Electromechanical Properties of Robocasted Barium Titanate Ceramics

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This work presents the fabrication of dense polycrystalline barium titanate (BaTiO$_3$, BT) for electromechanical transduction using robocasting and cold isostatic pressing (CIP). The use of CIP as post-treatment is proposed to eliminate defects and increase the density of robocasted parts to improve the piezoelectric performance. For robocasting, pastes containing 50 and 52 vol% are developed; the resulting green robocasted parts are CIPed at 100 and 150 MPa. Using this proposed technique, samples robocasted with BT52 and CIPed at 150 MPa display a relative density of $\approx 98\%$, comparable with reference polycrystalline samples. In addition, an increase in both the piezoelectric charge and voltage coefficient is observed in robocasted parts, with the values up to 195 pC/N and $12 \times 10^{-3}$ Vm N$^{-1}$, respectively. These values, which are comparable with previous studies of polycrystalline BT, indicate that the combined robocasting and CIP technique is a possible method for producing 3D printed piezoelectric sensors.

1. Introduction

Owing to their ability to convert mechanical to electrical energy and vice versa, perovskite-structured ferroelectrics are commercially important materials that are widely used in transducer applications, such as actuators, sensors, and energy harvesting systems.[1] The coefficients that describe the electromechanical conversion of these materials are, for one, intrinsically constrained by the crystal structure of the constituent material. Furthermore, the performance of polycrystalline piezoelectrics also depends on their microstructure, such as grain size and defects[2] as well as externally applied thermal, electrical, and mechanical fields.[3,4] These methods either depend on tuning the intrinsic properties of the material through, e.g., process optimization, chemical substitutions, or compositional modification, which might not be possible for a specific application, or implementing complex mechanical bias fields. Recent work, however, has demonstrated the possibility to enhance electromechanical properties with printed 3D ceramic structures,[5] where high piezoelectric charge coefficients and voltage constants were observed. As a result, the combination of additive manufacturing (AM) technologies with functional materials shows significant promise in optimization of electromechanical properties.

AM technologies for the fabrication of 3D parts possess advantages to the conventional forming techniques, such as injection molding, die pressing, tape casting, and gel casting. These techniques have long processing times and high cost and do not allow the production of precise structures with complex geometries or assemblies with interconnected holes. The AM techniques can overcome these issues by additively building 3D structures layer-by-layer from a computer model.[6] A few examples of these techniques are 3D printing (3DP) of powders,[7] selective laser sintering (SLS),[8] laminated object manufacturing (LOM),[9] stereolithography (SL),[10] inkjet printing (IJP),[11] and direct ink writing (DIW), also known as robocasting.[12–14]

Robocasting is a slurry-based method, which allows for the freeform 3D fabrication of dense ceramic parts by the extrusion of a colloidal gel or paste through a nozzle. The pastes are specifically designed to hold a high ceramic content with a low amount of binder (<1%) to prevent a viscoelastic paste response required for extruded parts to retain the printed shape after extrusion.[13,15] This makes robocasting suitable for assembling free-standing structures with high aspect ratio walls and spanning parts without the need of supports, which is also an advantage over other 3D techniques.[6,16] The flexibility of nozzle shapes and sizes is another benefit of this process, where the use of square, hexagonal, and hollow nozzles and sizes varying from 0.17 to $\times 1.5$ mm have been reported.[17,18] Fu et al.[19] for example, fabricated hollow filaments by extruding core–shell composites via robocasting and co-extrusion. In their work, the carbon filaments (core) were burned out, leaving only the Al$_2$O$_3$ hollow assemblies (shell). In addition, highly textured structures can be produced through the extrusion of particles with high aspect ratio, which can align themselves toward shear direction. Consequently, the combination of this technique and templated grain growth (TGG) can be used to produce assemblies with crystallographic alignment,[20,21] which leads to anisotropic...
properties, hence improving the material properties compared with a non-textured structure.[22,23] Compton and Lewis[24] fabricated fiber filled epoxy composites with excellent mechanical properties via robocasting and observed that the alignment of high aspect ratio fillers occurs toward the print direction. In addition, it was successfully used for tissue engineering applications[25–27] fabrication of solid monolithic part,[28] and complex porous scaffolds.[12] The interest in the development of functional devices using AM technologies,[29–31] such as energy storage systems and piezoelectric sensors, has significantly increased due to the ability to optimize functional properties and the commercial potential.[16,33] In particular, robocasting has specifically been studied for the assembly of functional ceramic parts.[34–36] Nevertheless, these studies primarily focused on the paste formulation and optimization of printing parameters. A study aimed at the manufacturing of highly dense structures with improved piezoelectric performance using robocasting has not been presented.

