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Hybrid inks for 3D printing of tall BaTiO₃-based ceramics

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ABSTRACT

Ink formulation is one of the main challenges with ceramic 3D printing. Here, we present a new, reactive-colloidal hybrid ink for 3D printing by robocasting of BaTiO₃-based ceramics. The hybrid ink combines a titanium isopropoxide-based sol-gel base with a colloidal dispersion of powder, here demonstrated with BaTiO₃, both as the sol-gel (by reaction of titanium isopropoxide and barium oxide) and colloidal (by addition of BaTiO₃ powder) parts. Addition of glycerol was necessary to avoid fast precipitation and poor dispersion of BaTiO₃ from the reaction of BaO and Ti-isopropoxide. With a solid loading of 40 vol% BaTiO₃, 10 mm tall structures could be printed with minimal deformation from slumping. The BaTiO₃ shows good piezo-, ferro- and dielectric properties after sintering, with a piezoelectric charge coefficient (d₃₃ = 159 pC/N) in the range commonly reported for BaTiO₃. The hybrid inks developed in this work are therefore suitable for robocasting of BaTiO₃-based electroceramics.

1. Introduction

Additive Manufacturing (AM) technologies, or 3D printing, have in the previous years been at the centre of attention for the development of three dimensional ceramic-based objects [1–7]. These shaping techniques build freestanding structures layer-by-layer until obtaining a defined shape. The latest development shows that AM techniques exhibit process flexibility, geometrical controllability (shape, thickness) and that 3D printed (3DP) devices have increased performance compared to devices made by traditional methods [8]. In some instances, 3DP materials can also allow a quicker and more cost-effective fabrication of complex shapes and structures [6]. Several techniques have been tried to fabricate complex ceramic-based 3D structures, including direct ink writing (DIW) [9], direct laser writing (DLW) [10], interference lithography (IL) [11], and phase-mask lithography (PML) [12].

DIW techniques are mainly in the centre of attention due to their ability to easily print and cure a wide range of multi-material systems in various shapes [13], their low cost and the absence of additional tools such as masks, screens, or dies [9,14]. DIW techniques include continuous fused deposition [15], filament approaches, micro pen writing [16] and robocasting.

Robocasting is one of the most promising DIW techniques. It is based on the extrusion of ink through a nozzle on a substrate. The ink is loaded into a cartridge and extruded through the nozzle by applying controlled air pressure to the cartridge piston. At the same time, a computer controls the position of the nozzle above the substrate [17]. The rheological behaviour of the ink is critical for successful printing, i.e. obtaining an object having a stable shape after printing. The ink must (1) exhibit a shear thinning behaviour to flow through a small nozzle when low air pressure is applied, (2) have sufficiently high yield stress (σy) so the object does not collapse under its own weight (also called slumping), without external contribution (temperature assisted drying, curing etc...). Such rheological behaviour is called “Herschel-Buckley” and is approximated with the following equation:

$$\sigma = \sigma_{\text{dyn}} + K \gamma^n$$

where σ is the shear stress (Pa), $\sigma_{\text{dyn}}$ the dynamic yield stress (Pa), K a model factor, $\dot{\gamma}$ the shear rate (s⁻¹), and n the flow index. The ink must also (3) have a sufficiently high solid loading to obtain a mechanically stable structure with the desired density after heat treatment.

There are different type of inks used for robocasting of ceramic-based objects. Colloidal inks i.e. stabilized suspensions of particles in an aqueous medium, are the primary type of inks used [18,19]. These inks...
require a long preparation time due to powder milling and stabilization of the colloidal powder to obtain suitable ink rheology [20]. The second type of ink used in robocasting are gels and hydrogels, based on the polymerization of an organic polymer to form a macro polymeric network [20]. The disadvantage of gel-based inks is that they require a very precise control of temperature and a multistep preparation protocol [21,22]. A new approach is to use a combination of colloids and sol-gels, called “hybrid sol-gel inks” [23,24]. This type of ink is a mixture of two parts, the colloidal powder and the stabilized sol-gel suspension. These two parts can either be based on the same material or different ones. Depending on the starting materials, their combination can yield systems with either a single-phase, a binary material that can enhance material properties [25], or a new phase synthesized by solid-state reaction at high temperature. The latter was demonstrated with the synthesis of pure bismuth titanate Bi$_4$Ti$_3$O$_{12}$ (BiT) by mixing bismuth oxide in a stabilized Ti-based sol-gel solution [25]. The concept has been further improved by adjusting the rheological properties of the ink to print 2D lines of BiT [26].

