Research Article

Reticulated Open-Celled Zinc Oxide Ceramic Foams: Manufacturing, Microstructure, Mechanical, and Thermal Properties

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Open-celled zinc oxide ceramic foams were prepared by the polymer sponge replication (Schwartzwalder) technique from aqueous ZnO dispersions with Sb_2O_3 and Bi_2O_3 as sintering additives, and mechanically stable ZnO foams with an average porosity of 93.6% were obtained. Their microstructure consists of ZnO grains with a Bi-containing grain boundary phase together with a Zn-Sb-O secondary phase with spinel structure. The obtained ZnO ceramic foams were characterized with respect to their morphology by computed tomography; in addition, the compressive strength and the thermal conductivity were determined, and the data were applied for modelling of the mechanical and thermal properties of the bulk ZnO strut material.

1. Introduction

Open-celled ceramic foams are used within several technological fields; with respect to the quantity, the most prominent applications are filter materials for metal melts in casting or catalyst supports [1]. Ceramic foams for the above-mentioned applications are manufactured on an industrial scale by the polymer sponge replication process established by Schwartzwalder and Somers in 1961 [2]. This results in a macrocellular foam-like structure similar to that of the polymeric sponge used as template in this process. A variety of cellular ceramic materials has been produced by this technique, an overview can be found in references [3, 4]. However, to our knowledge, no zinc oxide foams have been prepared by the sponge replication process yet.

Zinc oxide is a semiconductor material, which crystallizes in the wurtzite structure type in analogy to aluminum nitride or silicon carbide, for example. Therefore, it belongs to the class of adamantine compounds with a basic all-tetrahedral coordination of cations and anions [5]. As a consequence of this simple structure type, the phonon conductivity is high,

which results in a good thermal conductivity for adamantine compounds [6]. Consequently, pure zinc oxide has a thermal conductivity of $50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature, which is high for an oxidic compound [7].

A typical application for ZnO-based ceramics is varistors, which have a distinct nonohmic electrical conductivity, i.e., a very low conductivity below a characteristic breakthrough voltage and can be used for overvoltage protection [8]. The nonohmic properties of ZnO-based varistors are a complex function of the microstructure, for example, the amount and distribution of secondary phases [9, 10]. Common additives for sintering and microstructural control in these varistor ceramics are the antimony and bismuth oxides Sb_2O_3 and Bi_2O_3 [11]. Bismuth oxide forms a low-melting eutectic together with ZnO and promotes an effective low-temperature liquid phase sintering mechanism resulting in a distinct ZnO grain growth. On the contrary, antimony oxide reacts with ZnO to a ternary Zn-Sb-O phase, which restricts the ZnO grain growth by a pinning mechanism [12]. Consequently, the Sb/Bi ratio in the ceramic raw material is essential for the final microstructure and the electrical properties of ZnO ceramics.

In the present work, the established polymer sponge replication—Schwartzwalder—process has been adopted for the manufacturing of zinc oxide ceramic foams. As sintering aids, Sb_2O_3 and Bi_2O_3 were used in a fixed molar ratio of 2:1. The obtained foams were characterized with respect to their microstructure (SEM and phase composition by XRD) and their macroscopic properties mechanical strength and thermal conductivity as a function of the total porosity and morphology. Finally, the bulk properties of the ZnO strut material were extrapolated from the obtained data by applying established structure (porosity)-property relations.

2. Materials and Methods

2.1. Powder Preparation. The ceramic raw powder was prepared by ball-milling a dispersion of 200 g zinc oxide ($d_{50} = 0.2 \mu\text{m}$, Harzsiegel Standard, Norzinco GmbH, Goslar, Germany), 7.28 g Sb_2O_3 (1.0 mol% w. r. t. ZnO), and 5.82 g Bi_2O_3 (0.5 mol% w. r. t. ZnO) in 300 mL ethanol for 4 h. A planetary ball mill (PM 400, Retsch GmbH, Haan, Germany) operating at a milling speed of 300 rpm and equipped with two 250 mL alumina grinding bowls and 50 alumina balls each with $d = 10 \text{ mm}$ was used. Afterward, the ZnO- Sb_2O_3 - Bi_2O_3 powder was collected by vacuum filtration and dried at 100°C .

