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Assessment of flaws in cold-sintered ZnO via acoustic wave speed and attenuation measurements

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Abstract

The cold sintering process (CSP) is a low temperature processing technique that utilizes a transient phase to synthesize dense ceramics. However, some CSP parts contain microflaws that arise due to inhomogeneities in pressure, temperature, and transient phase. This work uses 20 MHz ultrasound to verify the presence of defects in CSP ZnO samples of varying densities (84%-97%). Acoustic metrics used in this work include wave speed, which is affected by differences in the effective elastic properties of the medium, and attenuation, which quantifies wave energy loss due to scattering from defects. Wave speed maps were inhomogeneous, suggesting density gradients which were verified with scanning electron microscopy. In addition, it was demonstrated that the pores produced by cold sintering are anisometric, which increases the anisotropy in the elastic properties. High attenuation regions (>300 Np/m) are present in all samples independent of relative density and correspond to defects identified in X-ray computed tomography (XCT) which were as small as 38 µm in effective diameter. However, some high attenuation spots do not correspond to visible defects in XCT, which suggests the presence of features undetectable with XCT such as residual secondary phases at the grain boundaries.

KEYWORDS

characterization, defects, sinter/sintering, ultrasonics, zinc oxide

1 | INTRODUCTION

Cold sintering has recently developed into a reliable low temperature processing method for ceramics^{1–3} and composites.^{4,5} In the cold sintering process (CSP), a transient phase, most commonly an aqueous solution, assists in the densification of powders upon the application of uniaxial pressures and moderate temperatures in an open system. In some ceramics, the densification is driven by a pressure dissolution-creep mechanism.^{3,5} Significant progress has been made on utilizing a range of chemistries to facilitate cold sintering for different ceramics. In many cases, relative densities exceeding 90% are obtained in a single step. However, some cold-sintered parts do not reach comparable mechanical or functional properties to those obtained via conventional sintering, even when high relative densities are achieved.^{6–9} These degraded properties are presumed to be in part a result of macroflows that

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Journal 4956

arise from poor die-filling, pressure gradients in the die, inhomogeneous distributions of the fluxes, or temperature gradients during the process. Densification can be further compromised in the case of inhomogeneous removal of transient phases or inability to reach the proper cold sintering temperatures and pressures everywhere in the part. Identification and characterization of the flaws in cold-sintered materials can assist in understanding their origin and so facilitate process optimization. Therefore, there is a need to develop a characterization method that can detect and assess the type, size, and distribution of defects in bulk CSP parts.

Ultrasonic testing (UT) allows nondestructive material analysis via sound waves, at frequencies generally in the tens of megahertz range that are sensitive to the elastic properties of the medium.¹⁰ Ultrasound is used industrially to detect flaws within parts and structures through diffraction-limited imaging, for which the imaged flaw size must be exceed half the wavelength used. In contrast, ultrasonic wave speed and attenuation can be used to image defects at a much smaller scale. Wave speed is sensitive to changes in the elastic properties of a material. Given that pores decrease the effective stiffness of the matrix material, an ultrasonic wave will travel slower through a porous region than a dense one. Attenuation is sensitive to regions smaller than the wavelength, which act as scattering sites for the ultrasonic wave. Thus, the presence of pores, secondary phases, and variations in microstructure morphology can increase attenuation in a material.

Previous studies have shown that ultrasonic wave speed and attenuation metrics can be employed to detect and quantify grain size,^{11,12} secondary phases,¹³ texturing,¹⁴ and porosity.^{15–19} Recently, Huang et al.¹⁶ explored the use of ultrasonic wave speed and attenuation as characterization techniques for additively manufactured 316 stainless steel and 316 stainless steel/bronze alloys. Regions of high attenuation and low wave speed correlated to regions of high porosity, an observation consistent with results on other alloys, ceramics, and composites.^{11,18,19} The orientation and shape of pores can also influence measured wave speed and attenuation. Pabst and Gregorová²⁰ showed using the Eshelby-Wu coefficients^{21,22} for an isotropic porous material that elastic modulus is strongly dependent on the aspect ratio of pores. Perfectly spherical pores produced the largest elastic modulus compared to disklike (oblate) and needlelike (prolate) pores. Ultrasonic wave speed measurements would in turn be sensitive to any reduction in elastic moduli resulting from nonspherical pores. More recently, Wang et al.²³ modeled pore morphology effects on attenuation in dry rocks and determined that smaller aspect ratios and pores at least 150 times below the ultrasonic wavelength had the greatest influence on atten-

uation with pore size dominating the ultrasonic response in cases where the aspect ratios exceeded 0.5.

