Evaluation of Stereolithography-Based Additive Manufacturing Technology for BaTiO₃ Ceramics at 465 nm

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Featured Application: Efficient 3D-printing of lead-free piezoceramic items using stereolithography-based additive manufacturing procedure.

Abstract: A piezoceramic BaTiO₃ material that is difficult for 3D printing was tested with a homemade laser-based stereolithography (SLA) setup. The high light absorbance of BaTiO₃ in the spectral range of 350–410 nm makes this material hardly usable with most commercial SLA 3D printers. The typical polymerization depth of BaTiO₃ ceramic pastes in this spectral range hardly reaches 30–50 µm for 40 vol % powder loading. A spectral change to 465 nm was realized in this work via a robot-based experimental SLA setup to improve the 3D printing efficiency. The ceramic paste was prepared from a preconditioned commercial BaTiO₃ powder and used for 3D printing. The paste's polymerization was investigated with variation of powder fraction (10–55 vol %), speed of a laser beam (1–10 mm/s, at constant laser power), and a hatching spacing (100–1000 µm). The polymerization depths of over 100 µm were routinely reached with the 465 nm SLA for pastes having 55 vol % powder loading. The spectral shift from 350–410 nm spectral region to 465 nm reduced the light absorption by BaTiO₃ and remedied the photopolymerization process, emphasizing the importance of comprehensive optical analysis of prospective powders in SLA technology. Two multi-layered objects were 3D-printed to demonstrate the positive effect of the spectral shift.

Keywords: BaTiO₃; 3D printing; stereolithography; SLA; lead-free piezoceramics

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1. Introduction

Additive manufacturing (AM) technology removes many restrictions in piezoceramics manufacturing related to the shape, size, and internal structure of the produced items. The AM implementation reduces the production cost of single items and small batches due to the exclusion from the manufacturing workflow of the expensive tools and molds, typical for traditional approaches [1]. Multiple tryouts of different AM technologies for piezoceramics manufacturing were demonstrated in the literature in the last decade [2]. Of the different AM approaches, the SLA/DLP-based methods (SLA—stereolithography apparatus; DLP—digital light processing) demonstrated the most promising results in terms of piezoceramics shaping, due to the high accuracy, reasonable dimensional control, and the usage of pastes and suspensions with high powder loadings (over 50 vol %) in the feedstock. Conventional piezo-materials based on lead zirconate titanate (PZT) have been used in industrial applications for decades. They demonstrate the best piezoelectric properties among piezoceramics when manufactured in a traditional or additive way [2]. However, due to the emerging ecological risks of PZT usage, a gradual replacement of these materials with lead-free contenders is ongoing. One of the most intensively studied lead-free ferroelectric materials is BaTiO₃ [3] (BT).

Since the beginning, the applications of SLA/DLP technology to BT was problematic [4]. This material was acknowledged as challenging to work with due to mediocre photopolymerization response of BT-based pastes and suspensions to UV laser light (for SLA) or UV masked light (for DLP). The photopolymerization depth of BT pastes was reaching no greater than 30–50 μm . The layer thickness in SLA/DLP had to be set to 10–20 μm in order to produce mechanically sound items. Some researchers even designed a particular subsystem to accurately prepare very thin layers of BT suspension for DLP-based processing [5].

The poor photopolymerization of materials in stereolithography-based 3D printing is traditionally attributed to the large difference in the refractive indices between powder and an organic binder [6,7]. In the spectral region of 350–410 nm, typical for conventional SLA/DLP technology, BT-based piezoceramic materials have a greater refractive index (2.65–2.81) than other technical ceramics, such as Al_2O_3 (1.79–1.8), ZrO_2 (2.22–2.26), or yttrium-stabilized zirconia (2.22–2.26), which are successfully used in SLA and DLP technologies.

In this work, we demonstrate that besides the refractive index differences, the significant factor affecting the performance of the SLA technology is the light absorption of BT ceramic powder in the selected spectral range. To demonstrate the effect of light absorption, we selected a wavelength of 465 nm, where BT piezoceramics absorbs little light, and conducted a photopolymerization study. We developed an SLA-based experimental setup featuring a 465 nm industrial laser connected to an industrial robot to assist with testing and 3D printing of simple BT greenbody items.

This work aimed to demonstrate that photopolymerization problems with BT-based pastes/suspensions may have a simple technological solution. The thermal processing of the samples and study of their properties and microstructure, concerning different 3D printing and thermal processing regimes, are out of the scope of this preliminary work—they are the subjects of the future research.

2. Materials and Methods

An optical response of BT powder in the spectral range of 350–800 nm was found in the scientific literature and analyzed in terms of light transmission and refractive index behavior. The results and the references are discussed in the Section 4. On the basis of the maxima locations in BT light transmission spectrum, we selected the wavelength of 465 nm for the laser source of the homemade SLA setup. Series of experimental tests were conducted with BT ceramic pastes to investigate the effect of the lower light absorption at 465 nm.