2.2. Dispersion Preparation. The ceramic dispersion for foam manufacturing was prepared by adding 100 g of the ZnO- Sb_2O_3 - Bi_2O_3 oxide mixture and 1.0 g ethanolammonium citrate deflocculant (Dolapix CE64, Zschimmer & Schwarz Chemie GmbH, Lahnstein, Germany) to 26.5 mL distilled water. The mixture was homogenized for 15 min using a planetary centrifugal mixer (THINKY Mixer ARE-250, THINKY Corp., Tokyo, Japan) operated at 2000 rpm. Afterward, 1.5 g polyvinylalcohol binder (Optapix PA 4G, Zschimmer & Schwarz Chemie GmbH) and 0.1 g polyalkylene glycolether defoamer (Contraspum K1012, Zschimmer & Schwarz Chemie GmbH) were added to the dispersion followed by a second mixing step for 15 min at 2000 rpm. The resulting dispersion has a solid content of 77.5 wt.%, which is 37.9 vol.%.

2.3. ZnO Foam Manufacturing. For the ZnO foam, manufacturing reticulated polyester polyurethane (PU) foams (SP30P20R, Koepp Schaum GmbH, Oestrich-Winkel, Germany) with 20 pores per linear inch (ppi) and a cubic geometry with $20 \text{ mm} \times 20 \text{ mm} \times 20 \text{ mm}$ were used as template structure. The PU foams were completely immersed into the ZnO dispersion and subsequently freed from the excess amount by manual squeezing of the foam template until its weight reached approximately 2.4 g (corresponding to $\approx 93.5\%$ porosity in the final foam piece after sintering). After drying under ambient conditions, the PU template was removed thermally in three steps ($110^\circ\text{C}/2 \text{ h}$, $250^\circ\text{C}/3 \text{ h}$, $400^\circ\text{C}/3 \text{ h}$, heating/cooling rate $1 \text{ K}\cdot\text{min}^{-1}$) in a circulating air furnace (KU 40/04/A, THERMCONCEPT Dr. Fischer GmbH, Bremen, Germany). Afterward, the samples were densified at 1100°C for 3 h in air (heating rate of $3 \text{ K}\cdot\text{min}^{-1}$) using a 30 L

sintering furnace (LH 30/14, Nabertherm GmbH, Lilienthal, Germany). For thermal conductivity measurements, rectangular PU templates with a dimension of $50 \text{ mm} \times 50 \text{ mm} \times 20 \text{ mm}$ were coated with the ZnO dispersion; the excess of slurry was extruded with a roller press to reach a total weight of 15 g for the coated PU foam. Template removal and sintering were performed as described above.

2.4. ZnO Foam Characterization. The total porosity of the foams ($V_{\text{pores}}/V_{\text{foam}}$) was calculated from the geometric foam density, which is the foam mass m_f divided by the geometric foam volume V_f , and the skeletal density of the strut material. A skeletal density of $5.65 \text{ g}\cdot\text{cm}^{-3}$ was calculated for the ZnO material by the rule of mixture. As an approximation, the density and weight fraction of ZnO, Sb_2O_3 , and Bi_2O_3 according to the initial starting powder were used. The strut porosity ($V_{\text{strut pores}}/V_{\text{struts}}$) and the strut pore volume were calculated from the dry, buoyant, and water-filled weight of the foams as determined by the water immersion/Archimedes' method according to the DIN EN 623-2:1993-11 standard [13]. To separate the porosity being present in the ceramic phase the volume of the hollow strut cavity caused by the removal of the PU foam template was subtracted from the overall strut porosity results. The volume of the hollow strut cavities was estimated from the average PU template weight of 0.244 g for a 8 cm^3 foam piece and a PU skeletal density of $1.1 \text{ g}\cdot\text{cm}^{-3}$ according to He-pycnometry. A volumetric shrinkage of the ZnO foam samples of 41% was considered in this estimation. For the porosity characterization, 37 specimens were analyzed, and the results were averaged.