In this article, ultrasonic wave speed and attenuation metrics are used to investigate density inhomogeneities, porosity, and other defects in cold-sintered zinc oxide (ZnO). ZnO is used in semiconductor, thermoelectric, and varistor applications and is a model ceramic system for cold sintering studies.^{7,24,25} Previous studies on coldsintered ZnO have investigated sintering mechanisms at elevated^{24,25} and near room-temperatures,²⁶ effects of different transient phases,^{9,27} and mechanical and functional properties.^{6,7,9,28} Gonzalez-Julian et al.²⁴ investigated the mechanisms of cold sintering ZnO and demonstrated the critical role both water and zinc acetate play in densification. Adsorbed water and zinc acetate increase defect formation within ZnO grains and in the grain boundary area which reduces the activation energy for atomic diffusion and promotes densification. Recently, Hérisson de Beauvoir et al.²⁸ investigated the cold sintering of ZnO using in situ electrochemical impedance spectroscopy. By cold sintering ZnO at 250°C, they demonstrated that elimination of residual acetate is essential for lowering grain boundary resistances. They also showed improved grain shape isotropy after acetate elimination, which is consistent with the Dargatz et al.²⁹ observation of coarsening of ZnO particles along [0001] in the presence of warmth, humidity, and acetic acid. Both Gonzalez-Julian et al.²⁴ and Hérisson de Beauvoir et al.²⁸ also suggested that residual acetate locally breaks the wurtzite crystal structure, which can result in diminished mechanical and electrical properties. Lowum et al.⁶ investigated the mechanical strength of ZnO cold sintered using zinc acetate as the transient liquid phase and found that, despite relative densities of 97%, the strength was approximately 40% lower than that for conventionally sintered ZnO counterparts. They hypothesized that the diminished mechanical strength was due to poor grain boundary bonding in cold-sintered materials compared to conventionally sintered materials. In contrast, Nur et al.⁷ reported similar elastic modulus and hardness in 99% dense cold-sintered ZnO, which used deionized water as the transient liquid phase, relative to conventionally sintered ZnO samples. Jabr et al.9 investigated effects of transient phase chemistries on the densification and mechanical strength of cold-sintered ZnO. Relative densities above 95% were obtained at 125°C using formic acid and acetic acid, but acetic acid samples showed significant grain growth, whereas formic acid samples retained their initial grain size. Biaxial characteristic strength for samples cold sintered with formic acid were twice the strength of the acetic acid samples and approximately 40% greater than the strengths from Lowum et al.⁶ Thus, variations in microstructure and presence of

TABLE 1 Cold-sintered ZnO samples of varying relative densities, their processing pressures, and corresponding average thicknesses.

Relative density (%)	Cold sintering pressure (MPa)	Average thickness (mm)	Average wave speed (m/s)	Average attenuation (Np/m)
84	530	1.66	4256 ± 20	224 ± 37
86	530	1.47	4259 ± 37	184 ± 40
87	530	1.55	4268 ± 21	388 ± 110
93	530	1.48	5075 ± 4	115 ± 42
95	700	1.43	5181 ± 9	121 ± 53
96	700	1.45	5223 ± 9	198 ± 47
97	530	1.46	5205 ± 74	208 ± 30

Note: The average ultrasonic wave speed and attenuation values (±standard deviation) obtained from the ultrasonic characterization are also listed. The maximum theoretical wave speed for ZnO is 5750 m/s.

transient phase are known to affect mechanical and electrical properties of cold-sintered ZnO.

