



Article

The Influence of Printing Parameters, Post-Processing, and Testing Conditions on the Properties of Binder Jetting Additive Manufactured Functional Ceramics

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Abstract: This article outlines the current state-of-the-art binder jetting (BJT) additive manufacturing of functional ceramics. The impact of printing parameters, heat treatment processing, and testing conditions on the observed performance of these ceramics is discussed. Additionally, this article discusses the impact of physical properties such as density and mechanical strength on the overall performance of these functional ceramics. Although printing parameters and initial feedstock are crucial for the printability of the desired parts, other factors play an important role in the performance of the ceramic. Thermal post-processing is crucial to achieve optimized functional properties, while the testing orientation is key to obtaining the maximum output from the part. Finally, future research directions for this field are also discussed.

Keywords: functional ceramics; binder jetting printing; additive manufacturing; ceramics

1. Introduction

Functional ceramics represent a class of materials that exhibit characteristic properties, in addition to those inherent to ceramics, such as chemical and thermal stability. Functional ceramics usually exhibit one or more unique properties in the biologic, elastic, electric, magnetic, or chemical regimes [1]. Among the most prominent type of functional ceramics are piezoelectric ceramics [2]. Piezoelectric ceramics are used for different applications such as sensors [3], energy harvesters [4], and actuators [5]. Other types of functional ceramics include those that are magnetic, such as magnetite [6], or hydroxyapatite, for its high compatibility in biological and biomedical applications [7], as well as those with electrochemical applications, such as titanium dioxide [8] and zirconium dioxide [9].

Ceramics in general are the most challenging materials to fabricate due to their brittle nature [10]. Functional ceramics exhibit the same challenges regarding their fabrication. The conventional route to fabricate bulk ceramics is rather rudimentary [11]. Firstly, the raw ceramic powder is mixed with a liquid medium to create a slurry. This slurry is then cast or pressed to create the desired shape. Finally, the fabricated part is heat-treated to remove the medium used to create the slurry, as well as consolidate and densify the ceramic part. This fabrication process greatly limits the geometries that can be manufactured using ceramics. In addition to the limited geometric freedom during fabrication, post-fabrication following heat treatment presents the same problem considering that it is extremely difficult to modify their geometry through machining or other subtractive manufacturing techniques. This geometry limitation due to the fabrication process was a topic of interest for years. The most promising technique to mitigate and alleviate this challenge is additive manufacturing (AM) [12].

Additive manufacturing of three-dimensional ceramics was explored using the techniques of paste extrusion (PE) [13], fused deposition modeling (FDM) [14], stereolithography (SLA) [15], and binder jetting (BJT) [16]. Parts produced through PE usually have high densities at the expense of lower resolutions. Parts fabricated using FDM have better resolution than PE parts, but the fabricated part is a polymer–ceramic composite. Resolution from SLA is the best of any additive manufacturing technology, but ceramic parts fabricated using this method have the lowest densities. BJT-printed ceramic parts have resolutions closer to those observed in SLA parts, but with much higher densities. BJT selectively deposits a liquid binder onto a powder bed of selected raw material using an inkjet printhead in a layer-by-layer fashion. The selectively deposited binder is then cured using heat to strengthen the fabricated part. After a de-powdering process, the BJT part is subjected to a further heat treatment process to densify the ceramic. A schematic depicting binder jetting 3D printing technology is provided in Figure 1.

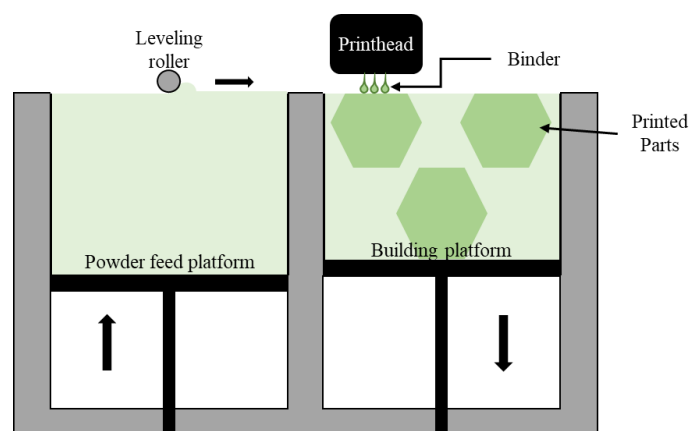


Figure 1. Schematic showing the working mechanism of binder jetting (BJT) additive manufacturing.

As discussed, the implementation of additive manufacturing for the fabrication of functional ceramic structures will eliminate the geometry limitations from conventional fabrication methods. Extensive research efforts were made in recent years to design and demonstrate the viability of using a rational design of geometries to tune the properties of different structures [17–20]. Both metamaterials and nature-inspired designs were demonstrated to have the potential to create highly efficient smart structures. These structures can be tailored to fulfill specific applications within a system by customizing its geometry. Having the ability to implement materials with multiple functionalities, such as in the case of functional ceramics, will further elevate and expand the possibilities of smart material systems for a wide range of applications.

Due to factors to be discussed in later sections, BJT was not proven to be successful in printing fully dense ceramics. For structural ceramics, low densities are perceived as a downside of the technology. However, the performance of functional ceramics is not only assessed by their density or strength, but also by their efficiency and overall functionality in specific applications. It was proven that material systems that incorporate functional ceramics benefit from designed porosity, as well as the increased surface area provided by lower-density structures. Therefore, BJT is a great candidate for the fabrication of highly efficient material systems where functional ceramics are utilized. In this manuscript, we discuss the impact of printing parameters, processing techniques, and testing conditions on the overall performance of functional ceramics fabricated using BJT additive manufacturing.

2. Printing Parameters

Parameters that affect the printability of functional ceramics are virtually the same as those that affect the printability of BJT ceramics. The parameters that were studied and how they affect the properties of structural and functional ceramics are discussed in this section.