In this work, we adapt the concept of hybrid sol-gel concept to the synthesis of barium titanate (BaTiO$_3$) and tailor the hybrid sol-gel ink rheology for the deposition of BaTiO$_3$ 3D objects by robocasting. The developed ink is based on the reaction between barium oxide (BaO) and a stabilized Ti- sol gel solution following the reaction:

$$\text{BaO (s) + TiO}_2\text{(aq)} \xrightarrow{\text{Deposition}} \text{BaTiO}_3\text{(s)}$$

BaTiO$_3$ is selected for its high applicability as an electroceramic, e.g. as lead-free piezoelectrics [27], capacitors [28] or high dielectric permittivity materials [25], and the recent growing interest in additive manufacturing of barium titanate [6,29–31]. Shape control is often crucial for such electroceramics, e.g. for ultrasound transducers the desired shape can vary from 2D structures [32] to annular [33] or fractal [34] configurations or curved surfaces for focusing the ultrasound [35].

Wet chemical synthesis of BaTiO$_3$ is often performed by a Pechini-based route with organic solvents [36–38], e.g. using ethylene glycol, citric acid, barium nitrate and titanium isopropoxide. An aqueous route was also recently developed [39]. Barium and titanium ions are found to be simultaneously stabilized with a 1:1 ratio as in the target compound BaTiO$_3$ [37]. Formation of intermediate carbonates, i.e. BaCO$_3$ has also been said to avoided, and BaTiO$_3$ free from BaCO$_3$ and TiO$_2$ can be obtained after curing in air at 500 °C for 8 h or at 600 °C for 2 h [37]. Typical sintering temperatures of BaTiO$_3$ powders are between 1200-1460 °C [40]. To our knowledge, no studies describe the formulation, characterization, and fabrication of BaTiO$_3$ hybrid sol-gel inks for robocasting. Here, we describe the preparation process of such ink and characterize the resulting object obtained after robocasting.

2. Experimental

2.1. Ink preparation

The hybrid ink preparation protocol was based on our earlier work described in Ref. [41]. A flow chart of the synthesis process is shown in Fig. 1. The chemicals stated below were mixed at room temperature in a glass bottle sealed with a silicon cork previously filled with Argon for 5 min to avoid uncontrolled reactions (i.e. hydrolysis and condensation) between air humidity and the metal precursor. Titanium (IV) isopropoxide (Ti(OPr)$_4$ (hereafter TTIP, Sigma-Aldrich)) and N-methyl-diethanolamine (hereafter MDEA, Sigma-Aldrich) were added in the argon-filled bottle using sterile syringes and mixed for 5 min. Barium oxide (Sigma Aldrich, 99.99%, <500 nm particle size) was added in the ink in stoichiometric proportions to obtain the desired composition.

![Fig. 1. Flow chart for the synthesis of the hybrid inks: (a) without glycerol and additional solid loading and (b) with glycerol and/or additional solid loading.](image-url)
BaTiO$_3$ and the mixture was stirred for 5 min to form a gel. The concentration of Ti$^{4+}$ in solution was 0.35 mol/l. The concentration of Ba$^{2+}$ in BaO was 0.04 mol/l. In order to study the influence of the solid loading on the hybrid ink properties, commercial BaTiO$_3$ powder (Sigma Aldrich, 99.5%, 1.3 µm particle size) was added to the ink preparation protocol. These inks are named “HI_G-BaTiO$_3$” (Fig. 1b).

2.2. Ink characterization

We investigated the rheological properties of the inks along with a commercial, water-based hydrogel without any solid loading (CELLINK© START), optimized for our robocaster. The measurements were done using an Anton Paar rheometer (MCR 302) in rotational mode and at a constant temperature of 21 °C. A plate-plate measuring system was used with a diameter of 25 mm (PP25) and at gap distance of 0.4 mm under a solvent trap. The experiments were performed using three steps of pre-treatment: the first one at 0.1 s$^{-1}$ for 1 min followed by 1 min at rest (0 s$^{-1}$ shear rate), and the third one at 1 s$^{-1}$ for 1 min. Flow curve measurements were conducted in step mode using 60 steps with a waiting time of 10 s. The shear rates investigated the range from 0.1 s$^{-1}$ up to 1000 s$^{-1}$, in the up-ramp, and from 1000 s$^{-1}$ to 0.1 s$^{-1}$ in the down-ramp.