To demonstrate the viability of UT for nondestructive evaluation of cold-sintered materials, samples were ultrasonically tested in a water immersion system using longitudinal bulk waves, in which particle displacement is in the direction of the wave propagation. Ultrasonic results are compared to X-ray computed tomography (XCT) images to assess ultrasonic sensitivity to defect size and aspect ratio. Further characterization was conducted using scanning and transmission electron microscopy (SEM/TEM). This work demonstrates that nondestructive ultrasonic evaluation allows the detection and analysis of microstructural homogeneity and flaws present in cold-sintered ZnO.

2 | MATERIALS AND METHODS

2.1 | Sample fabrication

Material preparation for cold sintering followed the process outlined by Kang et al.²⁶ For this study, ZnO nanopowder (99.9%, Alfa Aesar) was ball milled for 48 h in 4 wt.% 0.8 M aqueous ZnO(Ac)₂ solution. The compound was cold sintered at 120°C for 30 min at uniaxial pressures of 530 and 700 MPa depending on the density desired. Table 1 shows the relative densities achieved under various CSP pressures. Samples were 12.7 mm in diameter and between 1.43 and 1.64 mm in thickness, measured using digital calipers. Relative densities were measured via the Archimedes method using a material density of 5.61 g/cm³ for ZnO.

2.2 | Ultrasound measurements

Longitudinal ultrasonic measurements were performed in a water immersion system (Mistras Group, Princeton Junction, NJ, USA) using a pulse-echo configuration with inci-



Journal

4957

FIGURE 1 Schematic of the experimental configuration for thickness-independent wave speed measurements. The perforated section of the sample represents the absence of the sample for that specific reflection measurement.

dence normal to the sample surface as shown in Figure 1, resulting in longitudinal wave propagation. The immersion system consisted of a JSR DPR-500 pulser/receiver (Pittsford, NY, USA), a 20 MHz center frequency focused transducer (Olympus, Waltham, MA, USA, element diameter of 6.35 mm and focal length of 50.8 mm), an AD-8xG data acquisition card, and a computer-controlled positioning system. The beam width of the transducer used in this work is 0.6 mm which serves as the diameter for the circular spot size area of 0.283 mm². The volume interrogated is the thickness multiplied by the spot size, which will vary across all samples due to thickness variations. The transducer was focused on the back surface of the sample and raster-scanning across the top surface was performed at a 0.25 mm resolution. Time-dependent amplitude data were collected at each scanning point after 10 ensemble averages using a 1000 MHz sampling rate.

Two additional scans were performed to gather reflection from a plate placed behind the sample to enable thickness-independent measurements of the wave speed,



FIGURE 2 Wave speed maps (numbers in m/s) for cold sintered ZnO samples with (A) 84% – (G) 97% relative density. Scale bars vary for each sample but show a consistent range of 400 m/s. Large regions of missing data seen in (F) and (G) are due to delaminations in the samples.

following the process described by Kuo et al.³⁰ The time-dependent signals were post-processed in MATLAB (R2018b) to obtain spatial maps of longitudinal wave speed and attenuation through the thickness. The thickness-independent wave speed was calculated as

$$c_m = \left[\frac{t_w - t_m}{t_2 - t_1} - 1\right] c_w \tag{1}$$

where $(t_w - t_m)$ is the time delay between signals from the reflector without the sample (t_w) and with the sample (t_m) present along the propagation path, $(t_2 - t_1)$ is the time delay between front and back surface reflections from the sample, and c_w is the experimentally measured water wave speed.

Longitudinal attenuation calculations were completed according to the equal diffraction approach by Yu et al.³¹ where a fused silica sample (density 2214 kg/m³, thickness 1.59 mm, and longitudinal wave speed 6000 m/s) with assumed zero attenuation was used as a reference to account for the system effects and beam diffraction. Attenuation was then calculated by

$$\alpha_{s}(f) = -\frac{1}{2t_{s}} \ln \frac{|\Gamma_{s}(f)| \left(1 - R_{ref}^{2}\right) R_{ref}}{\left|\Gamma_{ref}(f)\right| \left(1 - R_{s}^{2}\right) R_{s}} + \alpha_{w}(f) \frac{W P_{ref} - W P_{s}}{t_{s}}$$
(2)

