permeability from in-plane behavior. In electromagnetic or acoustic response, alignment can modify scattering, impedance, and effective medium properties. However, alignment alone does not prove waveguiding. A waveguide claim requires boundary conditions and dimensions matched to the wavelength and contrast sufficient to confine or scatter the field.

5.3 Carbon residues and percolation networks

Carbon residue changes ceramics from purely dielectric bodies into composite systems. Depending on loading and connectivity, carbon can increase loss tangent, introduce electrical leakage, produce microwave absorption, or create resistive heating. The relevant transition is percolation. Below percolation, isolated carbon domains primarily contribute polarization and loss; near percolation, small changes in processing can produce large conductivity changes; above percolation, the body may become too conductive for dielectric resonator use but useful for absorption or heating. This makes carbon-bearing volatile templating attractive for lossy ceramics but dangerous for high-Q resonators.

5.4 Glass films, surface seals, and alkali-rich boundaries

Flux-derived glass films can seal pores, alter moisture uptake, lower sintering temperature, and introduce dielectric loss or ionic conduction. Surface-enriched salts or alkalis can also create a body whose external response differs from its interior. For applications involving field coupling at surfaces, this is a possible design variable. For reproducible materials science, it is also a major confound. Surface chemistry must be mapped before attributing measured response to bulk microstructure.

5.5 Rehydratable internal surfaces

Porous oxide surfaces can adsorb water and hydroxylate. Rehydration can change dielectric response, mass, outgassing, and thermal behavior. This matters because volatile-templated ceramics can retain high internal surface area even after firing. If pores are open and hygroscopic, ambient exposure becomes part of the property state. Humidity cycling, vacuum bakeout, thermally stimulated desorption, and impedance spectroscopy under controlled humidity are therefore required before assigning stable dielectric or RF behavior to the ceramic itself.

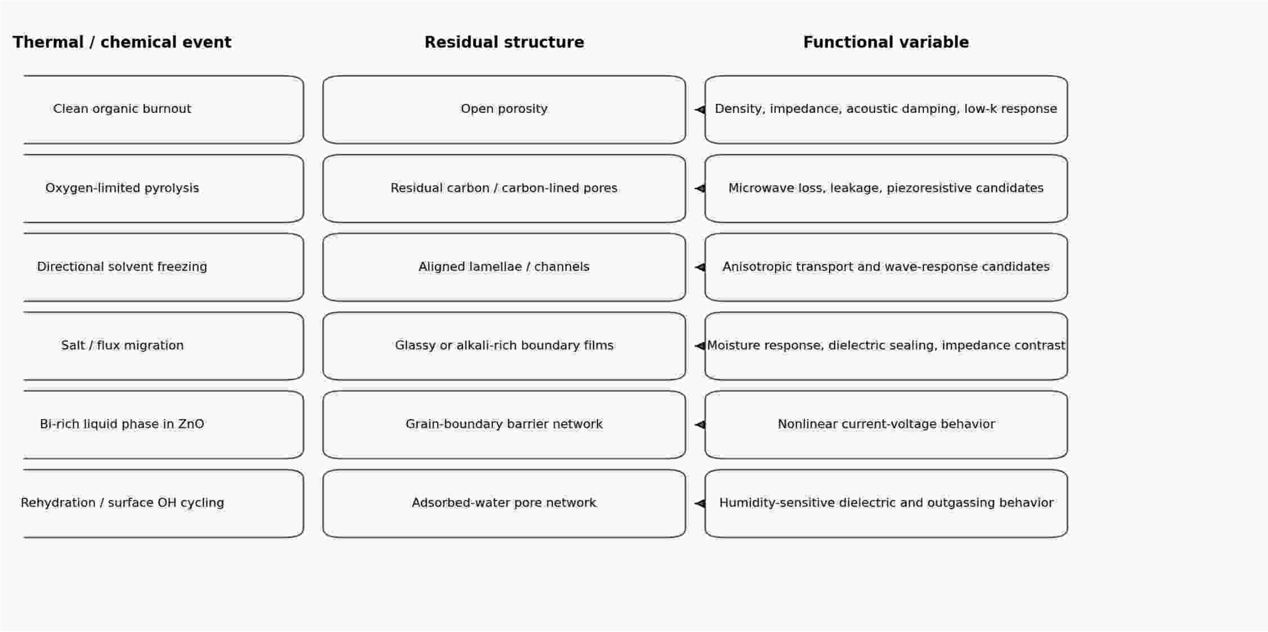

Figure 2. Volatile-templated pathway map. Each pathway is evidence-supported as a process route, but functional claims require direct measurement of the residual structure and response.