For this study, the effect of robocasting on the microstructure as well as the dielectric and piezoelectric properties of barium titanate (BaTiO$_3$, BT) was investigated. Discovered over 70 years ago,[37] BT is a well-known ferroelectric ceramic that was chosen here as a reference material.[38] Due to its high relative dielectric permittivity, BT is an important material for capacitor applications, but the use for piezoelectric applications is limited. This is due to a relatively low Curie temperature $T_C \approx 130$ °C and low electromechanical properties compared with lead-containing materials, such as lead zirconate titanate (Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$, PZT). However, international governmental regulations limit the use of lead and other toxic materials in electrical components, thereby increasing the interest in finding a lead-free alternative. Thus, despite its drawbacks, BT has received renewed interest, in particular, as an end member in lead-free solid solutions, such as (Ba,Ca)(Zr,Ti)O$_3$[39] and (Na$_{0.5}$Bi$_{1.5}$)TiO$_3$-BT.[40] In addition, over the last decades, several more compositions based on BT have been investigated and show promising results.[41] Recent studies have also demonstrated an enhancement in the electromechanical properties through, e.g., microstructure optimization, such as a relative dielectric permittivity up to 7000[42] as well as enhanced piezoelectric charge coefficients $d_{33}$ up to 425 pC/N through adjusting the grain size.[2,43] For example, Wada et al. achieved the $d_{33}$ values up to 788 pC/N by preparing textured BT via TGG.[44] Importantly, however, due to the relatively low Curie temperature, these high dielectric and piezoelectric properties have been achieved near room temperature, necessitating the characterization of the electromechanical response as a function of temperature. BT undergoes three first-order phase transitions while cooling from above the Curie temperature. As previously noted, BT transitions from a paraelectric cubic ($Pm3m$) phase to a ferroelectric tetragonal ($P4mm$) phase at $\approx 130$ °C, followed by a transition to a ferroelectric orthorhombic ($Pmm2$) phase at $\approx 0$ °C and a ferroelectric rhombohedral phase ($R3m$) at $\approx -90$ °C.[38] The phase transition temperatures have been shown to depend on several parameters, such as dopants,[45] grain size,[46] and internal stresses[47] as well as externally applied electrical[48,49] and mechanical fields.[50–53]

The aim of this study is to demonstrate that the freeform fabrication of highly dense structures with a variety of geometries is possible with a combination of robocasting and a cold isostatic pressing (CIP) post-treatment. For this, pastes containing a BT of 50 vol% and a BT of 52 vol% were produced and compared with a conventionally prepared reference sample. Bars were robocasted and subsequently cold-isostatically pressed at 100 and 150 MPa to determine the influence of post-processing on the microstructure and electromechanical behavior. To see the effect of robocasting on the functional properties, the piezoelectric charge coefficient and the relative permittivity were characterized as a function of temperature from 20 to 225 °C, above the ferroelectric-paraelectric phase transition temperature.