FIGURE 3 Porosity dependent wave speeds for cold-sintered ZnO where the triangle shaped points correspond to the mean wave speed for each sample and the error bars are the standard deviation. The solid dark redline represents analytical estimates of the wave speed dependence on porosity based on Hashin–Shtrikman limits.³³ The colored regions represent analytical estimates of the wave speed dependence on aspect ratio of porosity based on the Eshelby–Wu model,^{20,21,22} with colors denoting a range of aspect ratios.



where $|\Gamma_{ref}(f)|$ and $|\Gamma_s(f)|$ are the spectral amplitudes

of the back surface reflections for the reference silica and each scanning point on the sample, respectively, and t_s is the sample thickness at each scanning position as described by Cook et al.¹⁷ R_s and R_{ref} are the sample and reference silica reflection coefficients, respectively, calculated using the experimentally measured wave speeds. α_w is the attenuation in the water (10.1 Np/m). WP_s and WP_{ref} are the water paths for the sample and reference silica, respectively, where water path is defined as F—[$t_s(c_m/c_w)$] with F being the focal length of the transducer in water.

2.3 | Microstructural and defect imaging

XCT (General Electric vltomelx L300 nano/microCT) for defect characterization was performed with a 10-µm voxel size on all samples. Samples were stacked during the scan, and tomography slices were reconstructed using X-ray cone-beam back projections. Raw XCT data sets were imported into MATLAB (R2021a) for post-processing according to the process outlined in Chisena et al.³² Each sample data set was thresholded and segmented for porosity using a normalized histogram of voxel intensity. Segmentation was conducted according to mixed Gaussian distribution clustering which treats XCT measurement artifacts as random noise and models internal sample features as a mixture of Gaussian distributions. After segmentation, pores containing less than 27 voxels were removed for further denoising.¹⁶ Reconstructions of porosity in 2D were adapted from the thresholded data which constitute pore volumes summed through the thickness of the sample for enhanced visualization of porosity

distribution. Quantitative data, including pore volumes and aspect ratios, were extracted from the thresholded data sets using the *regionprops3* embedded MATLAB function.

The 87% dense ZnO sample was chosen for further imaging using field-emission SEM (ZEISS Gemini 500) for microstructural characterization on regions where ultrasonic techniques detected defects, but XCT did not. The sample was diced at the areas of interest and polished using an ion mill (Leica TIC3). An additional area on the 87% dense sample was chosen for imaging using TEM (Titan³ G2) prepared using focused ion beam (Helios 660), primarily focused on capturing residual transient phase along the grain boundaries.

3 | RESULTS AND DISCUSSION

Longitudinal ultrasonic wave speed and attenuation data are presented for nondestructive assessment of density homogeneity and characterization of micro and macroflows in cold-sintered ZnO. Ultrasonic results are validated by XCT, whereas SEM and TEM are used to further characterize the microstructure and defects in cold-sintered ZnO.

3.1 Wave speed

Figure 2 depicts the wave speed results for the cold-sintered ZnO samples; the average values are listed in Table 1. Note that the maps are not perfectly circular as the ultrasonic beam was blocked by the stainless steel standoffs used to hold the sample (hence the lack of data at the top and bottom of each map). Other areas of missing data are due to delaminations within the samples, which will be



FIGURE 4 Wave speed map (units of m/s) (A) of the 87% dense cold-sintered ZnO sample. An ion-milled cross-section indicated by the perforated black ellipse is shown in (B) showing bands of porosity. A magnified image of the microstructure is shown in (C).



FIGURE 5 Map of time of arrival of the maximum amplitude relative to the front surface reflection (in μ s) for the (A) 96% dense and (B) 97% dense cold-sintered ZnO samples. The yellow (0.6 μ s) indicates reflection from the back surface of the sample.

discussed in detail later in this section. Though average wave speed increases with increasing density (as shown in Table 1) variations in wave speed within single samples occur regardless of bulk relative density. For example, the 84% relative density sample in Figure 2A shows wave speeds of approximately 4100 m/s toward the lower half of the disc, increasing by as much as 300 m/s in the upper half of the disc. A similar trend is seen in Figure 2B-D with wave speeds across a single sample varying between 200 and 400 m/s. The sample with a relative density of 95% in Figure 2E has higher wave speeds around the perimeter of the sample and lower wave speeds toward the center. A similar observation is made in Figure 2F. Because wave speed is sensitive to differences in the effective elastic properties of the material, the variation in wave speed indicates microstructural inhomogeneities in each sample which are undetectable using geometrical or Archimedes density measurement methods. These inhomogeneities in sample densities could be caused by processing issues such as die press misalignment or die wear. Another possibility is inhomogeneous distribution of transient liquid phase

which Kang et al.²⁶ identified as vital for achieving densification in cold-sintered ZnO since the $Zn(OAc)_2$ transient phase serves as an additional driving force to pull particles together.

