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In situ probing of interfacial roughness and transient phases during ceramic cold sintering process

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ABSTRACT

The ceramic cold sintering process (CSP) offers an eco-friendly approach to producing fully dense ceramics at low temperatures. However, an incomplete mechanistic understanding hinders its optimization and widespread adoption. In this study, we analyze the microstructural and structural changes in ZnO, a model CSP system, using in situ synchrotron-based high-energy small-angle X-ray scattering and X-ray diffraction techniques. Our results reveal the time evolution of ZnO particles' surface area and roughness, reflecting the dissolution and reprecipitation processes that enable densification. The in situ measurements supply valuable kinetic data for these stages of CSP. Alongside microstructural changes and densification, we observed the evolution of secondary phases representing reaction products between ZnO and acetic acid, the solvent used. The initial ZnO/solvent mixture's dominant secondary phase is attributed to zinc acetate, which is gradually replaced by a zinc soap-type structure during CSP. This structure has a large (pprox 21 Å) lattice parameter and is assumed to have a layered nature. The formation of this soap phase, which is retained in the sintered product as an intergranular component, appears to be a signature of successful cold sintering as it facilitates mass transport, leading to densification. Our study underscores the potential of *in situ* synchrotron characterization for revealing microstructural and phase-evolution details during CSP. These findings, which would be challenging to obtain through ex situ measurements, provide crucial data to guide and validate theoretical models, ultimately enhancing CSP's effectiveness and adoption.

1. Introduction

Ceramic materials possess unique properties desirable for diverse structural and functional applications. The industrial utilization of ceramics is limited, among other factors, by the availability of cost-effective fabrication methods. Sintering, a crucial step in ceramic processing, presents a significant challenge as it requires prolonged exposure (hours) to high temperatures (> 1000°C), which increases the cost and carbon footprint while also creating technological hurdles, such as unwanted reactions, grain coarsening, and difficulties in integrating multiple materials [1].

A recently developed ceramic cold sintering process (CSP) mitigates these issues by allowing the densification of ceramics under uniaxial pressure at temperatures ranging from nearly ambient to just a few hundred degrees Celsius. CSP uses a liquid solvent, such as water, added to the ceramic powder to create a transient phase that facilitates densification. During the process, the material at the particle surfaces dissolves in the liquid and then reprecipitates, leading to the sintering of ceramic powders [2,3]. The method is simple to implement in a standard laboratory setting and has been demonstrated for over a hundred materials, including single-phase ceramics [4–10], mixed-phase ceramics [11,12], ceramic-polymer composite [13,14], and ceramic-metal composite [2]. This versatility has allowed for the exploration of cold-sintered parts for a variety of applications, including ceramic packaging [15], microwave dielectrics [16,17], solid-state batteries and electrolytes [18–22], and flexible electro-ceramic devices [23], with the list of applications growing rapidly.

Previous studies of CSP primarily focused on demonstrating its applicability to various materials systems and, to some extent, process optimization [9,14,24–26]. Recently, more attention has been given to understanding the mechanisms that facilitate densification. These studies, which used model systems, such as ZnO, and molecular

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Received 8 June 2023; Received in revised form 17 August 2023; Accepted 22 August 2023 Available online 23 August 2023 1359-6454/Published by Elsevier Ltd on behalf of Acta Materialia Inc. dynamics simulations [27–29], established the pressure and chemical potential gradients in the grain-contact regions as driving forces for CSP governing the dissolution, diffusion, and reprecipitation steps that facilitate mass transport [2,25,30–32]. The processes underlying CSP appear similar to pressure solution creep in sedimentary rocks [9,31,33, 34]. Despite the significant difference in time scales, with geological pressure solution creep taking thousands of years, compared to hours for CSP, pressure solution models have effectively predicted crucial aspects and kinetics of the latter process.

A recent comparison [32] of models using pressure solution creep to describe CSP identified three main aspects. Firstly, the faster time scale of CSP compared to traditional pressure solution compaction is due to smaller particle and initial pore sizes, larger stress-intensity factors at grain contacts, and the use of more reactive solvents in the former. Secondly, the rate of densification in early-stage CSP of systems like ZnO is limited by the rate of dissolution at grain-boundary necks, similar to pressure solution creep. Thirdly, island-channel networks at particle-contact regions, which are associated with rough grain boundaries and indicate non-equilibrium thermodynamics in pressure solution systems [32], are also present in cold-sintered specimens [35].

Observing and analyzing the evolution of grain-boundary roughness during pressure-solution-creep experiments is challenging. Previously reported observations were either limited to a single boundary or performed after the process had been completed, leading to questions about potential post-processing changes in the grain-boundary regions [36–40]. Models have been devised to describe the densification kinetics of pressure solution systems based on changes in grain-boundary roughness [33,41]. These models depict a multi-step process during pressure solution compaction, including developing intergranular protuberances or fluid-filled island-channel networks that facilitate mass transport. The growth of these protuberances leads to smoother grain boundaries and a cut-off of the island-channel network, ending mass transport. However, such models lack experimental validation due to the absence of *in situ* measurements of grain-boundary changes during pressure solution creep or CSP.