2.1. Material

A commercially available BaTiO_3 powder was purchased from a local supplier. An X-ray diffraction pattern of the powder (Figure 1) confirmed barium titanate as the main phase. The powder was ball milled in a planetary mill Pulverisette 6 (Fritsch, Idar-Oberstein, Germany) for 2 h in the presence of 2 mm zirconia balls and ethanol to reduce the size of powder particles to $<1 \mu\text{m}$. The powder was dried in a furnace at 70 $^\circ\text{C}$ for 3 h. The milled powder's particle size and morphology were characterized with scanning electron microscopy (SEM), using JSM-6390LA (JEOL Ltd., Tokyo, Japan) and FEI Quattro S (Thermo Fisher Scientific, Waltham, MA, USA) electron microscopes. The results of SEM imaging were processed with image analysis techniques to refine the size of the powder particles. The image analysis was conducted with FEI Avizo (Thermo Fisher Scientific, OR, USA) software. The phase of BT was assessed in X-ray patterns recorded with a Bruker D8 Advance (Bruker, Billerica, MA, USA) diffractometer. Phase analysis was carried out with the use of Match! software (Crystal Impact, Bonn, Germany) and Crystallography Open Database (COD) [8]. GSAS software [9] was applied for fitting powder diffraction pattern profile with Le Bail method and for the refinement of unit cell parameters with Rietveld method.

Figure 1. XRD pattern of a commercial BaTiO₃ powder, before milling.

After the particle size study, the powder was mixed with 2 wt % Disperbyk 100 (BYK-Chemie GmbH, Wesel, Germany) dispersant and homogenized in Retsch PM400 (Retsch, Haan, Germany) planetary ball mill for 30 min in order to uniformly distribute the dispersant over powder particles and break up the clusters. The homogenization resulted in the preconditioned powder. Ceramic pastes were prepared by mixing the preconditioned powder with a commercial organic photopolymerizable composition, Yellow Dental Clear (HarzLabs, Moscow, Russia).

2.2. The 465 nm Stereolithographic Experimental Setup

A handmade SLA experimental setup was built with the use of an industrial 465 nm laser LDM450-3-12 (Purelogic R&D, Voronezh, Russia). The laser was attached to a FANUC M-11A/0.5A (FANUC, Oshino, Japan) industrial robotic 6-axis manipulator to enable laser beam's mechanical XY-motion. A vat and a printing platform were designed and 3D-printed from ABS plastic, using an FDM 3D printer. The printing platform's ascending and descending functions were implemented with the vertical mechanical drive on the basis of Nema17 Stepper motor KS42STH48-1684A (HANPOSE 3D Technology Co., Guangzhou, China). The laser had a wide elliptical beam shape (approximately 3×2 mm) from the factory. A stainless-steel plate (a mask) with a 1 mm diameter pinhole was manufactured and inserted into the laser path to limit the exposed area. For some experiments, the mask was attached to the laser and aligned to the laser beam's center—this allowed us to crop the beam to a smaller diameter, trading off the intensity. For other experiments, the setup was used without the mask. When the mask was on, the laser light intensity was reduced 15-fold, but dimensional accuracy of contouring and shading was improved.

The printing operations with the experimental SLA setup were similar to those of commercial SLA machines, except that the paste portions were delivered to the printing platform by hands. The delivered paste was automatically spread over the printing platform by the robot, keeping the layer thickness of 100 μ m. The check of layer thickness consistency was made at multiple locations of the printing platform with an Elcometer wet film comb (Elcometer, Manchester, United Kingdom).

The laser power was measured with the Ophir Laser Power meter (Ophir Optonics, Jerusalem, Israel). The intensity of the laser beam was not adjustable. Hence, the amount of energy transferred to the material was regulated via the exposure time. For stationary testing, the exposure time was directly controlled by hardware. For the tests with laser

motion, laser marking speed and hatching spacing determined the local dosage of the light energy irradiated to the photopolymerizable material. There were three tests conducted with the experimental setup.

- (1) Test of the powder loading effect. There were six variants of ceramic paste prepared featuring powder loading of 10, 20, 30, 40, 50, and 55 vol %. The mask was attached to the laser for these testing series to mimic the realistic 3D-printing operations with this setup. The laser speed was set at 5 mm/s, and the hatching space was 200 μm —these parameters correspond to the energy intensity of 14.8 J/cm².
- (2) Test of the laser speed and hatching space variation. There were 20 vol % and 55 vol % ceramic pastes used in this test. The tested laser speeds were 1, 2, 3, 5, and 10 mm/s. The tested hatching spacings were 0.1, 0.2, 0.3, 0.4, 0.5, and 1 mm. The energy intensities investigated in this test, with the help of varying laser speed or hatching spacing, were in the range of 2.97–67.36 J/cm² for the masked laser and 45.76–1152.44 J/cm² for the unmasked laser. The optimal parameters for 3D printing operations were determined in this test.
- (3) Test of multi-layered objects 3D printing. The optimal process parameters selected for 3D printing were hatching spacing of 0.2 mm, laser speed of 3 mm/s, and paste powder concentration of 55 vol %. One 50 $\times$ 2 mm stripe and one 10 $\times$ 10 mm square sample were 3D-printed to demonstrate the technical possibility of BT's 3D printing using 100 μm thick layers. The stripe consisted of 20 layers and was printed using the unmasked laser. The square sample consisted of 50 layers (the total thickness was 5 mm) and was 3D-printed using the masked laser.