Variations in the average ultrasonic wave speed were further explored considering the relationship between wave speed and effective moduli for an isotropic solid given by

$$c_m = \sqrt{(K^* + 4G^*/3)/\rho}$$
(3)

where K^* is the effective bulk modulus, G^* is the effective shear modulus, and ρ is the sample density. Analytical relationships between moduli and porosity, dependent on pore distribution and aspect ratio, are given by the Hashin–Shtrikman³³ and Eshelby–Wu^{20–22} bounds that are described in more detail in the Appendix. The Hashin– Shtrikman bound for multiphase materials³³ assumes the special structural case of homogeneously distributed, spherical porosity. The Eshelby–Wu bounds, which are based on the Hashin–Shtrikman model, assume homogenously distributed porosity and consider the effect of pore



Attenuation (left, numbers in Np/m) and x-ray computed tomography (XCT) 2D reconstructions (right) for cold sintered FIGURE 6 ZnO samples with (A) 84% - (G) 97% relative density. Color intensity on the XCT images indicates the total dimension of the pores through the thickness (numbers in µm). Dashed circles show specific correlations between the attenuation map and XCT image.

aspect ratio. In this work, Voigt averages of the single crystal elastic stiffness constants for ZnO determined by Azuhata et al.³⁴ ($c_{11} = 190, c_{12} = 110, c_{13} = 90, c_{33} = 196$, c_{44} = 39, and c_{66} = 40 in GPa) were used to calculate K_0 and G_0 used in both models, given by (in GPa): $c_{11} = 185$, $c_{12} = 100$, and $c_{44} = 42.7$.

The mean wave speeds for the cold-sintered ZnO samples are plotted in Figure 3 which highlights the wave speed dependence on pore shape. The Hashin-Shtrikman upper bound (solid redline) was calculated according to Equations (A1) and (A2). The EshelbyWu bounds (colored regions) were calculated according to Equations (A3) and (A4) for aspect ratios from 0.1 to 1.5. A linear regression of the data shows a different slope than the Hashin-Shtrikman bound, which suggests that the sample microstructures differ from a Hashin assemblage (e.g., a porous material consisting of space filling hollow spheres with an infinitely wide size distribution); The CSP ZnO data falls clearly within between the cyan and purple regions which correspond to pore aspect ratios of 0.1-0.7 which are oblate (disklike).

4961

To support the wave speed data, the aspect ratios of the pores imaged by XCT were calculated and plotted as a histogram shown in Figure 3. XCT indicates that the majority of the pores detected are oblate with aspect ratios between 0.1 and 0.9. These data suggest that the pores dominating the wave speed response, and thus the effective elastic moduli, in cold-sintered ZnO, are disklike rather than spherical. This observation could help explain the diminished mechanical properties observed in cold-sintered ZnO since oblate pores reduce the effective elastic moduli of the material and decrease the overall compressive strength.⁶ These observations also highlight the versatility of nondestructive wave speed measurements in assessing not only microstructural homogeneity but also elastic moduli to infer mechanical strength.