Recently, we began to address this gap using the *in situ* characterization of CSP with synchrotron-based X-ray scattering and diffraction. Initial experiments employed a sample stage designed for mechanical testing, which allowed limited control over CSP parameters and low time resolution (approximately 5 min). Additionally, the moderate X-ray radiation energy used in these measurements limited the range of materials that could be studied. Nevertheless, our studies of CSP in potassium di-phosphate (KDP) [42,43] demonstrated the feasibility of *in situ* characterization and its potential for uncovering process details.

With this success, we developed a motorized stage dedicated to *in situ* studies of CSP. This stage allows for monitoring process parameters and material shrinkage while collecting high-energy X-ray scattering data. We used it to study the material processes involved in the cold sintering of ZnO [4–7,26,28,31,39,44,45], the most widely studied CSP material to date. Our results revealed changes in the surface area and roughness of the ZnO particles attributed to the dissolution and reprecipitation processes driving densification. We also observed the formation of an unreported phase, conjectured to exhibit a layered structure, at grain boundaries and junctions, which appeared critical for the successful sintering of ZnO (densification of powders into a solid, dense object). This methodology provides the capability for *in situ* characterization of theoretical models, and is applicable to other advanced ceramics processing technologies, such as spark plasma sintering.

2. Materials

We used zinc oxide (ZnO) powder with 99.99% purity sourced from Alfa Aesar[#] for our cold sintering experiments. The ZnO powder was mixed with a 1 mol/L aqueous acetic acid (HOAc, supplied by Fisher Scientific) solution, maintaining a 1:1 ratio in terms of powder-tosolution mass. We combined these components using an agate mortar and pestle. After this, the mixture was left to dry in the open air at room temperature, following which we broke up any agglomerated powder using the mortar and pestle. Before proceeding to the in situ measurements, we rehydrated the dried powder in a sealed, humidity-controlled chamber overnight. The relatively humidity of the chamber is ≈ 75 %. The water content in the humidified powder, as measured by TGA, is \approx 2.5 % mass. We promptly packed the capillaries with the humidified powder immediately prior to commencement of the in situ experiment. By adhering to this sequence of steps for each experiment, we ensured consistency and used an equivalent mixture of ZnO, HOAc, and H₂O every time. This hydration method is adapted from research conducted by Floyd et al. [45].

Our CSP stage (Fig. 1) features a machined aluminum heating block with an entrance and an exit aperture for X-rays. It holds a thick-wall fused silica capillary with an inner diameter of (0.75 ± 0.02) mm and an outer diameter of (3.0 ± 0.1) mm (Polymicro, Molex, LLC). We apply uniaxial pressure using pistons made of hardened stainless tool steel with a diameter of (0.742 ± 0.005) mm (McMaster-Carr). The gap between the piston and capillary wall averages 0.04 mm, which is tight enough to apply the required uniaxial stress and open enough to allow a solvent fluid to escape during densification. The top piston remains stationary, while the bottom piston, driven by a linear actuator stepper



Fig. 1. Schematic rendering of the setup for *in situ* X-ray scattering measurements during CSP. This sample stage enables monitoring of temperature, force (pressure), and motor position (sample height) at a frequency of 1 Hz. Combined, synchrotron-based high-energy simulatenous measurements of small-angle X-ray scattering and X-ray diffraction performed at approximately 0.1 Hz rate provide a real-time evaluation of the microstructural and structural evolution.

[#] Certain commercial products are identified in this paper to specify the materials used and the procedures employed. In no case does such identification imply endorsement or recommendation by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

motor, moves up to provide a target force (pressure). We monitor the force using an S-type load cell (ATO America). We read the temperature, pressure, and position of the linear actuator at a frequency of 1 Hz to enable a feedback loop for monitoring and controlling these parameters. The cold-sintering stage is integrated with the beamline controls using the EPICS communication protocol implemented at the Advanced Photon Source (APS), Argonne National Laboratory, and the information is passed to the stage via USB to an Arduino microcontroller. More details about this setup will be reported elsewhere.

We performed time-resolved small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD)/wide-angle X-ray scattering (WAXS) measurements using the high-energy SAXS/WAXS setup [46] at the 1ID-E beamline of the APS. We used monochromatic X-rays at 71.5 keV (wavelength $\lambda = 0.173$ Å), which is critical for sufficient transmission (approximately 70%) through the ZnO sample thickness in a 0.75 mm internal diameter capillary. We acquired the SAXS data using a Pixirad CdTe-based area detector at a sample-to-detector distance of 6.447 m, providing a *q* range from 0.008 Å⁻¹ to 0.34 Å⁻¹, where $q = 4\pi \sin(\theta)/\lambda$ is the magnitude of the X-ray scattering vector, and θ is one half of the scattering angle. For WAXS data, we used four GE-RT41 amorphous silicon-based integrating area detectors positioned at 2.705 m downstream from the sample to yield a q range of 0.9 Å⁻¹ to 12.9 Å⁻¹. We synchronized the SAXS and WAXS data acquisition, and the time interval between consecutive measurements was approximately 13 s. The SAXS data were reduced using a customized routine developed for this experiment in the Nika software package based on Igor Pro [47]. For SAXS data analysis, we used the Irena software package, a general-purpose SAS analysis software based on Igor Pro [48]. The XRD data reduction and analysis were conducted using a combination of GSAS-II [49], Irena, and a custom MATLAB-based code. In the reduction process of the SAXS and WAXS datasets, we conducted an azimuthal average across a full 360-degree range.