2.1. Raw Materials

The most important element to determine the properties of additively manufactured materials is the feedstock. In the case of BJT, the feedstock comprises two materials: the feed powder and the jetted polymeric binder.

2.1.1. Powder

The particle shape, size, and particle size distribution of the ceramic powder have a crucial role in the ability to three-dimensionally (3D) print the desired material, as well as the physical properties of the green body and sintered parts. The main properties affected by the powder selection are flowability, particle packing ratio, green body density, and potential sinterability of the finalized ceramic part.

Particle Size

The particle size of the powder employed was shown to have an impact on the properties of sintered ceramic bodies fabricated using BJT [21]. Bigger particles tend to have better flowability and are safer to operate than smaller particles [22]. Conversely, small particles exhibit better sinterability, as well as overall better functional properties [23].

Particle Shape

Particle shape was shown to have a strong influence on the flowability of the powder, as well as on the sinterability of the powder due to the number of contact points that each geometry offers [22,24]. This second point is discussed to a greater length in the next section.

Particle Size Distribution

Particle size distribution was demonstrated to have a considerable impact on the green body density of 3D-printed materials [21,25]. Multimodal particle size was shown to increase the density of BJT-printed ceramic and metallic parts. This increase was observed in both green body and sintered bodies, and it is attributed to smaller particles filling the voids left in between particles.

2.1.2. Binder

Powder–binder interaction is crucial to achieving better printability, as well as better properties in the printed parts. Despite the importance of the binder in the overall process, binder selection is very narrow due to compatibility with the commercial BJT equipment. Alternatively, infiltration of the 3D-printed parts with a secondary binder was proposed in the past to mitigate distortion of the part through filling the pores with functional ceramic precursors, thereby increasing the number of contact points between ceramics [26]. This infiltration process was demonstrated to enhance the shape retention of the fabricated ceramic after sintering, further validating the importance of binder in the performance of functional ceramics. Binders and binder chemistry must be tuned to accommodate and complement the behavior of ceramics to a similar extent to what was done with metals.

2.2. Printing Parameters

The quality of the printed ceramics is also greatly influenced by the printing parameters. Properties from the powder that affect the printability, such as poor powder packing ratio or low flowability, can be alleviated by the printing parameters. Additionally, ceramics have significantly different wettability, and this will also greatly influence their print quality. A key factor to control the amount of binder dispensed to the ceramic is the saturation level input in the printing parameters.

2.2.1. Layer Height

A key parameter for the quality of any BJT print is the layer height selected. This parameter controls the resolution of the print in the z-direction, but it also is dependent on the size of the powder used for the print. Common values for the layer height are, as a minimum, three times the max particle size present in the print, although this will vary based on the flowability of the feedstock powder. Intuitively, layer height should not be smaller than the feedstock powder.

2.2.2. Feed-to-Build Ratio

The feed-to-build ratio is a common parameter modified depending on the powder being used. This parameter controls the height of powder taken from the feed to be used for the build. As an example, a feed-to-build ratio of 2.0 set up to a BJT print would deposit a feed layer of twice the height from the height of the build. Feed-to-build ratio aids in improving the powder packing in the build side by pushing a higher amount of material than what is required by the print. This higher powder packing allows for higher green body densities, further contributing to better quality of the finalized product.

2.2.3. Saturation Level

Saturation was shown to impact the properties of BJT fabricated ceramics, especially in their green body form. Saturation is defined as the volume of binder jetted into the sample as a function of the empty space available due to packing. A volume of binder jetted equal to this empty space would represent a saturation level of 100%. At extremely low saturation levels, green bodies are not strong enough as there is not enough binder to keep the part together. In contrast, extremely high saturation levels yield distorted parts due to over-wetting and not enough curing during the layer stacking.

In this manuscript, we study the impact of saturation on the properties of BJT-printed functional ceramics. BaTiO_3 samples were fabricated with different saturation levels and then sintered under identical conditions. The green body and sintered body densities were studied as a function of the saturation level. The results from this study are shown in Figure 2. It was observed that green body density increased as binder saturation increased. This behavior is expected as a higher amount of polymer is being introduced in each layer. Conversely, the sintered density was found to initially increase as higher saturation was introduced; however, this density peaked at around 145% and 205% saturation. The initial increase in density is attributed to a higher green body density, aiding in the formation of higher-density sintered parts. However, as higher saturations are introduced, the excess binder “pushes” the particles from the feedstock powder apart, inhibiting the densification of the sintered parts.

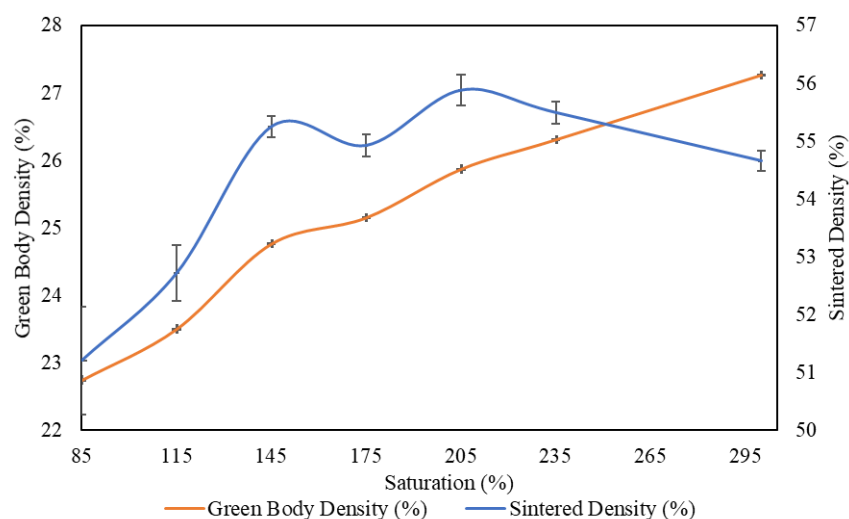


Figure 2. Binder saturation influence in green body and sintered density of BJT-printed BaTiO_3 functional ceramics.