2. Results and Discussion

2.1. Rheology

The rheological characterizations of pastes for robocasting containing BT50 and BT52 are shown in Figure 1. In Figure 1a, it is seen that the higher viscosity value at lower shear rate is attributed to the paste with BT52 due to the higher solid loading.[13] For both paste compositions, the exponential decrease in viscosity as shear rate increases is characteristic of a shear thinning behavior. This behavior allows the paste to flow through the print nozzle when a shear stress is applied and retain its shape after exiting the print nozzle.[12,18,28] Therefore, a yield stress is also
required for colloidal pastes to ensure the shape retention of the printed filaments. When the stress value is above the yield point of the paste, its viscosity starts to decrease due to the shear thinning response. After stress removal, the paste network recovers immediately, allowing the retention of the printed form. Thus, the yield stress is also an indication of the printed filament stiffness and, thus, ensures that the lower layers can support the weight of the upper layers. Figure 1b presents the storage ($G'$) and loss ($G''$) modulus as a function of shear stress for the pastes. Both paste compositions at low stress presented a linear viscoelastic response with the large $G'$ value characteristics of the formation of a stiff network. With an increase in the shear stress, $G'$ decreases and $G''$ increases until $G' = G''$, which is a characteristic of a yield point of 142 and 694 Pa for pastes with BT50 and BT52, respectively. These results indicate that the pastes developed in this work exhibited high stiffness ($G'$), high volume fraction of ceramics, and high yield strength, in addition to strong shear thinning. Hence, it is possible to affirm that suitable pastes for robocasting were developed.

2.2. Microstructural Analysis

Various parameters are crucial for the extrusion process to ensure successfully printed structures, such as print speed, raster pattern, rod spacing, and nozzle size. To reduce the building time and achieve a stable flow, faster printing speeds are usually desirable. For this work, a square nozzle was chosen to minimize the space between filaments during printing. Moreover, printing patterns with a filament and layer spacing of 1.35 mm were selected, corresponding to 90% of the nozzle size, which is small enough to ensure side-by-side contact during printing, but large enough to avoid overflow of printed areas. Figure 2 shows the printing patterns of robocasted bending bars as well as the schematic cross section of the printed structures and cross sections of the extruded structures after sintering with paste containing BT50 and BT52. Dotted lines are also included in the cross-sectional images of the sintered samples to represent the target structure. It is apparent from Figure 2, however, that the robocasted structures from both paste compositions presented voids between the printed filaments in the interface regions, i.e., approximately where the dotted lines cross. One reason for void formation may be assigned to the rotation of printed filaments along the extrusion direction, although the nozzle remains aligned parallel to this direction during patterning processing. This is most clearly evidenced by the first extruded layers of paste with BT50, which is denser in comparison with the upper layers. The first printed layer may have improved attachment to the printing substrate, hence impairing its rotation. From the second layer onward, the adhesion between the layers is likely lower, which facilitates filament rotation that can increase void size. Interestingly, the void geometry can be approximated to a triangle, which is most visible in robocasted structures with BT50 paste. This is most likely caused by the edge of the square filament, which, when rotated, forms triangular holes. Rao et al. also observed a similar behavior for hexagonal filaments for microfabrication of 3D periodic structures. An addition cause for void formation could be oil trapping during extrusion process. The oil can be trapped between the adjacent filaments, as they are printed in contact next to each other, hence leading to large voids after binder burnout. Feilden et al. investigated the influence of extrusion under oil and air on the microstructure of the extruded scaffolds, where they observed that only the parts printed in oil presented running voids in the extrusion direction.

Figure 2. Illustration of schematic cross section of robocasted structures and SEM images of samples cross section extruded with pastes containing BT50 and BT52.
A number of approaches can be applied to overcome these issues, such as performing extrusion in air or increasing the ceramic content of the extruded paste. However, extrusion in air usually leads to forming of drying cracks due to the fast drying rate. In addition, increasing ceramic content in the paste is also challenging, as the rheological response is directly influenced by the solid content. It is important to note that, as seen in the cross-sectional image of robocasted structures with BT52 paste, although there was a reduction in the void size between filaments compared with BT50, the voids did not completely disappear. Therefore, these are not alternatives that provide dense structures without defects. In this work, the application of CIP as a post-treatment to obtain dense structures via robocasting was investigated. Figure 3 shows the cross section of robocasted samples produced with and without CIP post-treatment.