Ex situ X-ray diffraction measurements were performed using a laboratory instrument with Cu K α radiation. Fractured surfaces of the cold-sintered samples were imaged in a JEOL 7100-FT FE scanning electron microscopy (SEM) operated at an accelerating voltage of 10 kV and a beam current of \approx 0.54 nA to minimize possible electron-beam damage.

Transmission electron microscopy (TEM) samples were prepared by sectioning the glass capillary containing the sintered ZnO rod perpendicular to the capillary axis with subsequent mechanical thinning of the resulting disks to $\approx 100 \ \mu m$ followed by dimpling to the final thickness of $\approx 28 \,\mu\text{m}$. The samples were further thinned until perforation using the Gatan Precision Ion Polishing System (PIPS-II) with the ion guns operated at 5 kV. (Multiple attempts to prepare samples at milder ion-beam conditions and with the sample kept at cryogenic temperatures were unsuccessful because of the ZnO part separating from the glass rim after completion of the milling process, presumably because of a groove generated at the glass/ZnO interface upon prolonged milling and mechanical stresses introduced by cooling and warming the sample.) Before insertion into the microscope, the ion-thinned sample was coated with a thin carbon layer to improve electrical conductivity. We performed TEM measurements using a Thermo Fischer Titan instrument at 300 kV in both fixed-probe and scanning modes.

3. Results and discussions

3.1. Stages of CSP in ZnO

Fig. 2 shows the pressure, piston position, and temperature as a function of time during CSP, with the target values for the pressure, heating rate, and temperature set at 50 MPa, 50° C/min, and 120° C, respectively. The pressure reached its target almost immediately, indicating easy compaction of the loose powder. Piston-position and temperature also changed rapidly during the first 2 to 3 min, consistent with powder rearrangement and compaction and the set heating rate. We refer to this initial period as Stage I, highlighted in yellow in Fig. 2. The



Fig. 2. Variations of the CSP parameters vs. process time. (a) pressure, (b) piston position, and (c) temperature. The target temperature and pressure were 120°C and 50 MPa, respectively. The heating rate was 50°C/min. For discussion purposes, we separated the process into Stages I, II and III.

applied heating rate at 50°C/min is within the range documented for ZnO in the literature, from 15°C/min in [28,50], to 80°C/min in [45] and 100°C/min in [51]. While ZnO can be sintered across this range of heating rates, the specific rate can significantly influence the diffusional processes, affecting the resulting material's microstructure. An in-depth investigation on this aspect was beyond the scope of our work, but its relevance to CSP's process optimization is undeniable.

Upon reaching its target value, the temperature fluctuated within a narrow range ($\pm 2^{\circ}$ C) defined by the controller's proportional-integralderivative (PID) parameters. The piston displacement rate slowed, reflecting the densification process. Even with slow and smooth piston motion, the pressure fluctuated around the preset 50 MPa by \pm 2 MPa. These fluctuations were unrelated to temperature oscillations, ruling out thermal expansion and contraction effects. Stage I is followed by the isothermal and iso-baric part highlighted in green and blue in Fig. 2. Previous works typically treated it as a single stage, thus describing cold sintering as a two-stage process. For example, Kang et al. described CSP of ZnO as proceeding through the "heating" and "isothermal" [26] stages, with the former characterized by rapid densification accompanied by significant liquid phase extrusion and the latter involving densification through mass transport. Such two-step densification has also been suggested to underlie cold sintering of SiO2 and polytetrafluoroethylene (PTFE) polymer composites [52]. Here, we propose that the isothermal/isobaric part of CSP includes two stages (Stages II and III in Fig. 2) characterized by distinct changes in the microstructures as will be described below.

The sample volume within the X-ray observation window changed noticeably during the experiment, complicating interpretations of the scattering data during Stage I with its rapidly varying process parameters. Therefore, for the quantitative analysis, we focused on Stages II and III.