Additionally, the impact of saturation level on mechanical properties was studied. As shown in Figure 3, it was found that higher saturations yield better mechanical properties. This phenomenon must be further studied, and other saturation levels must be evaluated to determine the optimal parameters for this ceramic, as well as the correlation between this parameter and the overall properties of the printed ceramics. The increase in mechanical properties should have an impact on other functional properties such as piezoelectricity.

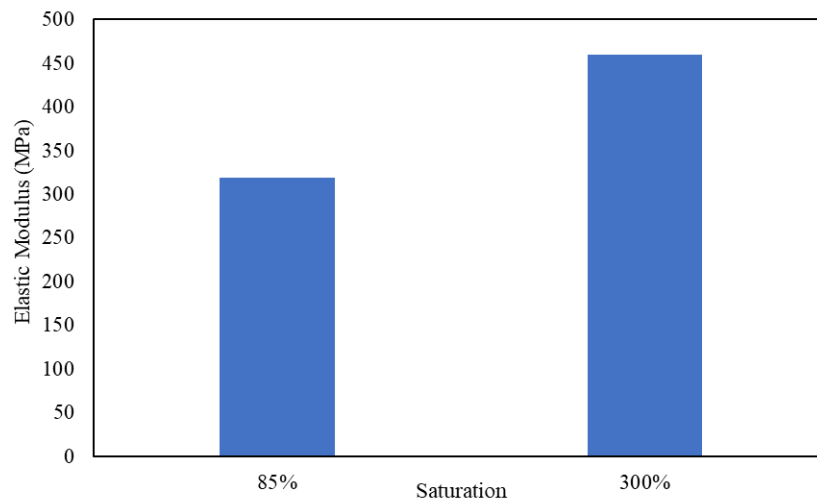


Figure 3. Influence of binder saturation on sintered strength of functional ceramics.

2.3. Impact of Printing Parameters on Functional Properties

The main factors and properties assessed to determine the optimal level of the described parameters were the packing ratio of the powder and the green body density. It is a common misconception in the literature that higher green body densities yield denser sintered parts. However, we demonstrated that this is not always the case. Additionally, density is not a good parameter to assess the performance of functional ceramics. As discussed in the next two sections, the microstructure and testing conditions are fundamental factors for the optimal operation and performance of additively manufactured functional ceramics.

3. Post-Processing Conditions

The key process to obtain the final 3D-printed ceramic structure is the heat treatment phase. During this process, the 3D-printed structure is densified, and its final dimensions are achieved. This process dictates key bulk physical properties of the ceramic such as density and strength [27]. In the case of functional ceramics, the heat treatment process is even more relevant as it also rules the functional ceramic performance due to the close relationship between the microstructure and functional properties [28,29]. Heat treatment processes influence microstructure properties such as grain size, grain boundary, and porosity of the sample [30], all of which are closely linked to the performance of functional ceramics.

A common heat treatment process for BJT-printed ceramics is shown in Figure 4 [31]. The heat treatment performed on ceramics fabricated using BJT usually consists of a curing process, in which the green body is subjected to temperature around 200 °C to strengthen the polymer. Once the curing process is completed, the sample is transported to a high-temperature furnace. In this furnace, the printed sample is subject to a binder burnout stage, during which the polymeric binder is removed from the sample. After the binder burnout stage, the sample is subject to a sintering stage, during which the ceramic is densified by subjecting it to high temperatures.

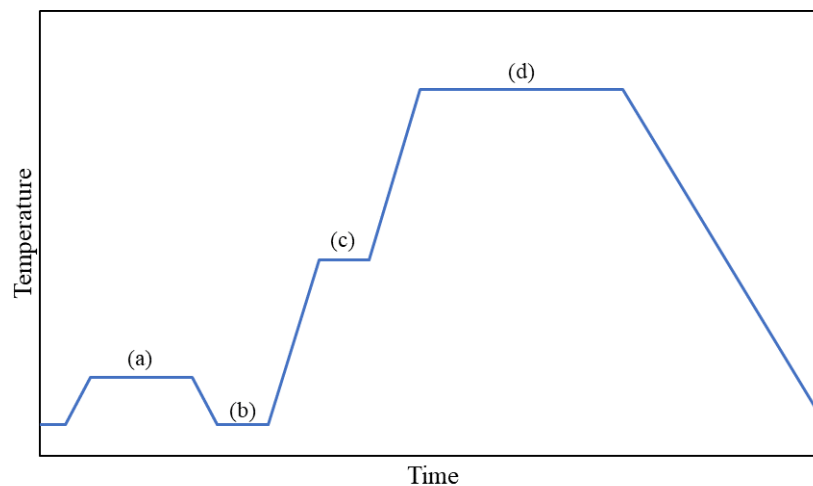


Figure 4. Common sintering profile of BJT-printed ceramics including (a) binder curing stage, (b) cool-down and sample transfer, (c) binder burn-out stage, and (d) sintering stage.

While all these steps are important to achieve a functional ceramic part with good properties, the sintering stage is the main contributor to the microstructure of the material and, therefore, to its functional performance. The significance of the microstructure of ceramics in their functional properties is discussed in this section. Additionally, factors that contribute during the sintering stage to dictate this microstructure properties are discussed.

3.1. Grain Size

3.1.1. Impact

Ferroelectric and ferromagnetic materials only exhibit these properties when they are in specific phases. In order to achieve these phases, the size of their grains should be above the critical domain dimension [32]. This critical domain dimension is dependent on the specific material being studied. The functional properties of ceramics are also influenced by the grain size even above this critical domain size. It was shown that piezoelectric properties are enhanced as grain size decreases, provided that this decrease is not past the previously mentioned critical domain [33]. Similarly, magnetic properties can be enhanced when the grain size decreases [34]. Therefore, the sintering process must be tuned for each functional ceramic, based on the initial particle size and the critical dimension required to achieve the desired functional properties.