The quantitative phase composition of the ZnO strut material was determined by powder X-ray diffraction (PANalytical X'Pert Pro Bragg-Brentano diffractometer, $\text{Co-K}\alpha_1/\alpha_2$ radiation) after ball-milling the respective sample for 5 min at 300 rpm. The grinded powder was filled into a backloading sample holder and measured in a θ/θ reflection geometry with a 2θ range from 10° to 160° . The obtained diffraction patterns were analyzed by the Rietveld technique using the Topas Academic 5 program package [14, 15].

The thermal conductivity of the ZnO foams was determined using the transient plane source (TPS) technique and a TPS 2500 S device (Hotdisk SE, Gothenburg, Sweden) by placing the sensor in between two $42 \text{ mm} \times 42 \text{ mm} \times 17 \text{ mm}$ foam samples with previously sanded surfaces [16]. A TPS sensor with 9.908 mm in diameter and a heating power of 200 mW for a 10 s measurement was used. The thermal conductivity was calculated from the sensor temperature change [17].

The compressive strength was determined using a TIRAtest 2825 universal testing machine and circular loading plates with 150 mm in diameter and a crosshead speed of $1 \text{ mm}\cdot\text{min}^{-1}$ (TIRA GmbH, Schalkau, Germany). To ensure a more homogeneous load on the samples, a cardboard piece with 1 mm thickness was placed between the foam and the loading plates. From the obtained data, the maximum force was extracted and used for the calculation of the compressive strength. The results of 35 specimens were evaluated using a two-parameter Weibull distribution and the Visual-XSel 14 program package [18, 19]. From this

distribution, the average compressive strength σ_{fc} (Weibull scale parameter) together with the modulus m (Weibull shape parameter) as a measure of the Weibull distribution's width were deduced.

The microstructure of selected specimens was characterized by scanning electron microscopy using a XL30 ESEM-FEG microscope (FEI/Philips, Hillsboro/OR, USA) equipped with a secondary electron (SE) and backscattered electron (BSE) detector. The grain size distribution in the ZnO strut material was determined from the BSE micrographs by manually measuring the dimension of 150 individual grains. The elemental composition of the ZnO strut material was analyzed by energy dispersive X-ray spectroscopy (EDAX-AMETEK GmbH, Weiterstadt, Germany). Beforehand, the grinded sample material was uniaxially pressed at 30 MPa for 2 min into slabs, which were used for the EDS characterization. Nine EDS spectra were recorded at different positions on the sample and were used for the subsequent elemental analysis.

Micro-computed tomography (μ -CT) was applied for the characterization of the foam macrostructure. For a measurement using a nanotom S tomograph (Phoenix/GE Sensing & Inspection, Wunstorf, Germany), a set of 1080 radiographs with a resolution of 2304×2304 pixels was collected using an exposure time of 750 ms per image. The distances between detector and X-ray source (FDD) and between object and X-ray source (FOD) were adjusted to result in a voxel size of $(9 \mu\text{m})^3$. Data acquisition and reconstruction were performed with the Phoenix Datos X 2.0 software package (Phoenix/GE Sensing & Inspection). For the calculation of the strut and cell size distributions, the CTAnalyser 1.17 program package was used after applying a 2×2 voxel binning to an effective voxel size of $(18 \mu\text{m})^3$ (CTAn, Skyscan/Bruker microCT, Kontich, Belgium). The import of the collected CT data into the CTAn software, and the differential thresholding-based binarization procedure preceding the actual calculations were performed as described elsewhere [20]. The cell size and strut thickness distributions were calculated after filling the hollow strut cavities by performing a morphological closing operation in CTAn using a round kernel with $r = 10 \mu\text{m}$ as described in a previous study [21]. The strut filament thickness distribution was calculated without closing of the hollow strut cavities.

3. Results and Discussion

The dispersion of the $\text{ZnO-Sb}_2\text{O}_3\text{-Bi}_2\text{O}_3$ powder mixture in water using an ethanolanmonium citrate-based deflocculant was successful with respect to the rheological behavior up to a solid content of 77.5 wt.%/37.9 vol.%. The obtained dispersion possessed the desired shear-thinning flow behavior and a viscosity suitable for the successful manufacturing of cellular ZnO ceramics by the polymer sponge replication technique [22, 23].