3.2. Surface roughness and surface area from SAXS

Fig. 3 displays the entire SAXS data sequence. A power-law slope is observed for *q* between $\approx 0.008 \text{ Å}^{-1}$ and $\approx 0.08 \text{ Å}^{-1}$. The absence of a Guinier region indicates that the scattering inhomogeneities



Fig. 3. Time-dependent evolution of the *in situ* SAXS data. The color gradient within the arrow denotes changes in the acquisition time. The inset shows the SAXS signal corresponding to the ambient conditions at the start of the experiment, with the intensity following a power-law having a slope of -4, which is indicative of smooth surfaces for the initial particles. Another significant feature of these data is a diffraction peak at $q \approx 0.3$ Å⁻¹.

contributing to this slope are larger than the detection limit of the SAXS setup ($\approx 2\pi/q_{min} = 785$ Å). At all *q*-values within this range, we observed a monotonic decrease in the scattered intensity with time. For a material consisting of a solid phase and pores, the scattered intensity is proportional to the volume fraction of the pores and the scattering contrast $(\Delta \rho)^2$, where $\Delta \rho$ is the difference in the scattering length densities of the solid component and the pores [53]. Thus, the reduction in the intensity can be attributed to the diminishing pore volume, which agrees with findings from prior small-angle-scattering studies of densification during conventional high-temperature sintering [54]. At time zero, the low-*q* SAXS data demonstrate an asymptotic q^{-4} power-law behavior, a hallmark of geometrically smooth surfaces for the starting powders [55].

We used the so-called unified analysis, a well-established heuristic method for small-angle scattering, to capture a general trend in the timeresolved SAXS data [56]. This method permits the extraction of the temporal evolution of morphological parameters using the following equation

$$I(q) = Gexp\left(-\frac{q^2 R_g^2}{3}\right) + B\left\{\frac{\operatorname{erf}\left(\left(\frac{qR_g}{\sqrt{6}}\right)^3\right)}{q}\right\}^p + c.$$
 (1)

Here, *G* is the exponential prefactor, R_g is the radius of gyration of the scattering object, erf() is the error function, *P* is the power-law slope, *B* is the power-law prefactor related to the scattering contrast and the surface area, and *c* is the background constant [57]. Given the lack of a Guinier region, in the power-law regime, we have $R_g \gg 1/q$, leading to $Gexp\left(-\frac{q^2R_g^2}{3}\right) \rightarrow 0$ and $erf\left(\left(\frac{qR_g}{\sqrt{6}}\right)^3\right) \rightarrow 1$. Eq. (1) is then simplified to $I(q) = Bq^{-P} + c$. (2)

We used this equation to fit the low-q power-law portion of the SAXS data and plotted the parameters *B* and *P* vs. time in Fig. 4.

During Stage I, both *B* and *P* vary stochastically, which precludes their interpretation. At the onset of Stage II, *P* decreased rapidly from \approx 4 at t = 0 min to \approx 3.7 at t = 15 min. This parameter is related to a surface-roughness metric (surface fractal dimension) as ds = 6 - P, where *ds* is the surface fractal dimension [58]. For three-dimensional objects, *ds* is between 2 and 3, with these limits corresponding to perfectly smooth (flat) and highly folded (rough) surfaces, respectively [53]. In the present case, *ds* was consistently above 2, with a maximum



Fig. 4. Time evolution of the (a) power-law prefactor (B) and (b) power-law slope (P) (See Equation 2) for the low-*q* portion of the data in Fig. 3. P and B are linked to the surface roughness and surface area, respectively, and their changes with time reflect the evolution of these characteristics. The background colors for Stages I, II, and III are identical to those in Fig. 2.

of \approx 2.3, suggesting significant roughening of the particle/grain surfaces. The changes in *ds* were non-monotonic, peaking at *ds* \approx 2.3 and then decaying over time but remaining greater than 2. (For a fractally-rough surface, *ds* is defined so that the total surface area per unit volume, *S*(*x*), measured down to roughness length, *x*, scales as $(1/x)^{(ds-2)}$, while the terminal scattering exponent scales as $q^{(6-ds)}$. For *ds* = 2, the surface area per unit sample volume is constant for all roughness lengths, the *q* exponent is -4, and the surface can be regarded as "smooth".)

The behavior of *ds*, deduced from *P*, suggests that the ZnO surfaces undergo a smooth \rightarrow rough \rightarrow less-rough transition, which is consistent with a commonly accepted picture [30,59], wherein both pressure and temperature promote the gradual dissolution of ZnO in acetic acid, followed by reprecipitation at the particle surfaces. Our *in situ* results show that the grain boundaries in the final sintered product retain some of the particle-surface roughness developed during the dissolution stage of the process. Hereafter, we will refer to the surface roughness when discussing both free particle surfaces during the early stages of CSP and the grain boundaries that form upon densification.

Interpreting the time evolution of B is more complex because this parameter depends on both the scattering contrast and surface area. We assumed a constant contrast during the later stages of the sintering when only gradual changes in the pore volume occur. Then, changes in B reflect the evolution of the surface area, which appears to grow significantly during Stage I and the first few minutes of Stage II. This growth can be attributed to the unavoidable compaction of powders into the Xray irradiated sampling volume, leading to an increase in the total surface area and to the surface roughening caused by the dissolution, with a concurrent increase in the total surface area. The surface area reached its peak value at t = 7 min, decreasing gradually afterward, consistent with a typical densification process proceeding through the formation of the interparticle neck regions with the subsequent decrease in the curvature gradient. The surface area plateaued after $t \approx 30$ min, which coincided with the power-law slope P (and ds) attaining its final value. These results suggest that both the total surface area and surface roughness can be used to evaluate the rate of surface reconstruction during cold sintering. As evident from Fig. 4, the isothermal/isobaric part of CSP indeed can be separated into two stages, II and III, dominated by the dissolution and reprecipitation processes, respectively; a significant part of the dissolution also happens already during Stage I.