It is shown that the CIP process after robocasting for both BT50 and BT52 pastes leads to a significant reduction of the pore content and their size in the sintered structures. The relative density was measured for all samples (Figure 4), showing an apparent increase in density with both BT content and applied CIP pressure. The grain sizes were averaged over 200 grains for each sample, revealing an average grain size of 24 ± 8 μm for the reference sample and 30 ± 10 μm for both robocasted samples. As shown in the microstructure images (Figure 4), the grain size distribution is homogeneous. However, robocasted samples displayed abnormal grain growth with sizes >100 μm, where one abnormally large grain is visible in Figure 4 for BT50. The volume fraction of these abnormal grains was estimated to be below 10%. A density of 98 ± 0.6% was observed in robocasted samples with BT52 paste that were CIPed at 150 MPa. Importantly, under these conditions, the density is comparable to the reference BT samples, which was also CIPed at 150 MPa and displayed a density value of 99 ± 0.5%. These results indicate that a CIP post-treatment of 150 MPa is a possible method to improve the density of robocasted structures. Furthermore, no additional defects, i.e., pores or cracks, were observed at the interface where two extruded bars met.

2.3. Temperature-Dependent Dielectric and Piezoelectric Behavior of BT

Microstructural characteristics, such as grain size and density, can have a great effect on the dielectric and piezoelectric properties of BT. Therefore, dielectric and piezoelectric properties were measured only for the samples cold-isostatically pressed at 150 MPa and compared with the reference sample. The results for the piezoelectric charge coefficient $d_{33}$ and the relative permittivity $\varepsilon_{33}$ are shown in Figure 5a–f. The room temperature values of $d_{33}$ for the reference, BT50, and BT52 samples were 150, 165, and 200 pC N$^{-1}$, respectively, measured at a frequency of 110 Hz. With decreasing frequency, the $d_{33}$
In addition, between the depolarization It is the piezoelectric charge coefﬁcient. These investigations have revealed that – at room temperature, which is comparable μ2 and, ﬁnally, to reduced piezoelectric properties. This is further corroborated by the lower permittivity. Interestingly, even though a similar grain size distribution was found for all samples, the explained by the lower area density of ~95 ± 0.9%. This is due to the fact that the electric field is concentrated in the pores with lower permittivity and reduces the effective electric charge in the ceramic material. This leads to a reduction of the remanent polarization P r and, finally, to reduced piezoelectric properties. This is further corroborated by the lower permittivity. Interestingly, even though a similar grain size distribution was found for all samples, the BT52 robocasted sample showed a higher d33. In all three cases, this value decreased with increasing temperature up to ~75 °C, which is likely due to the lower temperature orthorhombic-tetragonal phase. This is further conﬁrmed by the decrease in permittivity in the same temperature range. Due to increased intrinsic and extrinsic contributions to the electromechanical coupling in the vicinity of the phase transition temperatures, the piezoelectric and dielectric properties are maximized. Zheng et al. observed these maxima for BT with varying grain sizes. Other material classes with T o → T r, such as K 0.5 Na 0.5 NbO 3 (KNN), show an analogous maximum at ferroelectric–ferroelectric phase transition temperatures. At temperatures between 75 and 100 °C, the piezoelectric charge coefﬁcient remained constant at 110, 130, and 135 pC N−1, for the reference, BT50, and BT52 samples, respectively. With a further increase in temperature, an increase in d33 was observed, followed by a sharp decrease at the Curie temperature T c (Figure 5a–c), whereas ε′′ 33 (Figure 5d–f) showed a maximum at T c. Interestingly, the depolarization temperature, i.e., the loss of piezoelectricity, coincided with T c for all three samples at ~130 °C. Similar temperature-dependent d33 results were also observed by Anton et al., although the indirect piezoelectric coefﬁcient was presented. It should be noted that for other material systems, such as PZT or KNN, the depolarization temperature was found to be on the order of 6–10 °C lower than the Curie temperature, which might depend on the order of the transition as well as the thermal stability of ferroelectric domains in different materials. BT is well known to have the ﬁrst-order ferroelectric–paraelectric transition. The peak in the piezoelectric response before thermal depolarization can be described by

\[ d_{33} = 2Q_{11}P_3\varepsilon_0\varepsilon''_{33} \]  