3.1. Microstructure of ZnO Ceramic Foams. After sintering, mechanically stable ZnO ceramic foams were obtained which showed an intense yellow color (Figure 1). This is

FIGURE 1: Open-cellular zinc oxide ceramic foams with a pore count of 20 ppi and 93.6% total porosity after sintering at 1100°C . The yellow color is a consequence of structural defects in the ZnO lattice (oxide vacancies and interstitial zinc atoms).

characteristic for zinc oxide materials and can be attributed to the presence of structural defects like oxide vacancies and interstitial zinc atoms in the hexagonal wurtzite structure of ZnO [8, 24].

In the SEM micrographs of the strut material, a dense microstructure of well-sintered ZnO grains was observed (Figures 2(a) and 2(b)). The bright regions in the BSE images found at the grain boundaries indicate a homogeneously distributed Bi-containing secondary phase (Figures 2(b) and 2(c)). In accordance with literature data, this Zn-Bi-O grain boundary phase is formed during the liquid phase sintering process from the eutectic mixture of ZnO and the sintering aid Bi_2O_3 melting at 750°C [25, 26]. An antimony containing phase is found in form of octahedral crystallites with $0.3 \mu\text{m}$, on average, in diameter (Figure 2(e)), which can be assigned to the cubic polymorph of the $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ phase with spinel structure [26, 27].

Moderate ZnO grain growth from $0.2 \pm 0.07 \mu\text{m}$ in the starting powder to an average of $2.6 \pm 0.9 \mu\text{m}$ in the foam strut material was found after sintering at 1100°C (Figure 2(d)). This is significantly lower than grain sizes of $6 \mu\text{m}$ to $8 \mu\text{m}$ as reported in studies of dense ZnO ceramics made from similar powder mixtures [11, 28]. Most likely, this is a consequence of the pressureless preparation of the respective foam green bodies and the pressureless sintering procedure.

Powder X-ray diffraction reveals 89.0 wt.% of hexagonal wurtzite-ZnO as the main phase being present in the strut material (Figure 3, Table 1). As secondary phases, 10.3 wt.% of a cubic $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ spinel phase and 0.7 wt.% tetragonal $\beta\text{-Bi}_2\text{O}_3$ were found. Interestingly, the thermodynamically stable orthorhombic β -polymorph of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ as well as a $\text{Zn}(\text{BiSb})_3\text{O}_7$ pyrochlore phase were not detected. This is in contrast to other studies of the phase evolution in the $\text{ZnO-Sb}_2\text{O}_3\text{-Bi}_2\text{O}_3$ system. For compact ZnO ceramics prepared under comparable conditions (sintering at 1100°C , $\text{Sb/Bi} = 2$), a pyrochlore phase and/or $\beta\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ were reported as secondary phases [11, 26, 29].

In this context, the polymorphism of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is known, but not fully understood yet. In recent studies, the α -polymorph has been identified as thermodynamically

FIGURE 2: SEM micrographs of the strut fracture surface in zinc oxide ceramic foams: (a) SE image, (b, c) BSE images revealing the Bi-containing secondary phase in the grain boundaries, (d) grain size distribution in the ZnO strut material, and (e, f) BSE micrograph and EDS spectra of the strut surface (black O) and of individual grains of a Sb-containing secondary phase (red O).

stable phase above 1225°C, which, nevertheless, is formed preferentially as metastable phase below 900°C [27, 30]. In the temperature range between 900°C and 1225°C, α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ transforms into the orthorhombic β -polymorph. Consequently, the formation of β - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is expected for the ZnO foams sintered at 1100°C.