Our SAXS results complement the earlier studies of cold-sintered ZnO, pointing to a correlation between the surface roughness and grain-boundary defects affecting electrical properties. For example, Gonzalez-Julian et al. [60] used Kelvin Probe Force Microscopy to demonstrate that dissociated ions diffuse into the ZnO crystal, generating highly defective grain boundaries. The defects persist in the final sintered ZnO body, which displays a low electrical conductivity on the order of 10^{-4} S/cm. In another study, de Beauvoir et al. [61] showed that during cold sintering of ZnO, the grain boundary resistance, monitored by in situ electrochemical spectroscopy, exhibits a non-monotonic dependence with a maximum. Both trends parallel the behavior of the surface roughness inferred here from the SAXS data. Jing et al. [5] reported that a heat treatment at 500°C improves the electrical conductivity of cold-sintered ZnO from 0.0005 S/cm to 16.4 S/cm. suggesting a reduction in the grain-boundary defects during the post-processing. A follow-up SAXS/XRD experiment monitoring the microstructural evolution during a post-sintering heat treatment at higher temperatures than used for CSP could provide insight into the nature of this relationship.

3.3. Secondary phases from XRD and SAXS

The transformation of the atomic structure during the cold sintering of ZnO is complex. Fig. **5a** summarizes the *in situ* XRD data which consists of over 200 datasets with acquisition times indicated by a color-bar arrow. A 2D XRD pattern acquired at the end of the *in situ* run (Fig. **5(b)**, inset) features continuous diffraction rings with a nearly uniform azimuthal distribution of intensities, indicating no significant crystallographic texture. Fig. **5(b)** compares the room-temperature XRD pattern acquired at the beginning of the experiment with a stick pattern calculated for the hexagonal ($P6_3mc$) wurtzite ZnO structure (lattice parameters a = 3.24986 Å and c = 5.20662 Å [62]). The presence of additional weaker and broader peaks, marked with arrows, is evident. The most intense of these peaks persist through the entire duration of the experiment, while the weaker ones disappear after Stage I.

The intense extra peaks at 2.19 Å⁻¹ and 3.09 Å⁻¹, highlighted by red arrows in Fig. 5(a), inset, match the 440 and 632 reflections of zinc acetate, $Zn(CH_3CO_2)_2$ (space group *Pn-3n*; lattice parameter a = 16.256 Å [63]). This result, while consistent with a very recent work by Jabr et al. [64], contrasts with earlier XRD investigations of cold-sintered ZnO, which claimed the sintered material to be single phase [4,5,26,35,65]. As discussed below, this discrepancy in the XRD data could arise from the sensitivity of the zinc acetate phase to the level of moisture in the powder/solvent mixture.

The *in situ* SAXS data reveal the emergence of a diffraction peak at $q \approx 0.3 \text{ Å}^{-1}$ (*d*-spacing $\approx 21 \text{ Å}$) as the sintering progressed (Fig. 3). This



Fig. 5. (a) Time-dependent *in situ* XRD data recorded during cold sintering of ZnO. The color palette within the arrow denotes the acquisition time. The plot represents an overlay of >200 datasets. The inset shows a magnified view of the XRD patterns at selected times (0 min, 4 min, and 48 min, respectively) demonstrating changes of the weak peaks. The downward pointing red arrows highlight two weak non-ZnO peaks. (b) A comparison of the experimental room-temperature XRD data and a stick pattern calculated for the hexagonal ZnO structure having $P6_3mc$ symmetry and lattice constants a=3.24986 Å and c=5.20662 Å. The inset shows the diffraction ring collected by one of four XRD detectors, with the color bar indicating the intensity variation. (c) Time dependence of lattice parameter *a*; the inset shows a magnified view of this trend during Stages II and III. (d) Time dependence of lattice parameter *c*.

peak appeared in every successful sintering experiment over a broad range of processing conditions and, thus, was considered an attribute of the successful densification process. We tracked this peak's position, full width at half maximum (FWHM), and intensity as a function of time by fitting its profile with a Gaussian function (Fig. 6). All three peak characteristics changed rapidly and monotonically during the first few minutes after reaching the target temperature (120°C). The upshift in the peak position reflects lattice contraction of \approx 4 %, with the *d*-spacing value decreasing from (21.90 \pm 0.18) Å to (21.01 \pm 0.03) Å. During this period, both pressure and temperature remained approximately constant, suggesting stress is unlikely to be the sole cause of such lattice shrinkage, which may also be attributed to a continuous change in the stoichiometry of this presumed reprecipitated phase, possibly driven by the changing chemical potential. The monotonic increase in the integrated intensity of the peak indicates a growth of this phase's volume fraction. The size of the coherent scattering domains, estimated using Scherrer's formula (Scherrer limit \approx 150 nm for SAXS), varied from the initial ≈ 15 nm to ≈ 30 nm after ≈ 15 min, remaining approximately constant during the rest of the sintering process. This saturation of the crystallite size suggests that the phase growth may be geometrically confined.