Contributing Factors

The most practical factors to control during the fabrication and sintering of functional ceramics using BJT are particle size, sintering temperature, and sintering time.

Particle Size

The particle size utilized generally dictates the minimum grain size observed in the final part [35]. These particles coalesce and grow to form grains during the sintering; therefore, utilizing big particles from the start will yield poor to mediocre functional properties in the final part.

Sintering Temperature

Grain growth is required to achieve optimal density and is directly linked to sintering temperature. Grain growth is achieved through two main routes: grain coarsening and grain coalescence [36]. Grain coarsening refers to the growth of the individual particles when subject to high temperatures, while coalescence is related to mass diffusion of the particles through grain boundaries. The relationship between grain coarsening and temperature is expressed in the following equation [37]:

$$G^n - G_0^n = K_0 t \exp\left(-\frac{Q}{RT}\right),$$

where G is the average grain size at a given time, G_0 is the initial grain size, n is the kinetic grain growth exponent usually equal to 3, K_0 is the preexponential constant, Q is the apparent activation energy for grain growth of the specific material, R is the gas constant, and T is the absolute temperature during sintering.

From this equation, it can be observed that the sintering temperature plays a key role in determining the average grain size of the sintered ceramic. Therefore, sintering temperature is crucial in obtaining the optimal functional properties due to its impact on the microstructure of the ceramic.

Sintering Time

Equally as important to the microstructure of the finished sample is the sintering time. While sintering temperature determines the growth rate of the grain, the sintering time determines the final size of the grain. As is the case with sintering temperature, sintering time must be tuned and designed for the material being BJT-printed.

3.2. Grain Boundary

3.2.1. Impact

Grain boundaries were shown to lower the piezoelectric properties of functional ceramics due to a drop in the ferroelectric domain density [38]. Therefore, grain boundary concentration must be minimized.

3.2.2. Contributing Factors

At the high temperatures required for the sintering of ceramics, the different elements in the crystal structure segregate and precipitate in the grain boundaries. In the case of ABO₃-type functional ceramics, oxygen can be removed from the crystal structure and moved on to vacancies. Due to this mobility of oxygen, sintering in an oxygen atmosphere is beneficial to obtaining high-density ceramics [1].

The impact of sintering conditions in the functional properties of BJT printed ceramics was addressed in recent years [39]. A clear correlation in the piezoelectric and dielectric sensing capabilities of BaTiO₃ and the sintering temperature was observed, as shown in Figures 5 and 6. A linear increase in the dielectric properties was observed as the sintering temperature increased for the same sintering time. Additionally, the d_{33} piezoelectric coefficient of the printed ceramic was linearly influenced by the sintering temperature. Furthermore, a notable increase in density at higher sintering temperature was observed. Despite the clear trend observed for all of these properties as temperature was increased, it is still not clear if the higher dielectric and piezoelectric properties were due to an increase in density or to a change in the relevant microstructural properties of the printed ceramic. Recent studies showed that high piezoelectric properties can be attained in BJT-printed ceramics with much lower densities [31].

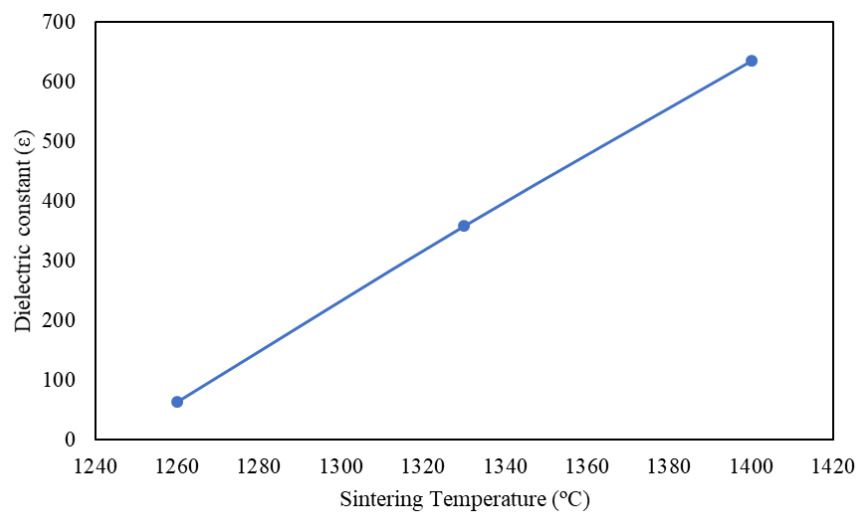


Figure 5. Sintering temperature impact in dielectric properties of BJT-printed BaTiO₃ [39].

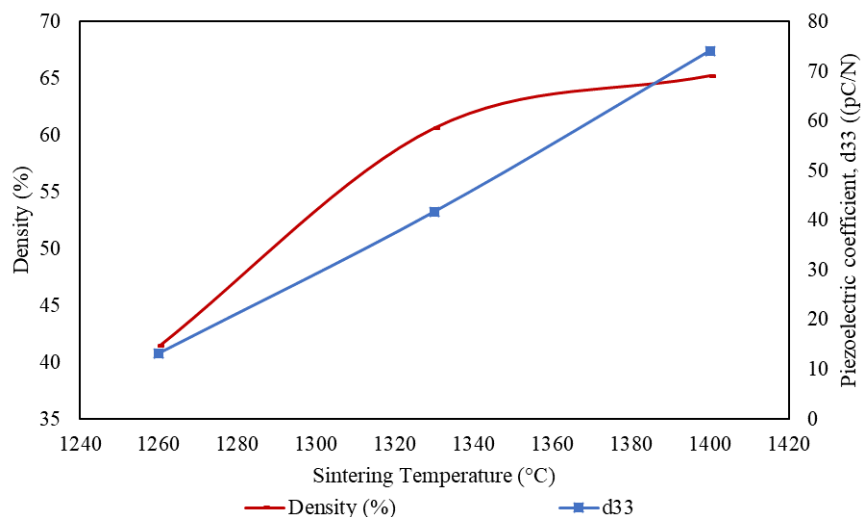


Figure 6. Sintering temperature impact on density and piezoelectric properties of BJT-printed BaTiO₃ [39].