Crystallographic phase identification was performed at room temperature using a monochromatic Cu-Ka radiation X-ray diffractometer (XRD: Bruker D8 Robot Tools X-ray diffraction, Bruker, Germany, and Rigaku Miniflex, Rigaku, Japan).

2.3. Robocasting

Cylindrical objects (height: 10 mm, diameter: 6 mm) with a curved top surface were designed with a CAD software (Solidworks) and printed with Bio X printer (Cellink AB, Sweden) at room temperature. Inks were first loaded into a 3 ml syringe and placed into the syringe holder of the robocaster. The ink was extruded through 22G nozzles (inner diameter: 0.410 mm) onto an alumina substrate in a layer-by-layer fashion. The extrusion speed was set at 5 mm/s, pressure at 40 kPa and infill density at 90%.

2.4. Thermal treatment and sintered sample characterization

The printed samples were transferred after drying to a platinum substrate for binder burnout and sintering. This was performed in stagnant air with a heating rate of 10 °C/h up to 300 °C, a 2 h isothermal hold, and heating at a rate of 60 °C/h to 1250–1350 °C, a 20 h isothermal hold, and finally cooling to room temperature at a rate of 200 °C/h.

The density of the sintered samples was measured by the Archimedes method in isopropanol. Scanning electron microscopy (SEM) was conducted on the as-sintered sample surface with a Hitachi TM3000 (Hitachi High-Technologies Europe GmbH, Germany).

X-ray micro computer tomography (µCT) scans were conducted using a lab-based Nikon XTH 225 instrument using a W reflection target. Scans were performed at a voltage of 210 kV, a power of 20 W, 1 mm Sn filter, detector binning 1, an exposure time of 4 s, 4 projections per angle and a total of 3142 projections over a 360° rotation, resulting in a pixel resolution between 4.6 and 5.3 µm. The recorded data was reconstructed using Feldkamp-Davis-Kress reconstruction algorithm with recon. The segmentation was challenging due to contrast variations and was carried out by using the commercial software Avizo in the following way. Filtering with three filters in this order: a median filter in 3D kernel size 3, neighborhood 18, Non-local means default settings, SNR default settings. Segmentation was carried out by using the local threshold tool for connected voxel called Magic wand with contrast setting = 3 to identify the bulk. Cracks and voids were manually segmented with the same tool and contrast setting. Islands were removed with default settings.

Ag paste (LVOC, SPI, West Chester, PA, USA) was used to apply electrodes prior to electrical characterization. The paste was painted on the top and bottom surfaces of the cylinder (~10 mm height, 6 mm diameter) with a fine brush and left to dry for a few hours. A multimeter was used to check that the electrode was conductive after drying. Polarization and strain vs. electrical field were measured at room temperature with a piezoelectric evaluation system (aixPES, aixACCT, Aachen, Germany) at a frequency of 1 Hz. The piezoelectric charge coefficient ($d_{33}$) was measured with a Berlincourt meter (APC International Ltd., Mackeyville, PA, USA).

3. Results and discussion

3.1. Ink properties and printing

Fig. 2 shows the rheological behaviour of the commercial, particle-free gel (CELLINK © START) optimized for robocasting. The ink exhibits relatively high yield stress (around 150 Pa), which means the ink does not flow at pressures lower than this value, and a shear-thinning behaviour illustrated by the shape of the flow curve.

The measurement protocol applied to the gel was also applied to the fabricated hybrid inks (HI) to observe their rheological behaviour relative to the commercial system. Fig. 2 shows the resulting rheological behaviour of the ink and indicates a rapid increase and decrease of shear stress in the low shear rate region (peak), followed by a linear increase of shear stress in the ramp-up stage. No peak is observed in the ramp-down phase. This sudden increase in shear stress, and hence in viscosity, is generally explained by the presence of poorly dispersed particles in the ink [42]. When such ink is subject to strain such as a flow curve test, particles rearrange at the low shear rate (an increase of viscosity) and, once mixed, normal flow is resumed. The presence of particles in the HI ink is believed to be Ba(OH)$_2$ mixed with some remaining BaO due to rapid precipitation between barium oxide particles and the titanium isopropoxide. Similar behaviour was observed on mixtures of titanium-based compounds with barium salts in alkaline pH, similarly to our case [43]. This precipitate formation leads to a non-suitable rheological behaviour for robocasting and has to be controlled.