We analyzed a 1:1 mixture of the starting ZnO powder and 1 mol/L acetic-acid solution in the as-mixed, wet state and after drying it overnight to understand the origins of the secondary phase(s). The XRD data collected for these mixtures using a laboratory instrument (Fig. 7(a)) cover a *q*-range from ≈ 0.2 Å⁻¹ to ≈ 4.5 Å⁻¹, thus, bridging the gap between ≈ 0.4 Å⁻¹ and ≈ 0.9 Å⁻¹ in the synchrotron measurements (dashed vertical lines in Fig. 7(a)). The weak reflections, marked with arrows, that are seen beside the strong ZnO peaks belong to zinc acetate, Zn(CH₃CO₂)₂, and another phase, presumably also representing a product of the reaction between ZnO and the acid solution. The lowest angle



Fig. 6. Evolution of parameters (peak center, intensity, FWHM) of the diffraction peak at q=0.3 Å⁻¹ in Fig. 3. The top panel shows the crystalline domain size, calculated from the FWHM values using Scherrer's equation. All error bars indicated for the XRD/SAXS data represent the standard deviation and are determined using the uncertainty analysis within *Irena*.

reflection of this latter phase occurs at the same $q \approx 0.3$ Å⁻¹ as the extra peak in question in the synchrotron data. None of the entries for the Zn-O-C-H chemistries in the most recent release of the Powder Diffraction File could completely account for these peaks. The closest match was the Zn-based soap phases, reported in Corbeil et al. [66], such as zinc linoleate (C₁₈H₃₁O₂)₂Zn and zinc oleate (C₁₈H₃₃O₂)₂Zn, which feature a large lattice parameter ranging from 38 Å to 42 Å. Structural details of these phases remain unknown, but given their long lattice periodicity along a single axis, we will assume a layered type, and we will refer to this phase as a soap-like phase.

The relative peak intensities for the non-ZnO peaks vary markedly between the "wet" and "dry" states (Fig. 7), indicating that structures of the underlying phase(s) are sensitive to the moisture levels. The changes in these peak intensities are not uniform: some peaks (denoted by the red downward arrows) grow stronger after drying, whereas others (indicated by the green arrows) weaken. Notably, the peak at $q \approx 0.3$ Å⁻¹, attributable to a soap-like phase increased in intensity upon drying, while other reflections, like the one at $q \approx 3.09$ Å⁻¹, assigned to the zinc acetate phase became less intense. Thus, the absence of the $q \approx 0.3$ Å⁻¹ peak during the initial stages of the *in situ* synchrotron experiment can be ascribed to a higher level of moisture in that mixture.

We performed a peak-profile analysis of the zinc acetate 3.09 Å^{-1} peak in the *in-situ* data (Fig. 7(b), inset). The integrated peak intensity (Fig. 7(b)) decreases monotonically, initially rapidly and then gradually. The similarly opposite trends observed for the two sets of non-ZnO peaks both during CSP and upon drying the powder-solvent mixture point to the concurrent disappearance of the zinc acetate phase and growth of the soap phase upon solvent evaporation. Given that the growing prominence of the soap phase correlates with the decrease in the particle-surface roughness, we conjecture that this phase is a transient product of the reprecipitation process from the acetic acid solution enveloping the ZnO grains before the reformation of ZnO itself. The presumed layered nature of the soap phase can be envisioned to facilitate diffusion.

3.3. Lattice strain and grain growth in ZnO

The evolution of the ZnO lattice parameters a and *c* with processing time is shown in Fig. 5(c) and 5(d), respectively. During the first several minutes, heating the sample (Fig. 2) is accompanied by the lattice expansion. Oscillations of the lattice parameters during the isothermal stage reflect the temperature fluctuations. Despite these oscillations, the lattice parameters contract (Fig. 5c, d), indicating that the ZnO lattice is compressed. A linear fit to the data (Fig. 5c) yields a slope of (-5.16 \pm 0.26) \times 10⁻⁶ Å/min. Over an isothermal period of \approx 43 min, this contraction rate translates into a compressive strain of \approx (-6.82 \pm 0.34) \times 10⁻⁵. Assuming the bulk Young's modulus of \approx 140 GPa [67], the corresponding stress is (-9.5 \pm 0.5) MPa, which is much smaller than the applied pressure of \approx 50 MPa. This difference suggests that the external pressure is dissipated, likely through the sample pellet sliding against the capillary wall and via the intergranular secondary phase (i.e., hence the contraction of the lattice dimensions for the soap phase).