However, the temperature at which this phase transformation occurs can be drastically affected by doping of

α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ with di- and trivalent metal ions like Cr^{3+} , Co^{2+} , or Ni^{2+} , whereas Cr^{3+} is most effective [31]. Complete suppression of the orthorhombic β -phase is found for α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ doped with at least 3.3 mol% Cr^{3+} according to the formula $\text{Zn}_{6.8}\text{Sb}_{1.9}\text{Cr}_{0.3}\text{O}_{12}$. Consequently, the α -polymorph with spinel structure is stabilized at room temperature by this doping effect. In the case of doping with trivalent metal ions, an unity of 1/3 Sb^{5+} and 2/3 Zn^{2+} in

FIGURE 3: Powder XRD pattern of the ZnO strut material and the corresponding Rietveld fit revealing the individual phase contents of hexagonal ZnO, cubic α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$, and tetragonal β - Bi_2O_3 . Deposition numbers of the crystal structure data used for the Rietveld analysis (Crystallography Open Database, COD/Inorganic Structural Database, ICSD): ZnO: COD-9004178, α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$: COD-1007077, and β - Bi_2O_3 : ICSD-41764.

TABLE 1: Phase and elemental composition of open-celled zinc oxide ceramic foams determined by powder XRD with Rietveld analysis and a comparative EDS measurement.

Phase composition (Rietveld)					
Phase (wt.%)	ZnO	α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$	β - Bi_2O_3		
ZnO 20 ppi	89.0 ± 0.14	10.3 ± 0.04	0.7 ± 0.01		
Elemental composition (calculated from Rietveld results)					
Element (wt.% at.%)	Zn	O	Sb	Bi	Al
ZnO 20 ppi	$76.6 \parallel 47.6$	$20.0 \parallel 50.8$	$2.4 \parallel 0.8$	$0.6 \parallel 0.1$	$0.4 \parallel 0.7$
Starting powder [#]	$75.4 \parallel 48.2$	$19.3 \parallel 50.3$	$2.8 \parallel 1.0$	$2.5 \parallel 0.5$	-/-
Elemental composition (EDS measurement)					
ZnO 20 ppi	$78.1 \parallel 52.2$	$16.5 \parallel 45.0$	$2.9 \parallel 1.1$	$1.7 \parallel 0.4$	$0.8 \parallel 1.3$

[#]Calculated for the initial powder mixture of 93.9 wt.% ZnO, 3.4 wt.% Sb_2O_3 , and 2.7 wt.% Bi_2O_3 .

α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ is substituted by one M^{3+} cation; a spinel phase with a general composition of $\text{Zn}_{7-2/3x}\text{Sb}_{2-1/3x}\text{M}_x\text{O}_{12}$ is formed. The end member of this homologous series with $x=6$ is the $\text{Zn}_3\text{M}_6\text{O}_{12}$ ($=\text{ZnM}_2\text{O}_4$) spinel [32].

In the case of the ZnO ceramic foams, a possible impurity is Al^{3+} originating from alumina abrasions during the ball-milling procedure of the initial $\text{ZnO-Sb}_2\text{O}_3\text{-Bi}_2\text{O}_3$ powder mixture. As the Al^{3+} and Cr^{3+} ions are similar in size and preferred coordination environment, a similar stabilization mechanism as described for the doping with Cr^{3+} may be expected. An indication for this hypothesis can be found in the lattice constant of α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ which is 848.7 pm for the spinel secondary phase in the ZnO strut material and therefore, 11 pm smaller compared to the literature values for the chemically pure α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ phase [27, 33]. The lattice parameter of 848.7 pm, as measured, is very similar to the value of 846.4 pm reported for a spinel with the composition $\text{Zn}_6\text{Sb}_{1.5}\text{Al}_{1.5}\text{O}_{12}$ [32]. By applying Vegard's law to the crystallographic data for pure α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ ($a_0 = 859.4$ pm) [33], $\text{Zn}_6\text{Sb}_{1.5}\text{Al}_{1.5}\text{O}_{12}$ ($a_0 = 846.4$ pm) [32], and the end

member of the homologous series, ZnAl_2O_4 ($=\text{Zn}_3\text{Al}_6\text{O}_{12}$; $a_0 = 809.1$ pm), [34], an aluminum content of $x=1.25$ was approximated (Figure 4) [35]. This corresponds to the composition $\text{Zn}_{6.17}\text{Sb}_{1.58}\text{Al}_{1.25}\text{O}_{12}$ for the spinel secondary phase in the ZnO strut material. Consideration of this Al^{3+} doping results in a significantly improved fit of the α - $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ reflections in the Rietveld analysis of the diffraction data (Figure 3).