(1)

where Q 11 is the electrostrictive coefﬁcient, P 3 is the macroscopic polarization, and ε 0 is the permittivity of free space. The signiﬁcant increase in relative permittivity at T c, coupled with the loss of macroscopic polarization at the sample temperature, resulted in an apparent increase of the piezoelectric properties. It is generally accepted that the electrostrictive coefﬁcient is relatively temperature invariant and, therefore, does not signiﬁcantly contribute to the temperature dependence of the piezoelectric properties.
The rate of decrease in $d_{33}$ from $T_{O-T}$ was found to vary between samples, where $d_{33}$ decreased for the reference and BT50 samples with $\approx 1 \text{pC N}^{-1} \text{ per } ^{\circ} \text{C}$, whereas the BT52 sample showed a two times larger decrease. These gradient changes could be due to the difference in grain size. As shown by Zheng et al., with decreasing grain size, a stronger $d_{33}$ gradient was observed as a function of temperature. Importantly, BT exhibits shifts in the phase transition temperatures with varying grain sizes,$^{[43]}$ due to changes in 90° domain wall density and width. Furthermore, it was shown that increasing grain sizes shifts $T_{O-T}$ to lower temperatures, whereas $T_C$ increased. However, the average grain of the robocasted samples was $\approx 10 \mu m$ larger and exhibited abnormal grain growth. In theory, these samples should have shown lower electromechanical coupling, lower gradient due to a lower $T_{O-T}$, as well, as an increased Curie temperature.

In addition to grain size, internal stresses can affect the piezoelectric and dielectric properties of BT.$^{[47]}$ Applied biaxial compressive stresses$^{[49]}$ as well as uniaxial compressive stresses$^{[51,52]}$ have been found to shift both the $T_{O-T}$ and $T_C$ phase transition temperatures to higher temperatures, whereas hydrostatic loading favors the paraelectric phase and reduces $T_C$.$^{[53]}$ Similarly, internal stresses, for instance, caused by $\text{ZrO}_2$ addition, different grain sizes, etc., were also observed to shift $T_C$ to higher temperatures and decrease the maximum permittivity.$^{[47]}$ In the present investigation, there was no observed $T_C$ shift between the reference and robocasted samples, although a decrease in the maximum relative permittivity in the robocasted sample was found. This, together with similar grain sizes across samples, indicates that there is no significant change in internal stresses by robocasting. As shown by Dellert et al.$^{[44]}$ for tape casting and by Fu et al.$^{[20]}$ for robocasting, standard particles show a predominant orientation in the green body due to the shear rate. As a result, shrinkage during sintering is anisotropic and can cause internal stresses.$^{[65]}$

It is also possible that this anisotropy in particle orientation is partially responsible for the improved piezoelectric properties in the BT50 and BT52 samples, similar to grain-oriented BT.$^{[44]}$

The piezoelectric voltage coefficient $g_{33}$, which is an important value for sensor applications, can be calculated using the following equation