To further assess the microstructural inhomogeneities present in cold-sintered ZnO, through-thickness SEM was performed on an ion-milled cross-section of the 87% dense sample, shown in Figure 4. The wave speed map from Figure 2C is shown for reference in Figure 4A with the circled region indicating the approximate area where the cross-section was imaged. Figure 4B shows a wavelike pattern and upon closer inspection, the "waves" are regions of low density surrounded by regions of higher density (Figure 4C). This bimodal density distribution could be caused by inhomogeneous distribution of the transient liquid phase. Liquid phase fraction and distribution is a key component for densification in cold-sintered materials and insufficient wetting of particles can inhibit particle rearrangement and densification under the applied pressure.^{25,26} Aside from the bimodal density distribution, the grains shown in Figure 4C are fairly isometric with an average grain size of 200 nm, which is consistent with previously reported results showing grains with sizes on the order of the particle size used.^{6,9,26}

Large regions of missing data in the wave speed maps are visible in the top Figure 2F and the right of Figure 2G. In these regions, a reflection was not detected in the narrow, predetermined time window placed at the expected arrival time for the back surface reflection. Instead, an earlier reflection was detected, potentially indicative of an internal delamination in the ceramics, as depicted in Figure 5. The time of flight map indicated the arrival times for the first reflection spatially, with the time scale denoting top surface reflections as 0 µs and back surface reflections as 0.6 µs. Macroscopic delaminations are indicated by a shorter wave arrival time; that is, the large regions corresponding to approximately 0.2-0.3 µs in Figure 5a,b are the same regions of missing data observed in Figure 2f,g, respectively. These large delaminations are not visible or detectable via standard relative density measurements. In addition, they were not visible in XCT due to the delaminations generating insignificant

TABLE 2 Number of defects detected via X-ray computed tomography (XCT) and the average volume of those defects for dense cold-sintered ZnO samples.

Relative density (%)	Number of defects in XCT	Average volume of defects (µm ³)
84	60	2.35×10^{5}
86	20	5.33×10^{5}
87	52	2.57×10^{5}
93	82	6.75×10^{5}
95	2	4.15×10^4
96	9	3.17×10^{5}
97	1	3.20×10^4

contrast with the selected X-ray settings. The presence of these delaminations is another explanation for the diminished macroscopic mechanical properties observed in cold-sintered ZnO.^{6,9}

3.2 | Attenuation

Average attenuation values are shown in Table 1 and were calculated excluding the high values around the perimeter which were impacted by scattering from the sample edges. Average attenuation for all samples exceeds 100 Np/m, with the 84%, 87%, and 97% dense samples having averages above 200 Np/m; the average values show no apparent correlation to relative density. The maps of attenuation coefficients plotted across the sample area are shown in Figure 6. Regions of high attenuation are seen throughout all samples. The 84% and 97% dense samples seen in Figure 6A,G have several highly attenuating areas located toward the perimeter of the disc. The remaining samples show several highly attenuating regions scattered randomly across the entire disc area. Unlike wave speed, which increased with increasing relative densities of the material, the amount and distribution of scattering events do not correlate with the average relative density. This random distribution suggests that microflaws, such as large pores or secondary phases, are not directly related to either average relative density or the conditions of the die and press. Other steps in the CSP, including powder packing or transient phase distribution around the powder, are possible explanations for the presence and distribution of these microflaws.

XCT was performed to visualize the defects causing scattering. Figure 6 depicts the 2D reconstructions of the XCT data summed through the thickness for each sample. Color intensity on the 2D reconstructions indicates the dimension of the pores through the thickness in μ m. Because features containing less than 27 voxels at a voxel size of 10 μ m were removed, the smallest features shown have



FIGURE 7 (A) Attenuation map of the 87% dense cold-sintered ZnO sample (units in Np/m). The white dashed circle indicates a region of high attenuation with no defects imaged via X-ray computed tomography (XCT) with arrows pointing to (B) the scanning electron microscopy (SEM) and (C and D) transmission electron microscopy (TEM) performed on this region.

volumes of at least $2.8 \times 10^4 \ \mu m^3$ and effective diameters of 38 µm. The number of defects detected and the average volumes of the defects for each sample are summarized in Table 2. Samples with 93% relative density or less show 20 or more defects while those with relative densities of 95% or greater show less than 10. It is important to note that while XCT showed fewer defects for the higher density (>95%) samples, these samples had large delaminations detected via ultrasound that were not imaged by XCT. The average volumes of the defects in the lower density samples (<93%) are also an order of magnitude higher than those in the 95% and 97% dense samples. Interestingly, the 96% dense sample shows more defects with larger average volumes than the other two high density samples.