The Bi_2O_3 amount of 0.7 wt.%, corresponding to 0.1 at.% Bi (Table 1), in the ZnO strut material as detected by XRD and Rietveld analysis was significantly lower than in the initial powder mixture (2.7 wt.% Bi_2O_3 /0.5 at.% Bi). This is an indication for the presence of an amorphous Bi-containing secondary phase, most likely formed during the liquid phase sintering process at the ZnO grain boundaries (Figure 2(c)) [25, 26]. As this amorphous phase is hidden for XRD and Rietveld analysis, an underestimation of the total Bi content is the result. Accordingly, a Bi content of 0.4 at.% was detected by EDS spectroscopy, which takes the amorphous material into account and is in good

FIGURE 4: Approximation of the Al^{3+} content in the cubic $\text{Zn}_{7-2/3x}\text{Sb}_{2-1/3x}\text{Al}_x\text{O}_{12}$ secondary phase in the ZnO strut material by applying Vegard's law on published crystallographic data of the pure spinels $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ and ZnAl_2O_4 ($=\text{Zn}_3\text{Al}_6\text{O}_{12}$) as well as an Al-doped spinel with the composition $\text{Zn}_3\text{Sb}_{1.5}\text{Al}_{1.5}\text{O}_{12}$.

agreement with the Bi amount in the initial powder mixture (Table 1). In addition, no indication for the partial loss of the sintering aid Sb_2O_3 by formation of volatile, molecular compounds like Sb_4O_6 was found [26]. The Sb content in the ZnO strut material measured by XRD and EDS analysis was 0.8 at.% and 1.1 at.%, respectively, and in good agreement to the Sb amount of 1.0 at.% in the initial $\text{ZnO-Sb}_2\text{O}_3\text{-Bi}_2\text{O}_3$ powder mixture. Furthermore, an aluminum concentration of 1.3 at.% was detected by EDS spectroscopy (Figure 5), which is in the same order of magnitude than the Al amount calculated from the results of the Rietveld analysis (0.7 at.%) and gives further evidence of the Al^{3+} doping of $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$. Nevertheless, it has to be noted that the accuracy of the EDS analyses for the trace elements (Sb, Bi, Al) is limited and a relative error of 4% to 12% has to be considered.

3.2. Macrostructure of ZnO Ceramic Foams. The total porosity of the obtained ZnO ceramic foams is high with a value of $93.6 \pm 0.4\%$ (Table 2). According to the Archimedes measurements and in conformity with the microstructure observed in the SEM investigations, virtually no residual porosity is present in the ZnO strut material ($<0.5\%$ w. r. t. the strut volume). Only the hollow strut cavities originating from the PU template are present; they contribute a porosity of $32 \pm 3\%$ w. r. t. the total strut volume. This value is in good agreement to alumina foams with a densely sintered strut material made from the same PU templates [36].

An isotropic linear shrinkage of $16 \pm 1\%$, equivalent to a volumetric shrinkage of $41 \pm 4\%$ in relation to the initial foam template dimensions, has been observed during the sintering process at 1100°C . This is in a good agreement to sintering studies of dense ceramics in the $\text{ZnO-Sb}_2\text{O}_3\text{-}$

FIGURE 5: EDS analysis averaged from 9 separate EDS spectra recorded on an uniaxially pressed slab of the ZnO strut material. *Inset:* Signals of the trace elements Al, Bi, and Sb.

TABLE 2: Properties of open-celled zinc oxide ceramic foams. The total porosity and cell porosity values refer to the geometric foam volume and the ratio $V_{\text{pores}}/V_{\text{foam}}$. The strut porosity is based on the strut volume and the ratio $V_{\text{strut pores}}/V_{\text{strut}}$ as determined by the water immersion technique.