$$g_{33} = \frac{d_{33}}{\varepsilon_0 \varepsilon_{33}}$$

At room temperature and a frequency of 110 Hz, $g_{33}$ was found to be $8.6 \times 10^{-3}$, $13.3 \times 10^{-3}$, and $12 \times 10^{-3}$ Vm N$^{-1}$, for the reference, BT50, and BT52 samples, respectively. These values are comparable to the $12.6 \times 10^{-3}$ Vm N$^{-1}$ observed in a previous investigation.$^{[31]}$ As $g_{33}$ is dependent on $d_{33}$, the lower value in the reference sample is to be expected, as well as the increase in value with decreasing frequency. Furthermore, the sample with 50 vol% BT showed a relatively high $g_{33}$ due to the lower density and permittivity. In general, the introduction of a porous structure is used to increase the piezoelectric voltage coefficient,$^{[55]}$ but in this case, the mechanical properties, such as fracture toughness, are decreased. Therefore, it would be preferable to increase $g_{33}$ while maintaining a high density. Increasing the temperature decreased the piezoelectric voltage coefficient, as shown in Figure 6a-c, which is most likely due to the decrease in $d_{33}$ with increasing temperature. Interestingly, unlike the piezoelectric charge coefficient, the piezoelectric voltage coefficient did not show a peak close to the Curie temperature. Combining Equation (1) and (2), one can see that the piezoelectric voltage coefficient is equal to $2Q_{11}P_3$, meaning that the decrease in $g_{33}$ depends only on the loss in polarization at the Curie temperature,$^{[48]}$ assuming that the electrostrictive coefficient remains relatively temperature invariant.$^{[61-63]}

Similar to tape casting, robocasting aligns anisotropic particles in the direction of extrusion. A special case for robocasting is the gradient in shear rate as a function of the position in the nozzle.$^{[20]}$ Due to this particle orientation, one could expect anisotropic behavior in the dielectric and piezoelectric properties. For this reason, X-ray diffraction has been conducted on the samples in parallel as well as perpendicular to the direction of extrusion (Figure 7a,b). The reference sample is used for the case of random distribution of the particles without any preferential orientation. This pattern confirms the tetragonal nature of BT and shows no signs of secondary phases. To describe the observed reflections, the pseudocubic notations are used. Looking at first at the parallel case, in particular, at the 200pc peaks (Figure 7b), one can see the change in the intensity ratio between these two peaks. The peak at lower angles describes the

![Figure 6. Piezoelectric voltage coefficient as a function of temperature at a constant stress of $-5 \text{ MPa}$ for a) poled reference sample, b) BT50, as well as c) BT52. The vertical dashed lines represent the Curie temperature for each sample.](image-url)
002 direction, whereas the peak found at higher angles describes the 200 and 020 directions, as they represent the c- and a-axes in a tetragonal crystal structure. This would suggest that the particles align in the 002 direction, or c-axis, parallel to the direction of extrusion. In particular with 52 vol% BT, the intensity of the 200 peak is significantly higher than any other signal. This could also be attributed to the density of the ceramic, as with increasing relative density, the degree of texturing increases.\textsuperscript{[65]} As 50 BT has a lower relative density, a lower degree of texturing is expected. Observing the X-ray diffraction pattern for the perpendicular case, a different behavior can be seen. Compared with the reference sample, the intensity ratio between the 200 peaks is reversed perpendicular to the direction of extrusion, where the intensity of the higher angle reflections, i.e., 200 and 020 orientations, is higher. This behavior is expected, as in parallel, the preferential direction is the 002 direction. It should be noted that only the surface of the samples can be observed, and thus, the results might change throughout the samples thickness. Nevertheless, these results are consistent and would, therefore, suggest an anisotropic response.