4. Testing Conditions

Ceramics fabricated using BJT tend to be highly orthotropic [40]. This is due to the voids formed throughout the ceramic during the fabrication and heat treatment processes. Some examples of the porosity of different BJT printed ceramics are shown in Figures 7 and 8. Although pores are formed throughout the sample, they are expected to be present to a higher extent with greater coordination between the printing layers. These porous arrays have an impact on the properties of the printed ceramics. The dependence on the loading direction was characterized for properties such as mechanical strength [40]. However, very little research was dedicated to studying the impact of the testing orientation on the functional properties of 3D-printed ceramics.

Recently, it was reported that the piezoelectric properties of BJT-printed functional ceramics is dependent on the testing orientation [31]. Samples in which the piezoelectric characterization was performed normally to the printing layers exhibited a piezoelectric response over 35% higher than those tested in a parallel condition to the printing layers. Additionally, the dielectric properties from functional ceramics were also influenced by the testing orientation. The dielectric properties of perpendicularly tested BJT-printed BaTiO₃ were 20% better than the samples tested in a parallel condition.

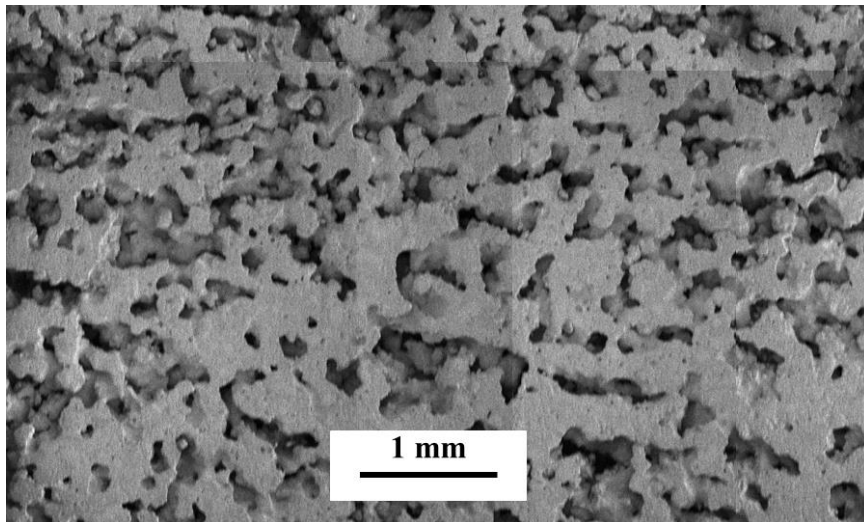


Figure 7. Cross-sectional SEM image of BJT-printed BaTiO₃ looking at the printing layers.

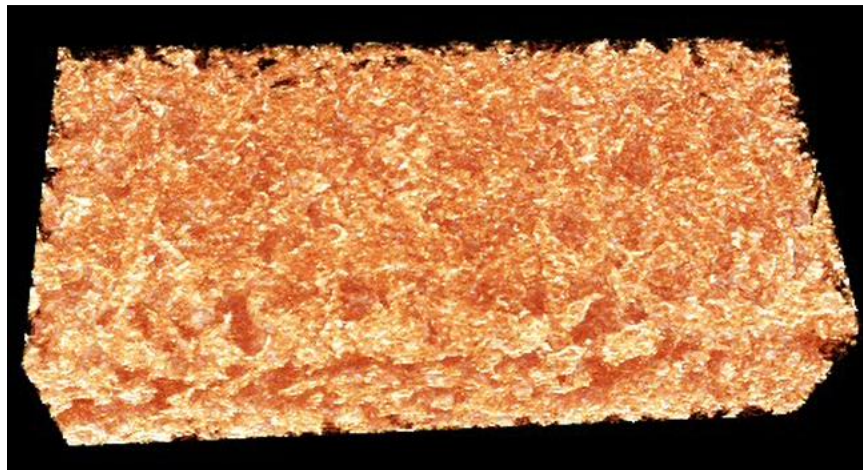


Figure 8. X-ray computed tomography of BJT-printed ceramic.

In this manuscript, the directional dependence of the functional properties in BJT samples was corroborated by fabricating samples of lead zirconate titanate (PZT). In order to test the piezoelectric properties of BJT-printed PZT samples as a function of building orientation, two sample sets were prepared using an ExOne M-Lab BJT printer. Samples from the same printing process were then sintered. After this, the two sample sets were electroded in two different orientations with respect to the build direction. The sample set defined as “parallel” was electroded parallelly to the deposited printing layers. Conversely, the “perpendicular” samples were electroded in a normal fashion to the deposited printing layers. After this electroding process, the samples were subject to a poling field of 0.5 kV/mm at 60 °C for two hours. Once the poling process was performed, the piezoelectric properties were characterized using a d_{33} m from American Piezo Ceramics, Inc.

A behavior like that observed in BaTiO₃ was observed for the PZT samples. Higher piezoelectric properties were obtained for the samples tested in a perpendicular manner to the ones tested parallelly. The results from this characterization can be seen in Figure 9. The average piezoelectric response for the PZT samples tested parallelly was found to be 468.5 pC/N, while the samples tested perpendicularly yielded an average piezoelectric charge coefficient of 541.4 pC/N. The orthotropic behavior in the functional ceramics is believed to be due to the porosity of the sample.