ZnO, 20 ppi		
Foam porosity ($V_{\text{pores}}/V_{\text{foam}}$)	Total	$93.6 \pm 0.4\%$
	Cell ^a	$93.5 \pm 0.9\%$
Strut porosity ($V_{\text{strut pores}}/V_{\text{strut}}$)	Total ^b	$32 \pm 5\%$
	Hollow strut ^b	$32 \pm 3\%$
	Strut material ^c	$<0.5\%$
Shrinkage	Linear	$15.8 \pm 1.1\%$
	Volumetric	$41 \pm 4\%$
Morphology (CT)	Strut thickness	$0.38 \pm 0.15 \text{ mm}$
	Cell size	$2.69 \pm 0.23 \text{ mm}$
Thermal conductivity	Foam	$0.82 \pm 0.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
	Bulk material ^d	$37 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Compressive strength	Average strength	$0.15 \pm 0.03 \text{ MPa}$
	Weibull modulus	5.6

^aIncluding the cavities resulting from the PU template burnout. ^bRelated to the overall strut volume; $V_{\text{hollow strut}}/(V_{\text{hollow strut}} + V_{\text{strut material pores}} + V_{\text{solid}})$ and $V_{\text{strut material pores}}/(V_{\text{hollow strut}} + V_{\text{strut material pores}} + V_{\text{solid}})$. ^cRelated to the volume of the strut material excluding the cavities resulting from the PU template burnout; $V_{\text{strut material pores}}/(V_{\text{strut material pores}} + V_{\text{solid}})$. ^dExtrapolated thermal conductivity of the bulk strut material according to Ashby's model [43].

Bi_2O_3 system, for which a linear shrinkage of 17% is reported for the same powder composition as used within this work [11].

The open porous structure of the ZnO ceramic foams is confirmed by computed tomography; a total porosity of 94% and a closed porosity $<0.1\%$ have been determined, which is in good agreement to the results of the Archimedes measurements. In addition, no significant pore window blocking is present resulting in a thoroughly open-cellular structure (Figure 6(b)). The cell size in the ZnO ceramic foams ranges

FIGURE 6: (a) Strut thickness and cell size distributions calculated from a three-dimensional μ -CT reconstruction of a 20 ppi ZnO ceramic foam; (b) three-dimensional reconstruction of the same ZnO foam.

between 1.8 mm and 3.2 mm with an average of 2.7 ± 0.2 mm according to a morphometric analysis of the three-dimensional reconstruction volume (Table 2, Figure 6(a)). The strut thickness and strut filament thickness amount to 0.38 ± 0.15 mm and 0.13 ± 0.08 mm on average. As expected, the morphological parameters of the ZnO ceramic foams are within the same range as previously reported for alumina cellular ceramics made from the same 20 ppi PU foam templates [21].

3.3. Mechanical and Thermal Properties of ZnO Ceramic Foams. The compressive strength data obtained on all 35 ZnO foam specimens could be satisfactorily modelled by a two-parameter Weibull distribution [18]. An average compressive strength σ_{fc} of 0.15 ± 0.03 MPa and a Weibull modulus m of 5.6 were calculated (Figure 7). The modulus

FIGURE 7: Compressive strength data of 20 ppi ZnO ceramic foams ($\square$) and the corresponding fit with the two-parameter Weibull function (red line).

m is in the expected range for brittle cellular ceramic structures [37, 38]. Essentially, the low compressive strength is a consequence of the high porosity of 93.6% in the ZnO ceramic foams; accordingly, the σ_{fc} value is in the same order of magnitude as the compressive strength of cellular alumina with a similar microstructure and porosity range ($\sigma_{fc} = 0.19$ MPa/0.34 MPa at 94.0%/93% total porosity) [37].