A method to avoid fast precipitation is to add a glycol-based solvent to the Ti-based solution to form an intermediate phase such as titanium glycolate or glyceroilate, depending on the used glycol [43]. In this work, we changed the solvent from pure water to a glycrol/water mixture (respectively 40/60 vol%) to see the effect of glycrol on the precipitation. The rheological behaviour of this ink, named HI_G (red line in Fig. 2) corresponds to a Newtonian one, illustrated by the linear relationship between shear stress and shear rate. This behaviour confirms that the precipitation was hindered by the glycrol addition. However, the ink rheology is still not suitable for robocasting in this state, as the ink has neither a yield stress nor shear thinning behaviour.
Another aspect to consider in the development of solid objects by robocasting is the solid loading in the ink. Crack-free and dense ceramics are obtained by minimizing the shrinkage due to various thermal treatments. Thus ceramic inks are formulated with a high solid loading that will allow a suitable particle percolation to reduce this shrinkage [43]. In the case of our ink, the amount of BaO is intimately linked to the concentration of titanium cations to keep a 1:1 stoichiometry between the cations, necessary to yield the desired BaTiO3. As such, the highest solid loading achievable in this process is 8 vol%, which is too low to obtain a 3D object with sufficient mechanical stability. In order to increase the solid loading and obtain a more suitable rheological behaviour, commercial BaTiO3 powder was added to the ink after the BaO addition (described in Fig. 1). Fig. 3 shows the rheological behaviour of three inks, named HI_G-BaTiO3, loaded with different amounts of commercial BaTiO3.

Fig. 3 shows that the ink viscosity increases with the solid loading and that all inks exhibit a Herschel-Buckley behaviour with different features. The inks with 30 and 35 vol% have a relatively weak shear thinning behaviour, while the ink with 40 vol% has a shear thickening behaviour. Moreover, the 40 vol% ink shows a “bump” in the ramp-up phase of the measurement that can be attributed to a non-optimal dispersion of the powder at high solid loading. The measurement was repeated on three different 40 vol% ink iterations (curves (a)–(c) on Fig. 3), and all showed similar behaviour. This significant rise of viscosity and rheological behaviour is commonly seen in powder-based inks with high solid loadings [42]. At low particle concentration (30 and 35 vol%), the suspension rheological behaviour is close to the carrier fluid rheological behaviour, i.e. the liquid phase part (sample HI in Fig. 2). As solid loading gradually increases, the suspension properties deviate from this behaviour as particle/particle interactions become greater and eventually dominate at a solid loading threshold. This effect would result not only in an increase of viscosity, but also in a change of rheological behaviour from Newtonian/quasi-Newtonian to shear thickening, which corresponds to the observation made in our case.

Another noticeable difference between the inks is their yield stress. The inks with 30 and 35 vol% show very low yield stress, while the ink with 40 vol% has a much higher yield stress. It is noticeable that the yield stress increases drastically between 35 and 40 vol%, while the difference is minimal between 30 and 35 vol%. These observations show that the yield stress is strongly correlated to the solid loading of the ink. In addition, to affect the printability of the ink, this parameter has another critical influence on the final printed object. During printing, the printing can be subject to shape deformation due to its weight by gravitational forces. This slumping occurs if the yield stress is not sufficiently high. Notably, the yield stress is correlated to the maximum printable height of the object, i.e. the highest achievable height before slumping starts. Equation (1) gives an estimation of the maximum printable height $h_{\text{max}}$.

$$h_{\text{max}} = \frac{\sigma_{\text{Dyn}}^{\text{rms}}}{\rho g}$$

where $\sigma_{\text{Dyn}}^{\text{rms}}$ is the dynamic yield stress (Pa), $\rho$ the density (kg.m$^{-3}$), and $g$ the gravitational acceleration ($g = 9.81 \text{ m s}^{-2}$) [17]. Table 1 reports the ink yield stress measured using Equation (3) together with the maximum printable height. Based on these results, only the 40 vol% ink was further characterized.

The phase composition of the hybrid ink was carried out by XRD. Fig. 4 shows that the ink forms the target BaTiO3 phase (tetragonal perovskite, space group P4mm) after thermal treatment at 850 °C and sintering at 1350 °C. This structure is also retained after sintering, without the formation of any significant secondary phases. The high background intensity, peaking around 20 ° 2θ is from the plasticine used to hold the sintered sample.