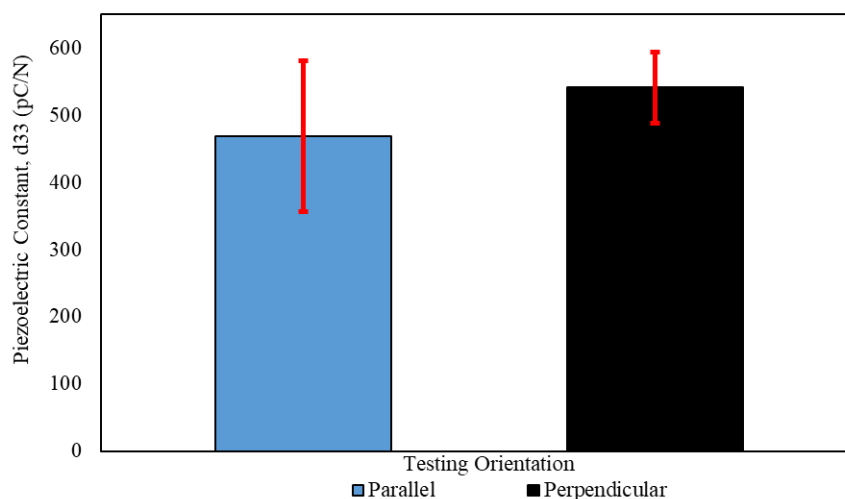


Figure 9. Piezoelectric performance of lead zirconate titanate (PZT) ceramics as a function of testing orientation.

Ceramic samples fabricated by BJT tend to have lower densities than samples obtained from metal BJT printing. One of the main reasons for this behavior is the lower powder packing density, and the air voids formed in between layers during the sintering process, as shown in Figure 7. This porosity was further characterized by performing X-ray computed tomography (XCT) in BJT-printed Al_2O_3 samples. The morphology of functional ceramics is very similar; however, this is harder to characterize using XCT due to the density of the elements present in materials such as PZT. One example of the results from this imaging is shown in Figure 8, as well as in Video S1 (Supplementary Materials). This microstructure is expected to affect the mechanical load transfer ability from the functional ceramics, as well as lower the overall piezoelectric response as a result.

Compressive mechanical tests were also been performed on this samples to validate this hypothesis. The results for this characterization, as well as the piezoelectric properties for BaTiO_3 under different loading conditions, are shown in Figure 10. From these results, it can be observed that higher structural properties also contribute to better piezoelectric properties in functional ceramics, further validating the importance of the testing conditions in the observed properties of functional ceramics.

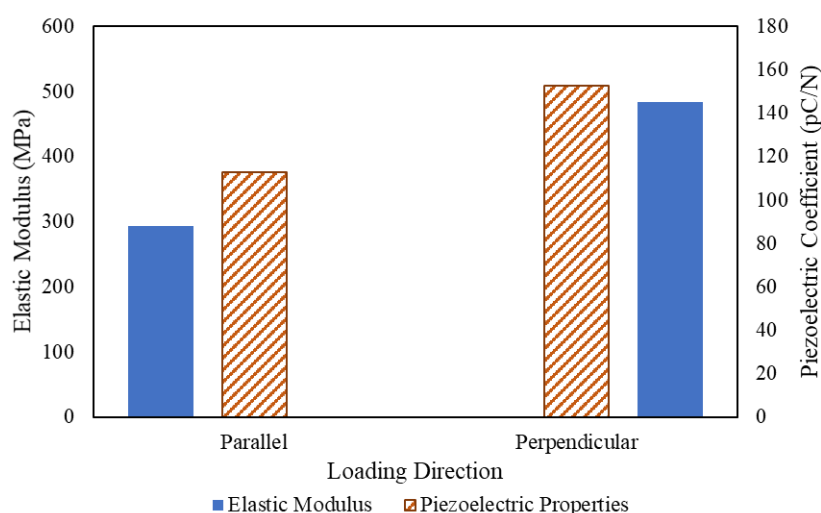


Figure 10. Correlation of mechanical and piezoelectric properties as a function of testing orientation.

5. Conclusions and Future Directions

In this brief review, the influence of relevant parameters in BJT printing of functional ceramics to attain ideal performance was discussed. It was found that particle shape and size distribution are crucial to achieving good printability. Although good printability is required to achieve successful BJT-printed parts, properties observed in the printed ceramics are also significantly influenced by printing parameters such as binder saturation. Binder saturation was found to affect green body density, as well as the density after sintering. The post-printing heat treatment processing is equally important to achieve high functional properties from the printed ceramics. The impact of sintering conditions on several functional properties such as dielectric and piezoelectric capabilities was also discussed. Finally, it was also demonstrated that BJT-printed ceramics tend to be highly orthotropic. It was observed that an increase in apparent piezoelectric properties of over 15% was observed for samples tested in different orientations with respect to the build direction. Finally, a correlation between the mechanical and piezoelectric properties of functional ceramics under different testing orientations was established.

Regarding future research directions for this growing field, some suggestions are provided below.

5.1. Material Design

As discussed in this review, the material interaction and evolution are critical to achieving high properties in functional ceramics, as well as ceramics in general. Most printing systems are designed for metals. Special attention must be paid to the development of binders compatible with ceramics that can also aid in increasing the density of the final part. Additionally, sintering and post-processing tailored for the multi-stage and material system printed by BJT must be developed to further aid in increasing the density and final properties.

5.2. Tailored Applications

Finally, applications in which the orthotropic nature and porosity can be used as an advantage of the material system must be explored. Systems that require the use of high-surface-area structures or directed response would greatly benefit from the use of BJT-printed functional ceramics.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2571-6131/3/1/8/s1>, Video S1.