Fig. 8(a) compares the FWHM of 012 and 002 ZnO reflections, after correcting for the instrumental broadening. During Stage II, both reflections sharpened between $t \approx 3$ min and $t \approx 25$ min and remained approximately unchanged afterward. Substituting these FWHM values into Scherer's equation (Fig. 8b) indicates that the crystallite size grows to a maximum of ≈ 200 nm, after which the growth stops (WAXS instrumental resolution limit corresponds to a crystallite size of ≈ 300 nm). This result contrasts with a continuous coarsening of ZnO grains reported for cold sintering at 305° C [4]. One possible explanation for this discrepancy is the existence of several grain-growth mechanisms, with the prevalent one determined by processing conditions. In our case, at T = 120° C, we observe liquid evaporating on heating (reported elsewhere). This evaporation creates a supersaturated solution favorable for epitaxial crystal growth. Such a mechanism was reported for the cold



Fig. 7. (a) Laboratory XRD patterns collected for 1:1 mixture of ZnO powder and 1 mol/L acetic-acid solution in its as-mixed, wet state (black) and after drying this mixture in air overnight (red). (b) Evolution of the integrated intensity of a diffraction peak at $\approx 3.09 \text{ Å}^{-1}$ attributed to the zinc acetate phase from the *in situ* dataset in Fig. 5a. The inset shows a magnified view of this peak with the acquisition time indicated by the color-bar arrow.



Fig. 8. Parameters of the 012 (red) and 002 (green) ZnO peaks vs. process time. (a) FWHM and (b) crystallite sizes estimated from the FWHM values of 012 and 002 reflections using Scherrer's equation.

sintering of BaTiO₃, with a clear evidence presented for recrystallized BaTiO₃ epitaxial layers forming on the grain surfaces [9]. Higher temperatures can promote Oswald-ripening-type growth, with a coalescence of neighboring grains reducing the total surface area. Previous studies of heat treatments for ZnO cold-sintered at 250° C showed that temperatures above 300° C are required to activate the coalescence [5], which is also consistent with the results by Funahashi et al. [4]. Hence, the plateauing of the crystallite size suggests recrystallization as the primary growth mechanism. The presence of a secondary phase at grain boundaries and triple junctions can also preclude Oswald ripening.

Hence, by optimizing the processing conditions, CSP has the potential to limit grain coarsening and achieve desired mechanical, thermal, and electrical properties.

3.4 SAXS: Evolution of the pore volume

We used a scattering invariant analysis of the SAXS data to follow the volumetric evolution of pores during CSP. The scattering invariant Q for a two-phase system is defined as:

$$Q = \int_{0}^{\infty} I(q)q^{2}dq = 2\pi^{2}\phi_{1}\phi_{2}\Delta\rho^{2},$$
(4)

where ϕ_1 and ϕ_2 are the volumes of phases 1 and 2, and $(\Delta \rho)^2$ is the scattering contrast. In our case, the sample contains three components: crystalline ZnO, the secondary nanocrystalline phase, and pores. However, SAXS data are dominated by components yielding higher scattering contrast. The pores exhibit larger sizes and stronger contrast (compared to ZnO) than the nanocrystalline phase and are expected to provide a much more significant contribution to the scattering intensity. Hence, for a quantitative analysis of the trend in pore volume versus sintering time, we neglected the presence of the secondary phase and treated our sample as a two-component system consisting of ZnO and pores.

We considered the data from the power-law region in Fig. 3 to avoid the diffraction peak. We determined the background using the Bonart method and performed the numerical integration according to a previously described procedure [68]. We calculated the scattering contrast assuming a ZnO-pore two-phase system with the X-ray scattering length densities for ZnO (mass density: 5.61 g/cm³) calculated at $\rho_{ZnO} = 4.445$ $\times~10^{11}~cm^{-2}$ and for the pores set at ρ_{pore} = 0. The resulting X-ray scattering contrast between ZnO and pores is $(\rho_{ZnO}-\rho_{pore})^2=1.976$ \times 10^{23} cm⁻⁴. Fig. 9 displays a volume fraction of the pores calculated using this contrast. The pore volume decreases monotonically after Stage I. following a trend similar to that observed for the surface area (Fig. 4). suggesting the pores were stable during the later stages of the sintering process, with a concurrent smoothing of the grain boundaries. This inference is also supported by the lack of piston movement (Fig. 2) during the later stage of the sintering, which is consistent with the ceasing of densification. The kinetics of grain growth observed in our experiments (Fig. 8) align with those for pore volume (Fig. 9), pointing to the concurrent recrystallization-induced grain growth and pore closure. We should also note that the cold sintering process did not completely eliminate porosity. A detailed characterization of the remaining pores will be reported separately.

3.5. Ex situ microstructural characterization using SEM and TEM

SEM images of ZnO (Fig. 10a), sintered using the same setup and parameters as employed in our *in situ* measurements, revealed pores residing primarily at triple grain junctions and constituting ≈ 2.3 % of the image area (image analysis performed in ImageJ [69]). The characteristic chord length of the pores, calculated as (average area)^{1/2}, was ≈ 0.033 µm. The average particle size estimated from the SEM



measurements was ≈ 0.4 µm. The average chord length for pores expected for a random close packing of uniform spheres of this size is ≈ 0.2 µm, significantly greater than the estimate from the SEM images. This difference is consistent with pore shrinkage during the densification process. Furthermore, the inset SEM image, acquired from a fractured surface, clearly shows the equiaxed and faceted grains and indicates a uniform sintering within the observation window. The presence of these grain structures confirms the successful sintering process. The faceted grains signify a high degree of crystallinity. Simultaneously, the equiaxed nature of the grains implies isotropic material properties. Our results are similar to the previous SEM observations of CSP [45,70] (often higher temperatures and pressures) as well at as of conventionally-sintered ZnO.