6. Functional consequences

6.1 Dielectric constant, loss tangent, and effective-medium behavior

Porosity lowers effective permittivity because air replaces higher-permittivity ceramic. The exact change depends on pore fraction, pore shape, connectivity, orientation, and matrix permittivity. Loss tangent is more complex: clean porosity can reduce dielectric loss in some systems by reducing polarizable volume, while residual carbon, alkali films, water adsorption, and grain-boundary defects can increase loss. Dielectric response therefore cannot be inferred from porosity alone. It must be measured across frequency, temperature, and humidity. Porous $TiO2$ and other oxide studies show that pore generation route can affect dielectric loss and effective properties through differences in pore geometry and surface area, not merely total void fraction [20,21].

For resonant dielectric components, porosity introduces a tradeoff. Lower permittivity and density can be useful, but scattering and surface losses can degrade Q factor. For absorbers, the same loss mechanisms may be desirable. The design question is therefore not whether volatile templating improves dielectric function in general, but whether the target is high-Q storage, controlled loss, impedance matching, or environmental sensitivity.

6.2 RF and microwave absorption

RF and microwave absorption require a mechanism for converting field energy into heat or for impedance matching incident waves into a lossy body. Carbon residues, semiconducting phases, magnetic additives, ionic glass films, and interfacial polarization can all contribute to dielectric or conductive loss. Porosity can improve impedance matching by lowering effective permittivity, while carbon or conductive residues provide dissipation. However, uncontrolled carbon distribution can make response irreproducible. A rigorous volatile-templated absorber program requires VNA measurements, sample thickness control, density normalization, and comparison to dense and randomly porous controls.

6.3 Acoustic damping and sound absorption

Porous acoustic absorption depends on the interaction between oscillating air and pore walls. Flow resistivity, tortuosity, viscous boundary layers, pore connectivity, and surface roughness govern dissipation [10-13]. Burnout-derived pore networks are therefore directly relevant to acoustic function when pores are open and coupled to the incident pressure field. Historical porous acoustic tiles and modern mineral foams demonstrate that mineral and ceramic-like porous bodies can be engineered for sound absorption, especially when pore connectivity and perforation control are treated explicitly [12,13]. In ceramic systems, the most credible acoustic claims involve damping, absorption, and impedance matching rather than narrow resonant filtering unless the structure includes intentional cavities or periodic features at the appropriate acoustic scale.

6.4 Nonlinear conduction and field-limiting behavior

The varistor case shows that ceramic nonlinear electrical behavior can be controlled by grain-boundary microstructure [14,15]. It is the strongest warning against bulk-composition reasoning. A material can be mostly ZnO by volume and yet derive its decisive electrical function from nanoscale or microscale boundary states. For volatile-templated ceramics, nonlinear conduction is plausible when process-derived boundary phases, dopant segregation, oxygen vacancies, or carbon networks create field-dependent transport. But plausibility is not evidence. Required tests include I-V sweeps, impedance spectroscopy, thermal stability, microstructural mapping, and cycling durability.

6.5 Photonic, phononic, and THz hypotheses

Structured porosity can, in principle, produce photonic or phononic effects when periodicity and contrast match the wavelength regime. Freeze-cast ceramics and sacrificial templating can create periodic or quasi-periodic structures, but many reported pore spacings are too small for ordinary acoustic Bragg effects and too large or too lossy for optical photonics. THz and millimeter-wave regimes are more plausible for tens-to-hundreds-of-micrometers features, but only with sufficient periodic order and low enough loss for band behavior to be resolved. Therefore, this review classifies photonic, phononic, and THz filtering as design hypotheses unless supported by S-parameter measurements, transmission spectra, band-structure modeling, or angle-resolved response.