Author Contributions: SEM imaging, results analysis, and discussion were performed by L.A.C. Sample fabrication and testing, as well as data processing were performed by P.I. and B.W. D.A.IV and C.S. provided expertise and resources to perform XCT testing. R.W. provided with resources, expertise, and guidance in the additive manufacturing. Finally, Y.L. provided with resources, as well as oversight and guidance throughout the project. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yin, Q.; Zhu, B.; Zeng, H. *Microstructure, Property and Processing of Functional Ceramics*; Metallurgical Industry Press, and Springer: Shanghai, China, 2009.
2. Eichel, R.A.; Erusalimskii, E.; Drahus, M.D.; Smyth, D.M.; Van Tol, J.; Acker, J.; Kungl, H.; Hoffman, M.J. Local variations in defect polarization and covalent bonding in ferroelectric Cu₂₊-doped PZT and KNN functional ceramics at the morphotropic phase boundary. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8698–8705. [[CrossRef](#)]
3. Lin, X.; Yuan, F.G. Diagnostic lamb waves in an integrated piezoelectric sensor/actuator plate: Analytical and experimental results. *Smart Mater. Struct.* **2001**, *10*, 907–913. [[CrossRef](#)]
4. Chavez, L.A.; Jimenez, F.O.Z.; Wilburn, B.R.; Delfin, L.C.; Kim, H.; Love, N.; Lin, Y. Characterization of thermal energy harvesting using pyroelectric ceramics at elevated temperatures. *Energy Harvest. Syst.* **2018**, *5*, 3–10. [[CrossRef](#)]

5. Zhao, X.; Gao, H.; Zhang, G.; Ayhan, B.; Yan, F.; Kwan, C.; Rose, J.L. Active health monitoring of an aircraft wing with embedded piezoelectric sensor/actuator network: I. defect detection, localization, and growth monitoring. *Smart Mater. Struct.* **2007**, *16*, 1208–1217. [\[CrossRef\]](#)
6. Lakeman, C.D.E.; Payne, D.A. Sol-gel processing of electrical and magnetic ceramics. *Mater. Chem. Phys.* **1994**, *38*, 305–324. [\[CrossRef\]](#)
7. Oonishi, H. Orthopaedic applications of hydroxyapatite. *Biomaterials* **1991**, *12*, 171–178. [\[CrossRef\]](#)
8. Brezesinski, T.; Wang, J.; Polleux, J.; Dunn, B.; Tolbert, S.H. Templated nanocrystal-based porous TiO₂ films for next-generation electrochemical capacitors. *J. Am. Chem. Soc.* **2009**, *131*, 1802–1809. [\[CrossRef\]](#)
9. Bai, Y.; Wu, J.; Xi, J.; Wang, J.; Zhu, W.; Chen, L.; Qiu, X. Electrochemical oxidation of ethanol on Pt-ZrO₂/C catalyst. *Electrochem. Commun.* **2005**, *7*, 1087–1090. [\[CrossRef\]](#)
10. Diaz, O.G.; Luna, G.G.; Liao, Z.; Axinte, D. The new challenges of machining ceramic matrix composites (CMCs): Review of surface integrity. *Int. J. Mach. Tools Manuf.* **2019**, *139*, 24–36. [\[CrossRef\]](#)
11. Wang, F.F.Y. *Ceramic Fabrication Processes: Treatise on Materials Science and Technology*; Elsevier: London, UK, 2016; Volume 9.
12. Lv, X.; Ye, F.; Cheng, L.; Fan, S.; Liu, Y. Binder jetting of ceramics: Powders, binders, printing parameters, equipment, and post-treatment. *Ceram. Int.* **2019**, *45*, 12609–12624. [\[CrossRef\]](#)
13. Kim, H.; Renteria-Marquez, A.; Islam, M.D.; Chavez, L.A.; Rosales, C.A.G.; Ahsan, M.A.; Tseng, T.L.B.; Love, N.D.; Lin, Y. Fabrication of bulk piezoelectric and dielectric BaTiO₃ ceramics using paste extrusion 3D printing technique. *J. Am. Ceram. Soc.* **2019**, *102*, 3685–3694. [\[CrossRef\]](#)
14. Jafari, M.A.; Han, W.; Mohammadi, F.; Safari, A.; Danforth, S.C.; Langrana, N. A novel system for fused deposition of advanced multiple ceramics. *Rapid Prototyp. J.* **2000**, *6*, 161–175. [\[CrossRef\]](#)
15. Eckel, Z.C.; Zhou, C.; Martin, J.H.; Jacobsen, A.J.; Carter, W.B.; Schaedler, T.A. Additive manufacturing of polymer-derived ceramics. *Science* **2016**, *351*, 58–62. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Du, W.; Ren, X.; Ma, C.; Pei, Z. Binder jetting additive manufacturing of ceramics: A literature review. In Proceedings of the ASME 2017 International Mechanical Engineering Congress and Exposition, Tampa, FL, USA, 3–9 November 2017.
17. Cui, H.; Hensleigh, R.; Chen, H.; Zheng, X. Additive manufacturing and size-dependent mechanical properties of three-dimensional microarchitected, high-temperature ceramic metamaterials. *J. Mater. Res.* **2018**, *33*, 350–371. [\[CrossRef\]](#)
18. Chen, Z.; Song, X.; Lei, L.; Chen, X.; Fei, C.; Chiu, C.T.; Qian, X.; Ma, T.; Yang, Y.; Shung, K.; et al. 3D printing of piezoelectric element for energy focusing and ultrasonic sensing. *Nano Energy* **2016**, *27*, 78–86. [\[CrossRef\]](#)
19. Babaei, S.; Shim, J.; Weaver, J.C.; Chen, E.R.; Patel, N.; Bertoldi, K. 3D Soft Metamaterials with Negative Poisson's Ratio. *Adv. Mater.* **2013**, *25*, 5044–5049. [\[CrossRef\]](#)
20. Cox, S.C.; Thornby, J.A.; Gibbons, G.J.; Williams, M.A.; Mallick, K.K. 3D printing of porous hydroxyapatite scaffolds intended for use in bone tissue engineering applications. *Mater. Sci. Eng. C* **2015**, *47*, 237–247. [\[CrossRef\]](#)
21. Gonzalez, J.A.; Mireles, J.; Lin, Y.; Wicker, R.B. Characterization of ceramic components fabricated using binder jetting additive manufacturing technology. *Ceram. Int.* **2016**, *42*, 10559–10564. [\[CrossRef\]](#)
22. Kaerger, J.S.; Edge, S.; Price, R. Influence of particle size and shape on flowability and compactibility of binary mixtures of paracetamol and microcrystalline cellulose. *Eur. J. Pharm. Sci.* **2004**, *22*, 173–179. [\[CrossRef\]](#)
23. Coble, R.L. Effects of particle size distribution in initial stage sintering. *J. Am. Ceram. Soc.* **1973**, *56*, 461–466. [\[CrossRef\]](#)
24. Hassan, M.S.; Lau, R.W.M. Effect of Particle Shape on Dry Particle Inhalation: Study of Flowability, Aerosolization, and Deposition Properties. *Aaps Pharmscitech* **2009**, *10*, 1252–1262. [\[CrossRef\]](#)
25. Bai, Y.; Wagner, G.; Williams, C.B. Effect of particle size distribution on powder packing and sintering in binder jetting additive manufacturing of metals. *J. Manuf. Sci. Eng.* **2017**, *139*, 081019. [\[CrossRef\]](#)
26. Grant, L.O.; Carazzone, J.R.; Cordero, Z.C. Mitigating distortion during sintering of binder jet printed ceramics. In Proceedings of the 29th Annual International Solid Freeform Fabrications Symposium—An Additive Manufacturing Conference, Austin, TX, USA, 13–15 August 2018.
27. Wang, W.; Fu, Z.; Wang, H.; Yuan, R. Influence of hot pressing sintering temperature and time on microstructure and mechanical properties of TiB₃ ceramics. *J. Eur. Ceram. Soc.* **2002**, *22*, 1045–1049. [\[CrossRef\]](#)