To observe an anisotropic behavior, Figure 8a–d compares the piezoelectric charge coefficient and relative permittivity parallel and perpendicular to the extrusion direction. Figure 8e shows a schematic representation of particle orientation, as shown by Fu et al.\textsuperscript{[20]} together with the measurement direction. The significant differences in parallel and perpendicular direction in BT50 could be due to the relatively low density of 95 ± 0.9%. Due to statistical distribution of pores, cutting out samples can lead to a strong variation between samples. Furthermore, pores could orient in a similar fashion as particles, thus changing the anisotropy of the properties. Zhang et al. showed that the reduction of the remanent polarization with increasing porosity is lower in case of pores aligned to the applied electric field,\textsuperscript{[56]} indicating that the effect on the piezoelectric charge coefficient is lower for aligned pores. Thus, pores seem to be the major contributor of the BT50 samples, which is even more apparent when compared with the BT52 samples. Here, only minor differences could be observed, albeit the BT52 sample showed a more pronounced preferential orientation (Figure 7). This could be explained by looking at how particles theoretically align during robocasting. While extruding the BT slurry, the particles aligned in the center of the nozzle predominantly perpendicular to the extrusion direction, whereas on the wall, mostly parallel orientation occurred. As a result, there are two predominant orientations that coincide with the poling and measurement directions. Especially, the perpendicular case is, therefore, dependent on the depth of the observation. Using transmission synchrotron or grinding the sample step-by-step would be necessary to get a depth profile. However, this particle alignment during robocasting could explain the improvement when compared with the reference sample, where the particles are randomly distributed. Nevertheless, internal stresses cannot be ruled out as another explanation for the observed results. Extrusion of platelets, which show higher particle orientation,\textsuperscript{[64]} and measurements that focus on internal stresses would be needed to see the major contributor of the enhanced properties in robocasted samples.

3. Conclusions

Robocasting is a feasible method to produce simple samples and showed improved behavior in comparison with reference samples and traditionally produced samples. These results, therefore, suggest the possible application of the robocasting method for electromechanical transducer applications. As more complex structures can be printed with this method, certain structures...
Figure 8. Comparison between a,b) piezoelectric charge coefficient and c,d) permittivity as a function of temperature for two different poling directions in regards to printing direction. e) Schematic representation of particle orientation after robocasting.

could lead to improved $d_{33}$ and lower permittivity, which in return would increase the important figures of merit. This could be achieved by tailoring the robocasting parameters and paste composition as well as texturing through use of anisotropic ceramic particles.

The fabrication of dense polycrystalline BT structures with robocasting and CIP is presented. The robocasted samples, using a ceramic content of 50 and 52 vol%, were post-treated by CIP at 100 and 150 MPa. This post-treatment was found to improve the relative density and, as shown by microstructure analysis, drastically reduce the presence of running voids formed during extrusion under oil as well as enhance the piezoelectric properties. Here, the optimized parameters were found at 52 vol% BT and a CIP pressure of 150 MPa, as lower ceramic content lead to lower density and reproducibility. Further investigations, however, are necessary to determine the origins of the improved piezoelectric properties compared with the reference sample, as no significant variations in the microstructure or phase transition temperatures were observed. Therefore, the combination of these techniques is a promising fabrication method for textured or highly complex structures and core–shell composites with improved relative density and reduced defects, making it promising for sensing or energy harvesting applications.

4. Experimental Section

During robocasting, pastes containing 50 vol% BT (BT50) and 52 vol% BT (BT52) ($d_{50}$ of 1.2 μm, Ferro GmbH, Frankfurt am Main, Germany) were used together with 2 vol% of binder (Bermocoll E 320 FQ, Akzo Nobel GmbH, Düren, Germany) and 1.7 vol% of dispersant (Darvan C14, Vanderbilt Minerals LLC, Norwalk, USA), both in relation to ceramic content. Distilled water was used as solvent. To reach the required viscoelastic properties for robocasting, 0.3 and 0.11 vol% of coagulant (PEI branched; average MW ≈25 000, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used for pastes containing BT50 and BT52, respectively. The pastes were produced using a planetary mixer (ARE-250, Thinky Co., Tokyo, Japan) and subsequently filled into 30 ml syringes and degassed.

The rheological behavior of the pastes was measured using a viscometer (MCR 302, Anton Paar Germany GmbH, Ostfildern, Germany) at 20 °C. A cone-plate measuring setup with a plate diameter of 25 mm and a cone angle of 1° was used to investigate the viscosity as a function of shear rate in a range from 1 to 100 s$^{-1}$. For the dynamic viscoelastic test, the storage ($G’$) and loss modulus ($G’’$) were measured using an oscillatory measurement. Therefore, a sweep analysis with amplitude ranging from 0.001% to 100% at a constant frequency of 1 Hz was required.