The attenuation and XCT figures are compared in Figure 6 with examples of visibly correlated regions of highly attenuating areas and XCT imaged defects shown within the circled regions. Defects exceeding 5 μ m in the through-thickness dimension corresponded well with the attenuation maps. However, some regions of high attenuation do not correspond with defects imaged in XCT which suggests that different types of defects are scattering the ultrasonic waves. As XCT at the laboratory scale is only sensitive to density differences within the sample,¹⁶ additional microstructural features such as grain size, micro-textured regions, or secondary phases with sim-

ilar densities to ZnO can go undetected with this method. To assess the presence of highly attenuating microstructural features that went undetected in XCT, a low density (87%) sample was chosen for further characterization by SEM and TEM. More specifically, a region of high attenuation but no XCT anomaly was chosen for imaging as indicated in Figure 7A.

Initially, mechanical polishing was done to prepare the samples for SEM; however, the samples experienced significant grain pullout making microstructural features, such as porosity, impossible to identify. This grain pullout is likely a result of weak grain boundaries in cold-sintered samples as hypothesized by Lowum et al.⁶ Therefore, ion milling was performed to create a polished microstructural surface while avoiding grain pullout. The corresponding SEM image is given in Figure 7B. The same heterogeneously dense microstructure seen in Figure 4C is observed, but the highly densified regions here are smaller and more isolated. These isolated densified regions have defined boundaries separating them from the lower dense material surrounding them which might cause the ultrasonic wave to scatter since changes in grain size increase attenuation.¹¹ A few grains that exceed several microns in size were observed, so the possibility of increased attenuation due to crystal anisotropy was considered. However, the ultrasonic wavelength ($\sim 265 \,\mu m$) is much larger than

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the largest observed grain diameter (~10 μm) which indicates the attenuation coefficient due to grain scattering is within the Rayleigh regime and no increased attenuation from grains is expected. 11

Further analysis of this sample was conducted using TEM and Figure 7C.D shows the resulting images of the grain boundaries. These images reveal an amorphous secondary phase located between ZnO grains which is presumably residual $Zn(OAc)_2$. This amorphous phase is a result of incomplete extrusion and/or conversion of the $Zn(OAc)_2$ during the CSP. This residual phase has been attributed by Kang et al.²⁶ to the cold sintering temperatures not exceeding the necessary thermal decomposition temperature of Zn(OAc)₂ in cold-sintered ZnO, which is consistent with the observations made by Hérisson de Beauvoir et al.²⁸ and Jabr et al.⁹ that residual acetic acid is present until sintering temperatures of 250°C are reached. Though ultrasonic attenuation is sensitive to differences in acoustic impedance between phases, it is unlikely that the attenuation response seen in Figures 5C and 7A is caused only by the presence of residual acetate phase.

It is important to note that a single lower limit for defect detection via ultrasonic attenuation is difficult to identify to due dependence on matrix material and inclusions, inclusion size, inclusion shape, and inspection frequency.^{11–14} However, ultrasonic attenuation has shown to be sensitive to features such as MRTs and secondary phases,^{11–14} which suggests the presence of some of these microstructural features within cold-sintered ZnO.

4 | CONCLUSIONS

This study demonstrates the viability of ultrasonic nondestructive evaluation for characterization of cold-sintered ZnO. Microstructural characteristics, such as poor grain boundary bonding, inhomogeneously distributed porosity, and macroscopic delaminations, can diminish mechanical and electrical properties of cold-sintered ceramics. Ultrasonic wave speed measurements, which are sensitive to changes in the elastic moduli of the material, indicated density gradients and macroscopic delaminations in cold-sintered ZnO; such flaws can go unnoticed in standard relative density measurements such as the geometrical method. SEM showed a bimodal distribution of densities producing a "wave" pattern, most likely caused by inhomogeneous transient phase distribution during processing. Analytical models (Hashin-Shtrikman³³ and Eshelby-Wu²⁰⁻²² models) were used to assess the wave speed dependence on pore distribution and shape. The wave speed values of cold-sintered ZnO deviate from the Hashin assemblage of inhomogeneously distributed nonspherical pores. CSP ZnO wave speed values fall within the Eshelby-Wu bounds which predict average pore aspect ratios between 0.2 and 0.7. The majority of pores imaged in XCT had aspect ratios between 0.2 and 0.9 in agreement with the wave speed data. Ultrasonic attenuation measurements indicated the presence of randomly distributed and relative density independent microflaws that were confirmed via XCT imaging. Attenuation measurements corresponded well to defects exceeding 5 µm in the through-thickness dimension and showed sensitivity to flaws undetectable via XCT. These regions were assessed through SEM and TEM. SEM showed isolated regions of densified material in the 87% dense sample which could have served as large scattering sites. TEM showed residual Zn(OAc)₂ present between grains which is unlikely to have contributed significantly to the attenuation response but may have contributed to the slower than predicted wave speeds. The results of this study underscore the value of a nondestructive technique such as ultrasound for analysis of cold-sintered parts as a rapid feedback approach for process optimization.