28. Vergara, L.; Olivares, J.; Iborra, E.; Clement, M.; Sanz-Hervas, A.; Sangrador, J. Effect of rapid thermal annealing on the crystal quality and the piezoelectric response of polycrystalline AlN films. *Thin Solid Film.* **2006**, *515*, 1814–1818. [\[CrossRef\]](#)
29. Jarupoom, P.; Munpakdee, A.; Eitssayeam, S.; Pengpat, K.; Rujijanagul, G. Effects of thermal treatment on piezoelectric and dielectric properties of zirconium modified barium titanate ceramics. In Proceedings of the 2013 Joint IEEE International Symposium on Applications of Ferroelectric and Workshop on Piezoresponse Force Microscopy (ISAF/PFM), Prague, Czech Republic, 21–25 July 2013.
30. Mazaheri, M.; Zahedi, A.M.; Sadrnezhad, S.K. Two-step sintering of nanocrystalline ZnO compacts: Effect of temperature on densification and grain growth. *J. Am. Ceram. Soc.* **2007**, *91*, 56–63. [\[CrossRef\]](#)
31. Chavez, L.A.; Wilburn, B.R.; Ibave, P.; Delfin, L.C.; Vargas, S.; Diaz, H.; Fulgentes, C.; Renteria, A.; Regis, J.E.; Liu, Y.; et al. Fabrication and characterization of 3D printing induced orthotropic functional ceramics. *Smart Mater. Struct.* **2019**, *28*, 125007. [\[CrossRef\]](#)
32. Bastani, Y.; Schmitz-Kempen, T.; Roelofs, A.; Bassiri-Gharb, N. Critical thickness for extrinsic contributions to the dielectric and piezoelectric response in lead zirconate titanate ultrathin films. *J. Appl. Phys.* **2011**, *109*, 014115. [\[CrossRef\]](#)
33. Hoshina, T.; Takizawa, K.; Li, J.; Kasama, T.; Kakemoto, H.; Tsurumi, T. Domain size effect on dielectric properties of barium titanate ceramics. *Jpn. J. Appl. Phys.* **2008**, *47*, 7607–7611. [\[CrossRef\]](#)
34. Berkowitz, A.E.; Schuele, W.J. Magnetic properties of some ferrite micropowders. *J. Appl. Phys.* **1959**, *30*, S134. [\[CrossRef\]](#)
35. Powers, J.D.; Glaeser, A.M. Grain boundary migration in ceramics. *Interface Sci.* **1998**, *6*, 23–29. [\[CrossRef\]](#)
36. German, R.M. Coarsening in sintering: Grain shape distribution, grain size distribution, and grain growth kinetics in solid-pore systems. *Crit. Rev. Solid State Mater. Sci.* **2010**, *35*, 263–305. [\[CrossRef\]](#)
37. German, R. *Sintering: From Empirical Observations to Scientific Principles*; Butterworth-Heinemann: Oxford, UK, 2014.
38. Huan, Y.; Wang, X.; Fang, J.; Li, L. Grain size effect on piezoelectric and ferroelectric properties of BaTiO₃ ceramics. *J. Eur. Ceram. Soc.* **2014**, *34*, 1445–1448. [\[CrossRef\]](#)
39. Gaytan, S.M.; Cadena, M.A.; Karim, H.; Delfin, D.; Lin, Y.; Espalin, D.; MacDonald, E.; Wicker, R.B. Fabrication of barium titanate by binder jetting additive manufacturing technology. *Ceram. Int.* **2015**, *41*, 6610–6619. [\[CrossRef\]](#)
40. Farzadi, A.; Solati-Hashjin, M.; Asadi-Eydivand, M.; Osman, N.A.A. Effect of layer thickness and printing orientation on mechanical properties and dimensional accuracy of 3D printed porous samples for bone tissue engineering. *PLoS ONE* **2014**, *9*, e108252.



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