A robocaster (Rob-Fab, Battenberg Robotic GmbH and Co.KG, Marburg, Germany) was used for the extrusion process, which consisted of a six-axis robotic arm responsible for the movement in the $x$- and $y$-directions and a movable table responsible for the $z$-direction. Bending bars were pneumatically extruded using a 1.5 × 1.5 mm$^2$ square nozzle onto an Al$_2$O$_3$ substrate in an oil bath (Renolin MR 0 VG 2, Fuchs GmbH, Mannheim, Germany) at 20 °C with an extrusion velocity of 5 mm s$^{-1}$ and a feed speed of 11 mm s$^{-1}$. The robocasted structures were dried for 24 h at room temperature, following which were CIPed. For the CIP process, the robocasted samples were first vacuum encapsulated in a plastic bag and then placed into a wet bag press machine (LOOMIS PRODUCT Kahlefeld, Kaiserslautern, Germany). Two sets of samples were divided and pressed at 100 and 150 MPa for 300 s. The higher density values were obtained by robocasted samples pressed at 150 MPa. Thus, a reference sample of as-received BT powder was produced only by CIP at 150 MPa for the piezoelectric measurements. For the reference sample, no organic additives, such as dispersant or binder, were added. All samples were then heated to 600 °C for 1 h with a heating and cooling rate of 1 K min$^{-1}$ to burn out the binder, dispersant, and coagulant, followed by sintering at 1350 °C for 3 h in air with a heating and cooling rate of 5 K min$^{-1}$. The reference sample was sintered under the same conditions, however, without the binder burnout step.

The robocasted samples were cut and surface ground to cuboid samples with a height of 2 mm and a length and width of 4 mm. The reference sample was ground to 2 mm height, however, remained a cylindrical shape with a diameter of 8 mm. The density of all samples was measured using
the Archimedes method according to DIN-EN 623-2. The samples were then sputtered with Pt electrodes on the 4 mm × 4 mm and circular surfaces, respectively, and annealed at 200 °C for 1 h to reduce domain reorientation caused by the grinding process. The samples were poled at room temperature in an oil bath under an electric field of 2 kV mm⁻¹ for 30 min. Electrical characterization was performed at least 24 h after electrical poling.

The piezoelectric charge coefficient $d_{33}$ and relative permittivity $\varepsilon_{r33}$ were measured as a function of temperature in a screw-driven load frame (5967, Instron, USA) outfitted with a thermal chamber (TK 26.600.LN2, Fresenberger, GmbH, Wipperfürth, Germany) and a custom piezoelectric and dielectric measurement system, described in detail elsewhere. During testing, the samples were heated up to 225 °C with a heating rate of 2 K min⁻¹, during which the direct piezoelectric charge coefficient and capacitance were simultaneously characterized. The samples were applied with bias stress of ~5 MPa to maintain electrical contact throughout the measurement. The piezoelectric charge coefficient was directly measured using a piezoelectric actuator, which applied a sinusoidal stress signal with an amplitude of ±0.5 MPa at varying frequencies $(f=10$–110 Hz). A custom-built LabView-based control and analysis program collected the polarization, which was determined by a Sawyer–Tower circuit, and the force signal from the load cell to determine the frequency-dependent $d_{33}$. The relative permittivity was measured at a frequency of 1 kHz with an LCR meter (E4980AL, Keysight, USA). The LabView-based control and analysis program switched between the piezoelectric and dielectric measurements during testing.

Scanning electron microscopy (SEM; Quanta 200, FEI, Czech Republic) was used for the microstructure characterization of robocasted structures. Furthermore, to ensure phase purity, the surfaces of the samples were measured using a laboratory X-ray diffraction (D8 Advance Eco diffractometer, Bruker) in reflection geometry.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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