7. Case families

Case family	Volatile / transient event	Residual architecture	Review conclusion
Starch-consolidated alumina	Starch granules consolidate and later burn out	Porous alumina with pore population tied to starch loading	Strong evidence for process-to-porosity; function must be measured
Freeze-cast alumina	Ice crystals reject particles, then sublime	Aligned lamellae and channels	Strong evidence for anisotropy; wave-response claims require scale matching
Polymer debound ceramics	Binders decompose and leave gas pathways	Void defects, cracking, residual carbon risk	Strong evidence as defect-control system
Cellulose/sawdust-templated bodies	Fibers pyrolyze or burn out	Open fibrous pore networks	Strong practical evidence; acoustic/filter function plausible
Carbon-containing refractories	Oxygen-limited carbon retention	Carbon-bonded or carbon-bearing microstructure	Strong for thermal/refractory function; RF loss must be measured
ZnO-Bi2O3 varistors	Bi-rich boundary phase during liquid-phase sintering	Double-Schottky barrier network	Established nonlinear electrical function
Fluxed low-temperature bodies	Mobile ions melt/segregate	Glassy films and enriched surfaces	Supported; functional response composition-specific

The case families show the boundary of the argument. Established literature already proves that transient phases shape microstructure. Established functional ceramics prove that microstructure can dominate response. The integration step is to build a controlled library that connects the two without skipping measurement. A publication-grade claim must not say, for example, that sugar-templated alumina is an RF material. It can say that saccharide burnout can generate pores or carbon residues, and that those residues may alter dielectric or microwave response, which must be tested against controls.

8. Characterization framework

A volatile-templated ceramic study needs a characterization stack that follows the causal chain rather than only the final coupon. Thermal analysis identifies what leaves and when. Evolved gas analysis identifies whether the gas is water, CO2, CO, hydrocarbons, sulfur species, chlorine species, or other volatiles. Microscopy and tomography identify the residual architecture. Phase and surface analysis identify what remains or segregates. Functional measurements test whether the architecture matters.

Measurement domain	Question	Recommended method	Critical control
Thermal evolution	What leaves, when, and under what atmosphere?	TGA/DSC; staged firing; mass balance	Additive-only and matrix-only controls
Gas chemistry	Which species evolve during burnout or decomposition?	EGA-MS, EGA-FTIR, gas trapping	Blank furnace and known decomposition standards

Pore geometry	What architecture remains?	SEM, optical microscopy, micro-CT, image analysis, porosimetry	Dense matrix and untemplated porous control
Phase structure	Did new phases form?	XRD, Raman, FTIR	Starting powders and fired matrix control
Boundary chemistry	Did mobile species segregate?	SEM/EDS, XPS, TEM-EDS if needed	Nonvolatile dopant route or no-flux control
Carbon state	Is residual carbon present and connected?	Raman D/G bands, conductivity, TGA in air	Clean-burnout control
Dielectric response	How do permittivity and loss change?	Impedance spectroscopy, dielectric analyzer, cavity perturbation	Dense and randomly porous references
RF/microwave response	Does the body absorb, reflect, or resonate?	VNA S-parameters, waveguide fixture, resonant cavity	Air line, metal short, known absorber/dielectric
Acoustic response	Does porosity change damping or absorption?	Impedance tube, ultrasonic pulse-echo, ring-down	Dense ceramic and known porous absorber
Environmental memory	Is response humidity or outgassing dependent?	Humidity cycling, vacuum bakeout, TPD, repeated impedance tests	Dry baked and saturated states

The most important methodological point is that each functional measurement must be tied to a structural variable. Reporting a dielectric spectrum without pore metrics does not prove volatile templating. Reporting porosity without dielectric, RF, or acoustic data does not prove function. Reporting unusual response without controls does not identify mechanism. A robust study must therefore track at least three linked variables: process history, residual architecture, and measured response.

9. Design rules for volatile-templated functional ceramics

The following design rules are evidence-bounded. They are not recipes; they are constraints for building testable process-property experiments.

- Define the target response before selecting the volatile pathway. High-Q dielectric components, lossy absorbers, acoustic dampers, humidity sensors, and nonlinear electrical elements have incompatible optimum microstructures.
- Separate porosity from residue. Clean pores, carbon-lined pores, glass-sealed pores, and hydrated pores can look similar at low magnification but produce different functional response.
- Control atmosphere as a first-order variable. Oxidizing and oxygen-limited firing can turn the same organic additive into either a clean pore former or a carbon source.
- Use feature-size matching for wave claims. Acoustic, microwave, THz, and optical functions require different length scales and contrast regimes.
- Include dense, randomly porous, and composition-matched controls. Without these controls, functional response cannot be attributed to volatile-templated architecture.
- Treat boundary phases as active structures. Grain-boundary films, alkali-rich surfaces, and Bi-rich varistor phases can dominate response even when they occupy small volume fractions.
- Stabilize environmental state. Open porous oxides may adsorb water; humidity and bakeout state must be specified for dielectric and RF measurements.
- Report failure modes. Pore collapse, cracking, carbon over-percolation, flux volatilization, and batch-to-batch segregation are not side observations; they are part of the process map.