A cylinder (10 mm high, 6 mm diameter) with a curved top surface, imitating the shape of a focusing transducer [35], was printed using the 40 vol% ink. The cylinder was dried at room temperature for 24 h before sintering. Fig. 5 shows images of the sample as printed and after drying. Fig. 5a) shows that the printed object differ slightly from the programmed dimensions: the cylinder is wider at the bottom, narrower on the top, and shorter than the programmed, meaning that the object slumps slightly during printing. This effect can be due to either a slightly insufficient yield stress compared to the height of the printed item, which is close to the theoretical maximum value predicted in Table 1 or not

![Fig. 3. Flow curve of the HI_G-BaTiO3 with solid loadings of 30, 35, and 40 vol %, the latter measurement being repeated 3 times (a, b, and c). The upper part of each curve is always ramping up in shear rate. Inset shows ramp down curves at low shear rates.](image)

![Fig. 4. XRD of BaTiO3 commercial powder and the hybrid ink HI_G-BaTiO3, both after calcination at 850 °C and sintering at 1350 °C.](image)

| Solid loading | Yield stress | Estimated maximum height |
|---------------|--------------|--------------------------|
| %            | Pa           | mm                       |
| 30            | 10           | 0.7                      |
| 35            | 32           | 2.4                      |
| 40            | 198          | 14.4                     |

Table 1

Measured yield stress and estimated maximum printable height for different ink solid loadings. The value for 40% is an average of the 3 performed measurements.
Fig. 5. Photographs of the printed sample (a) as printed, (b) after drying for 24 h, and (c) after drying, top view.

Fig. 6. SEM observations of the surface of the robocast BaTiO₃ after sintering at a) 1250 °C, and b) 1350 °C.

Fig. 7. Tomography results of BaTiO₃ printed with hybrid ink after sintering at 1250 °C (top row, images a-d) and 1350 °C (bottom row, images e-h). Figures a,e) show a central 2D vertical tomographic slice of the sample, while the cracks and pores from the entire sample volume are illustrated with 3D renderings in Figures (b,f) and (c,g), respectively. Figures (d,h) show the size distribution of the pores based on the segmentation of the CT data shown in Figures (b,f).
optimal printing parameters. However, measurements made after drying (Fig. 5a-b) are similar, showing that the sample does not undergo more slumping during drying.

3.2. Sintering and functional properties

No defects from binder burnout were visible on the surface after sintering by applying low heating rate. Some defects at the bottom of the sample due to sticking to the substrate were introduced when the sample was transferred to the Pt substrate for sintering. The microstructure of the surface after sintering at 1250 °C is shown in Fig. 6a. The grains are rounded and relatively uniform in size (≈2 μm), and some pores (0.5–2 μm) are present. These pores are assumed to be related to limited densification at this sintering temperature, rather than being introduced during printing. The density measured by the Archimedes method is 94%.

The sintering temperature was then increased to 1350 °C to improve the densification of the sample. The resulting microstructure is shown in Fig. 6b. The increased sintering temperature promoted both grain growth up to ≈100 μm and densification. The smaller pores related to limited densification have mostly disappeared. The darker phase visible mainly at the grain boundaries are Si impurities, most likely contamination from the furnace deposited on the sample surface during sintering. The density measured by Archimedes method increased from 94% at 1250 °C to 96% after sintering at 1350 °C.

We used X-ray tomography to study the internal structure of the BaTiO3 samples. As shown in Fig. 7, the samples contain pores (voids) rendered in blue in b) and f) and some cracks visualized in green in c) and g), but there are no large print-related defects associated with the print lines or infill pattern during printing. The pores are isometric and homogeneously distributed throughout the volume. Note the renderings in b) and f) are projection images throughout the entire volumes exaggerating the appearance of the number of pores. From the pore size distributions in c) and g), we can see that while there are a few pores above 200 μm (in equivalent spherical diameter), most pores are in size range 20–100 μm. These pores are likely from air bubbles in the hybrid ink that were introduced during preparation. Since the spatial resolution in the x-ray tomograms is approximately three times the voxel size (4.6 and 5.3 μm, in samples sintered at 1350 and 1250 °C, respectively), pores smaller than this (14 and 16 μm) are not segmentable from the image data and they are not included in the histograms. This lower threshold explains why the sample sintered at 1350 °C appears more porous than at 1250 °C as the sub-resolution pores are not visible in Fig. 7. Still, such smaller pores are likely also present to some extent, as evident from the SEM image in Fig. 6, but most likely originate from lack of densification rather than defects during printing.