For the evaluation of the strength-porosity correlation, the compressive strength data obtained for the cellular ZnO specimens were modelled with the Gibson–Ashby (GA) relation for the description of the crushing behavior of brittle, cellular materials (equation (1)) [39]:

$$\sigma_{fc} = C_6 \cdot (\rho_{rel})^n \cdot \sigma_{fs}. \quad (1)$$

According to equation (1), the compressive strength σ_{fc} of a brittle, cellular sample is a function of its relative density and the bending strength σ_{fs} of the bulk strut material. The density exponent n describes the effect of the porosity on the mechanical strength; for open-celled foams, a value of 1.5 is commonly used. The constant C_6 is related to the cellular geometry of the foam; for cellular ceramics made by the polymer sponge replication, usually a value of 0.16 is applied for C_6 [40]. The strength-porosity correlation for the ZnO ceramic foams is shown in Figure 8; the bending strength σ_{fs} was varied to fit the Gibson–Ashby model to the compressive strength data of the ZnO foams. An adequate GA fit is the result, and a bending strength of 54 ± 2 MPa is approximated for the bulk ZnO strut material. This is in the same order of magnitude than the bending strength of compact zinc oxide varistor ceramics, which ranges between 80 MPa and 120 MPa [41, 42].

The thermal conductivity of the obtained ZnO ceramic foams determined by the transient plane source technique was $0.82 \pm 0.07 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 93.6% total porosity. In order to evaluate the thermal properties of the ZnO strut

FIGURE 8: Compressive strength data of 20 ppi ZnO foams (□) and the corresponding fit with the Gibson–Ashby model for the strength–porosity correlation (red line).

material, the bulk thermal conductivity λ_b has been approximated. As the strut material contains virtually no microstructural porosity, a simple model derived by Ashby based on the rule of mixture was applied (equation (2)) [43]:

$$\lambda_b = \frac{\lambda_f - P_{\text{cell}} \cdot \lambda_g}{(1/3) \cdot (1 - P_{\text{cell}})} \quad (2)$$

The parameter λ_g is the thermal conductivity of the gas phase (air; $\lambda_g = 0.0264 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), [44] λ_f is the thermal conductivity of the foam and P_{cell} is the cell porosity of the ZnO foams including the hollow strut cavities ($P_{\text{cell}} = 93.5\%$) [36]. The calculated bulk thermal conductivity of the ZnO strut material is $37 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is slightly lower compared to experimental and theoretical values reported for chemically pure ZnO ($\approx 50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) [7, 45]. The reduced thermal conductivity of the ZnO strut material can be explained by the presence of the Bi_2O_3 and $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ secondary phases, which have a very low thermal conductivity of $1.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $2.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively [46]. The thermal conductivity of $37 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ of the bulk ZnO strut material is in good agreement with the value of $43 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ extrapolated by Landauer’s theory of effective percolation for a mixture of 90.2 vol.% ZnO and 9.8 vol.% $\alpha\text{-Zn}_7\text{Sb}_2\text{O}_{12}$ [47]. Consequently, for commercial ZnO-based varistor ceramics containing the same Sb_2O_3 and Bi_2O_3 sintering additives, a reduced thermal conductivity in the range between $20 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ and $35 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ is found as well [46].

4. Conclusions

The manufacturing of cellular ZnO ceramic foams with the established polymer sponge replication technique and an

aqueous ZnO dispersion and Sb_2O_3 and Bi_2O_3 as sintering additives has been demonstrated. The obtained open-celled ZnO foams show a high total porosity of 93.6% including the characteristic hollow strut cavities typical for this processing technique. The strut material itself is almost fully densified; its microstructure consists of ZnO grains with an amorphous Bi-containing grain boundary phase. In addition, an Al-doped spinel secondary phase with the composition $\text{Zn}_{6.17}\text{Sb}_{1.58}\text{Al}_{1.25}\text{O}_{12}$ was formed. The dopant Al^{3+} originates from a contamination during the ball-milling process of the raw powders and leads to a stabilization of the thermodynamically metastable spinel phase at room temperature.

The mechanical and thermal properties of the obtained ZnO ceramic foams were evaluated, and an average compressive strength of 0.15 MPa and a thermal conductivity of $0.82 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ were measured. The strength–porosity correlation was modelled with the Gibson–Ashby law for brittle, cellular structures; a bending strength of 54 MPa for the bulk ZnO strut material being in good accord to published data on comparable ZnO-based varistor ceramics was estimated. From the thermal conductivity data, a bulk thermal conductivity of $37 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ was determined for the ZnO strut material, which is in good agreement with the thermal conductivity of ZnO varistor ceramics of similar composition.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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