10. Research gaps

The first gap is quantitative process libraries. Porous ceramic literature often reports one material, one additive, and one firing condition. A volatile-templating library would instead report decomposition path, gas species, residual carbon, pore metrics, phase segregation, and property response across a formulation matrix. This is more laborious but is the only way to distinguish general rules from anecdotal outcomes.

The second gap is scale-resolved wave measurement. Many proposed resonant functions depend on a match between structural periodicity and wavelength. Without S-parameter, cavity, impedance-tube, or transmission measurements, claims of guiding, filtering, or bandgap behavior are unverified. A useful research program should publish negative results as well: structures that look periodic but show no relevant wave effect are essential for narrowing the design space.

The third gap is carbon and moisture state control. Residual carbon and adsorbed water can dominate dielectric and microwave response, yet both are sensitive to firing atmosphere and post-firing storage. A volatile-templated ceramic intended for dielectric function must define whether carbon and water are design variables, contaminants, or environmental states to be excluded.

The fourth gap is translation from mature electroceramic examples to broader systems. ZnO-Bi2O3 varistors prove that boundary segregation can produce nonlinear electrical function, but that proof cannot be generalized without corresponding barrier physics. Future work should identify which low-temperature fluxed or segregated ceramic systems can create field-dependent transport without relying on the full mature varistor chemistry.

11. Proposed validation matrix

A minimal validation program should use a small number of matrix materials, volatile classes, and functional endpoints. The objective is not to survey all ceramic additives. It is to prove or falsify whether volatile-pathway control improves predictive access to functional response.

Variable class	Recommended levels	Reason
Matrix	Alumina, silica-rich clay, TiO2, ZnO-based comparator	Covers low-loss oxide, glass-forming body, high-k oxide, nonlinear comparator
Volatile route	Starch/saccharide, cellulose fiber, PVA binder baseline, freeze-cast solvent, salt/flux, carbonizing binder	Spans clean pore, fibrous pore, debinding control, aligned pore, boundary film, carbon residue
Firing atmosphere	Air, limited oxygen, staged burnout	Separates clean oxidation from carbon retention
Structure endpoint	Porosity, pore size, connectivity, residue, boundary chemistry	Creates process-structure data
Function endpoint	Dielectric loss, RF response, acoustic absorption, nonlinear I-V	Tests whether structure matters
Controls	Dense matrix, untemplated porous body, additive-free firing, composition-matched nonvolatile dopant	Prevents false attribution

A strong initial test is a paired process comparison rather than a broad survey: one oxide matrix, one volatile pore former, one carbonizing route, one salt/flux route, and one freeze-cast route. Each route should produce three replicate coupons and a control. The measured question is whether process-derived architecture produces statistically separable dielectric, RF, or acoustic response. If not, the hypothesis narrows. If yes, the next study can optimize feature size and phase chemistry for one application domain.

12. Conclusion

Burnout, outgassing, volatilization, and phase segregation are not merely subtractive events. They are formative operations that can define the architecture of a fired ceramic. The literature already supports the individual components of this claim: sacrificial pore formers generate controlled porosity; freeze casting generates aligned channels; binder burnout controls defects and residual carbon; porous media govern acoustic damping through transport parameters; dielectric response changes with pore geometry, surface state, and loss pathways; and ZnO-Bi2O3 varistors demonstrate the functional power of segregated grain-boundary phases.

The synthesis is therefore credible but must remain evidence-bounded. Volatile-templated ceramic microstructures should be treated as a process-structure-property framework, not as a universal shortcut to resonant function. The correct research program tracks what leaves, what remains, what architecture is produced, and what response is measured. Where those four elements align, burnout-derived structures become intentional design variables. Where they do not, the result is only porous ceramic anecdote. The strongest conclusion is consequently operational: the path by which material exits or transforms during firing can be engineered, measured, and used as a design surface for low-temperature ceramic function, provided the claimed wave, dielectric, acoustic, or nonlinear behavior is validated against explicit controls.

References

[1] Lyckfeldt O, Ferreira JMF. Processing of porous ceramics by starch consolidation. Journal of the European Ceramic Society. 1998;18(2):131-140.