The crack features observed in Fig. 7c) and g) are defects that appear to be associated with sintering, which in the present case appear to be more severe with the higher sintering temperature. The majority of cracks after sintering at 1350 °C are aligned parallel with the vertical axis and lie approximately 1 mm from the outer surface. The volume of cracks is very low in both samples; 0.004% and 0.034% of the total sample volume after sintering at 1250 and 1350 °C, respectively.

We calculated the density of the samples from the volume(s) obtained by the tomographic reconstructions. Using the volume of pores and cracks relative to the volume of the entire sample results in very high densities; 99.6 and 99.1% for samples sintered at 1250 and 1350 °C, respectively. These high calculated densities reflect the large volume of pores present below the pore segmentation thresholds and therefore not accounted for here. Using the mass of the samples divided by the volume of the entire samples (from the tomographic reconstruction), we obtain densities of 92% after sintering at 1250 °C and 93% after 1350 °C. These values correspond reasonably well with the 94% and 96%, respectively, measured by the Archimedes method. Compared with the high density values (99.6 and 99.1%) calculated by the segmented pore and crack volumes, they also demonstrate that the major part of the pore volume comes from pores of size below 14 and 16 μm.

Fig. 8 shows the ferroelectric and piezoelectric properties of BaTiO3 hybrid ink robocast and sintered at 1350 °C. The polarization-electric field hysteresis loop is well developed, with a coercive field of 0.1 kV/mm, a remanent polarization of 5.4 μC/cm² and saturated polarization of 8.5 μC/cm² (Fig. 8a). From the initial, small-signal polarization-electric field loop with a maximum voltage amplitude of 3 V, we estimated the relative dielectric permittivity to 1900. Ferroelectricity is also apparent from the switching current peaks at ±0.1 kV/mm (Fig. 8b). The sample did not display significant leakage current or signs of imminent dielectric breakdown. The strain-electric field loop shows the typical butterfly shape of ferroelectric materials, highly symmetric and with a maximum strain of 0.02% at ±0.5 kV/mm. Field-induced strain, often denoted d33+ or Smax/Fmax was 430 p.m./V at 0.5 kV/mm (average of 10 unipolar measurements). The direct piezoelectric effect measured on a Berlincourt meter showed a piezoelectric charge coefficient, d33, of 159 pC/N.

The piezo-, ferro- and dielectric properties of our print are all in the range of typically reported values for conventionally shaped [40,44] and 3D-printed [6] BaTiO3. This is notable considering the defects illustrated in Fig. 7 both in terms of the porosity and the large planar cracks. In this case it appears for the electrical properties, vertically aligned near surface cracks do not have a catastrophic effect. The measured properties show that despite the near conventional values attained, there is still opportunity for further optimization of ink preparation, robocasting and sintering procedures with respect to the internal structure of printed objects.

This work demonstrates the concept of hybrid inks for robocasting of undoped BaTiO3, where BaTiO3 is both the base of the hybrid ink and the additional ceramic powder. In addition to preparation of undoped BaTiO3, this system could easily be modified for robocasting of other piezo-, ferro- and dielectric ceramics of BaTiO3 with dopants or in solid solutions, e.g. (1-x)BaZrO2-xTiO2-x/3K2O/3Ta2O5 [45], BaTiO3–K0.5Na0.5 NbO3–Bi0.5Na0.5 TiO3 [46], or BaTiO3–BiFeO3 [47] etc., just by replacing the additional ceramic powder. The BaTiO3 from the hybrid ink is also expected to be adjustable to other titanates, e.g. PbTiO3, Bi0.5Na0.5TiO3, BixTi3O12 already demonstrated in hybrid inks for inkjet printing [41].
4. Conclusions

Hybrid inks containing both solid loading and reactive metalorganic molecules were successfully developed for robocasting of BaTiO3-based ceramicomers. The water-based hybrid inks combine a BaTiO3 sol-gel part, made by reaction of Ti-isopropanol and BaO, and a BaTiO3 colloidal part consisting of commercial BaTiO3 powder. Addition of glycerol was helpful to both increase the shear-thinning rheological behaviour required for robocasting and to avoid fast precipitation of the sol-gel BaTiO3. Solid loadings of 40 vol% were achievable in the hybrid ink, thus enabling printing of self-supporting 10 mm tall cylinders with a curved top surface without significant slumping after drying or print-related defects after binder burnout and sintering. A density of 96% and piezoelectric charge coefficient (d33) of 159 pC/N was obtained after sintering at 1350 °C, in line with previous reports on BaTiO3, demonstrating the applicability of the hybrid inks for robocasting of BaTiO3-based ceramicomers of complex shape.

Declaration of interests

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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