The SEM images displayed distinct contrast for the grain boundaries and grain interiors. Bright-field TEM images, shown in Fig. 10(b), revealed the presence of an amorphous-like component at many grain boundaries and triple junctions. According to energy dispersive spectroscopy, these regions contain Zn and O with only a hint of C. The surfaces of the ZnO grains in contact with the amorphous component appeared relatively rough, in line with the SAXS results on the surface roughness. Previous studies that combined Raman Spectroscopy and microscopic measurements also revealed an intergranular amorphous phase within cold-sintered ZnO [26]. The amorphous-like regions in our TEM images can be hypothesized to represent a soap phase yielding the $q \approx 0.3 \text{ Å}^{-1}$ peak in the XRD data, which became amorphized during the ion-thinning of the sample. Given the likely metalorganic chemistry of this nanocrystalline phase, such damage can be difficult, if not impossible, to avoid. The characteristic dimensions of the amorphous component are consistent with the size of a coherently scattering domain estimated from the FWHM of the diffraction peak. We lack conclusive evidence for a direct transformation between the zinc acetate and the soap-like phase. However, the similar kinetic time scales shown by their integrated XRD intensities (Figs. 6 and 7) suggest that these two phases may be related.

3.6. Hydrothermal conditions

Previous work on cold-sintered ZnO claimed the existence of a temperature-dependent pressure threshold and the importance of transient hydrothermal conditions for successful sintering. For example, Kang et al. [26], who used 1.66 mol/L acetic acid as a solvent and process temperatures between ambient and $\approx 140^{\circ}$ C, indicated a critical pressure of ≈ 140 MPa was required for the cold sintering of ZnO at $\approx 120^{\circ}$ C. In contrast, we densified ZnO with 1mol/L acetic acid at 120°C using a pressure of only 50 MPa, suggesting the requirement for the hydrothermal conditions is not universal.

4. Conclusions

We used a custom-designed cold-sintering stage optimized for *in situ* synchrotron measurements to study cold sintering of ZnO, the most studied cold-sintering material to date, with a combination of small-angle X-ray scattering and X-ray diffraction while simultaneously monitoring pressure, temperature, and sample dimensions. These measurements were augmented by *ex situ* characterization using X-ray diffraction and electron microscopy. We densified ZnO at a pressure of \approx 50 MPa, questioning a requirement for the hydrothermal conditions as critical for cold sintering. The CSP of ZnO is shown to proceed through three stages. Stage I is characterized by the most volumetric shrinkage and the dissolution of the particle surface. Stage II is dominated by the continuing dissolution process manifested in the surface reprecipitation resulting in smoother particle/grain surfaces and gradually reduced surface area with eventual densification.

We demonstrated the presence of nanocrystalline non-ZnO phases evolving during CSP. In the initial powder/solvent mixture, the





Fig. 10. (a) SEM and (b) TEM images of the cold sintered ZnO. SEM reveals the remaining pores reside primarily at grain triple junctions. The inset of (a) shows a fractured surface. TEM uncovers an amorphous-like phase at the grain boundaries and triple junctions.

dominant secondary phase appeared to be zinc acetate, presumably resulting from a reaction between ZnO and acetic acid solution. As CSP progresses with the liquid gradually squeezed out of the mixture, this phase was replaced by another one, tentatively attributed to a zinc soap compound exhibiting a large lattice dimension along one of the axes and therefore assumed to have a layered nature. This latter phase was retained in the final sintered part, residing at grain boundaries and triple junctions. An ex situ analysis of the wet and dried mixtures of ZnO and acetic acid solution under ambient conditions demonstrated that the soap-like phase emerges as the solvent evaporates. A transformation of zinc acetate to this phase is possible but still unconfirmed. The formation of the soap phase accompanied every successful CSP experiment. We, therefore, hypothesize that this layered-type phase promotes cold sintering by facilitating the mass transfer and grain sliding. Overall, the in situ measurements demonstrated here provide the kinetic datasets characterizing particle surfaces and microstructural evolution at different length scales that can be used to validate the modeling and simulation efforts and would be difficult to obtain by other measurements. While many of our conclusions are specific to ZnO, we believe the core principles and *in situ* monitoring techniques we've established can serve as a blueprint for probing and understanding the essential phase and microstructure transformation pathways during CSP, vital for determining the sinterability and performance of a broad spectrum of cold-sintered materials. Our approach sheds light on the intricacies of the cold sintering process, contributing to a better understanding of the fundamental materials science of CSP and opening doors for potential advancements in the field.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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