[2] Studart AR, Gonzenbach UT, Tervoort E, Gauckler LJ. Processing routes to macroporous ceramics: a review. Journal of the American Ceramic Society. 2006;89(6):1771-1789.

[3] Deville S. Freeze-casting of porous ceramics: a review of current achievements and issues. Advanced Engineering Materials. 2008;10(3):155-169.

[4] Scotti KL, Dunand DC. Freeze casting - a review of processing, microstructure and properties via the open data repository FreezeCasting.net. Progress in Materials Science. 2018;94:243-305.

[5] Deville S, Saiz E, Tomsia AP. Ice-templated porous alumina structures. Acta Materialia. 2007;55(6):1965-1974.

[6] Shao G, Hanaor DAH, Shen X, Gurlo A. Freeze casting: from low-dimensional building blocks to aligned porous structures - a review of novel materials, methods, and applications. Advanced Materials. 2020;32(17):1907176.

[7] Lewis JA. Binder removal from ceramics. Annual Review of Materials Science. 1997;27:147-173.

[8] Chartier T, Ferrato M, Baumard JF. Influence of debinding on defects and microstructure in ceramic processing. Journal of the European Ceramic Society. 1995;15:899-903.

[9] Reed JS. Principles of Ceramics Processing. 2nd ed. New York: Wiley; 1995.

[10] Biot MA. Theory of propagation of elastic waves in a fluid-saturated porous solid. I. Low-frequency range. Journal of the Acoustical Society of America. 1956;28(2):168-178.

[11] Johnson DL, Koplik J, Dashen R. Theory of dynamic permeability and tortuosity in fluid-saturated porous media. Journal of Fluid Mechanics. 1987;176:379-402.

[12] Allard JF, Atalla N. Propagation of Sound in Porous Media: Modelling Sound Absorbing Materials. 2nd ed. Chichester: Wiley; 2009.

[13] Christensen J, Romero-Garcia V, Pico R, Cebrecos A, Garcia de Abajo FJ, Mortensen NA, Willatzen M, Sanchez-Morcillo VJ. Extraordinary absorption of sound in porous lamella-crystals. Scientific Reports. 2014;4:4674.

[14] Clarke DR. Varistor ceramics. Journal of the American Ceramic Society. 1999;82(3):485-502.

[15] Matsuoka M. Nonohmic properties of zinc oxide ceramics. Japanese Journal of Applied Physics. 1971;10(6):736-746.

[16] Colombo P. Conventional and novel processing methods for cellular ceramics. Philosophical Transactions of the Royal Society A. 2006;364:109-124.

[17] Fruhstorfer J, Aneziris CG. Carbon-containing refractories: current status and future prospects. Ceramics International. 2014;40:8999-9013.

[18] Brosnan DA. Corrosion of refractories. In: Schacht CA, ed. Refractories Handbook. New York: Marcel Dekker; 2004.

[19] Bueno PR, Varela JA, Longo E. SnO2, ZnO and related polycrystalline compound semiconductors: an overview and review on the voltage-dependent resistance behavior. Journal of the European Ceramic Society. 2008;28:505-529.

[20] Kim YW, Kim SH, Wang C, Park CB. Processing of porous silicon carbide ceramics from carbon-filled polysiloxane by extrusion and carbothermal reduction. Journal of the American Ceramic Society. 2003;86(12):2231-2233.

[21] Penn SJ, Alford NM, Templeton A, Wang X, Xu M, Reece M, Schrapel K. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. Journal of the American Ceramic Society. 1997;80(7):1885-1888.

[22] Gibson LJ, Ashby MF. Cellular Solids: Structure and Properties. 2nd ed. Cambridge: Cambridge University Press; 1997.

[23] Rao CNR, Raveau B. Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides. 2nd ed. New York: Wiley-VCH; 1998.

[24] Barsoum MW. Fundamentals of Ceramics. 2nd ed. Boca Raton: CRC Press; 2019.

[25] Kingery WD, Bowen HK, Uhlmann DR. Introduction to Ceramics. 2nd ed. New York: Wiley; 1976.

[26] Jonscher AK. Dielectric relaxation in solids. Journal of Physics D: Applied Physics. 1999;32:R57-R70.

[27] Bergman DJ. The dielectric constant of a composite material - a problem in classical physics. Physics Reports. 1978;43(9):377-407.

[28] Sihvola A. Electromagnetic Mixing Formulas and Applications. London: Institution of Electrical Engineers; 1999.