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APPENDIX

An analytical relationship between moduli and porosity is given by the Hashin-Shtrikman bounds for multiphase materials³³ where for the special case of materials with homogeneously distributed porosity, the upper bound for bulk modulus (K^{HS}), and shear modulus (G^{HS}) is given by

$$K^{HS} = \left(1 - \left[\frac{3K_0 + 4G_0}{9K_0c_1 + 4G_0}\right] [1 - \varphi]\right) K_0$$
(A1)

$$G^{HS} = \left(1 - \left[\frac{15K_0 + 20G_0}{9K_0 + 8G_0 + (6K_0 + 12G_0)(1 - \varphi)}\right] [1 - \varphi]\right) G_0$$
(A2)

and the lower bound degenerates to zero. Here, φ is the volume fraction of porosity, and K_0 and G_0 and the bulk and shear moduli of the fully dense medium, respectively.

Another relationship between effective moduli and porosity, known as the Eshelby–Wu^{21,22} model, considers the effect of pore aspect ratio on the elastic moduli of the medium. The Eshelby–Wu model is given by

$$K^* = \left(1 - \left[K^{EW}\right]\varphi\right) K_0 \tag{A3}$$

$$G^* = \left(1 - \left[G^{EW}\right]\varphi\right) \ G_0 \tag{A4}$$

where K^{EW} and G^{EW} are the Eshelby–Wu coefficients for the bulk and shear moduli, respectively, which are given in the Appendix. A more detailed explanation of the Eshelby– Wu model can be found in Pabst and Gregorová.²⁰

As presented in Pabst and Gregorová, the Eshelby–Wu coefficients are given by

where R is the aspect ratio of the inclusion and q is a function of the aspect ratio, given by

$$q = \frac{R}{(R^2 - 1)^{3/2}} \left[R(R^2 - 1)^{\frac{1}{2}} - \operatorname{arcosh}(R) \right]$$
(A7)

$$q = \frac{R}{\left(1 - R^2\right)^{3/2}} \left[\arccos(R) - R(1 - R^2)^{1/2}\right]$$
(A8)

$$q = 2/3 \tag{A9}$$

where (A7) is used for prolate (R > 1) pores, (A8) is used for oblate (R < 1) pores, and (A9) is the special case for spherical (R = 1) pores, respectively.

$$[K] = \frac{1-\nu}{6(1-2\nu)} \times \frac{4(1+\nu)+2R^2(7-2\nu)-\left[3(1+4\nu)+12R^2(2-\nu)\right]}{2R^2+(1-4R^2)q+(R^2-1)(1+\nu)q^2}q$$

$$[G] = \frac{4(R^2 - 1)(1 - \nu)}{15\{8(1 - \nu) + 2R^2(3 - 4\nu) + [(7 - 8\nu) - 4R^2(1 - 2\nu)]q\}} \times \left\{ \frac{8(1 - \nu) + 2R^2(3 + 4\nu) + [(8\nu - 1) - 4R^2(5 + 2\nu)] *q + 6(R^2 - 1)(1 + \nu)q^2}{2R^2 + (1 - 4R^2)q + (R^2 - 1)(1 + \nu)q^2} - 3\left[\frac{8(\nu - 1) + 2R^2(5 - 4\nu) + [3(1 - 2\nu) + 6R^2(\nu - 1)]q}{-2R^2 + [(2 - \nu) + R^2(1 + \nu)]q}\right] \right\}$$
(A6)