3. Results

3.1. Material Characterization

The analysis of XRD data revealed that the main phase in the initial powder was BaTiO₃ in tetragonal modification (COD #96-152-5438) (Figure 2a,b). Calculated cell parameters were as follows: $c = 4.02287 \text{ \AA}$, $a = b = 3.99337 \text{ \AA}$; tetragonality $c/a = 1.0074$. Besides barium titanate, minor phases of barium zirconate (BaZrO₃, COD #96-153-8370), zirconium oxide (ZrO₂, COD #96-210-8454), and barium carbonate (BaCO₃, COD #96-100-0034) were found in the powder. The appearance of zirconium oxide and zirconate phases, which were not presenting in the as-purchased powder, was attributed to the milling procedure. The tetragonal BT has a density of 6.02 g/cm³ and a melting point of 1625 °C—the density was needed to convert wt % to vol % during mixing of BT ceramic pastes.

SEM images of the milled powder (Figure 2c) indicate that the particles had no spherical shape, but their aspect ratio was close to 1. While there were many particles of $\approx 1 \mu\text{m}$ in size, plenty of them were smaller than one micrometer. They were attached to the larger particles or sited between them. The particles were not agglomerated, which improved the homogenization of the BT pastes.

The estimation of particle size carried over with the image processing methods (Figure 2d) resulted in distribution with an average particle size of 267 nm. The use of the equivalent diameter measure for particle size analysis was rational since particles' aspect ratio was close to 1. The presence of multiple submicron-sized particles in the milled powder complicated polymerization of BT pastes due to the enhancing of the light scattering phenomena. Such pastes typically demonstrate decreased polymerization depths. Thus, the polymerization testing of BT pastes conducted in this study was done under unfavorable conditions in terms of light propagation into the bulk of feedstock material.

Figure 2. Properties of the milled BT powder: (a) XRD results with major and minor phases identified, (b) the zoom-in to the 45° intensity peak of XRD results, (c) SEM image, and (d) particle size distribution based on SEM results.

3.2. Photopolymerization Using the 465 nm SLA Method

The experimental laboratory setup produced high light intensity at 465 nm. The BT material has low light absorption around this wavelength. The amount of energy deposited by the laser was measured with an Ophir power metering sensor while the laser was shading a 10×10 mm area. The typical pattern of the laser power evolution, recorded while marking the square area, is shown in Figure 3a. The recorded data were numerically integrated to compute the total energy deposited to the area. The laser's marking speed was varied to obtain the dependence between the marking speed and the energy delivered to the printing platform (Figure 3b,c). The test was conducted for the masked laser (Figure 3b) and for the unmasked laser (Figure 3c). The addition of the mask decreased the energy density by ≈ 15 times, on average. The energy density in the worst-case scenario (masked laser moving at the fastest speed) was 7.3 J/cm^2 .

Figure 3. Results of laser power analysis for a 465 nm industrial laser, attached to a FANUC robot: (a) a typical laser exposure pattern recorded with a laser power meter, (b) the energy intensity of the masked laser, and (c) the energy intensity of the unmasked laser.

The polymerization test conducted for BT ceramic pastes with powder loadings of 10–55 vol % demonstrated great polymerization thicknesses of almost $100 \mu\text{m}$, even for the

paste with 55 vol % of powder (Figure 4a). The dependence of polymerization thickness on the laser speed (Figure 4b) and the hatching spacing (Figure 4c) demonstrated the expectable decrease in polymerization depth with increased laser speed and increased hatching spacing. In the first case, the exposure time became shorter. In the second case, the overall amount of energy deposited to the unit area became smaller due to fewer laser passes. On the basis of these results, we determined the optimal parameters for the 3D printing procedure—the laser speed of 3 mm/s and the hatching spacing of 0.2 mm (indicated with the red box in Figure 4b). The polymerization thickness at these values was around 125 μm when the mask was used. The 100 μm thick layers could be used during 3D printing operations.

Figure 4. The results of 55 vol % BT paste polymerization test, using a 465 nm industrial laser: (a) the effect of powder loading, (b) the impact of laser marking speed variation, (c) the effect of hatching spacing variation.

The 3D printing approach was first tested with the unmasked laser. It provided reduced dimensional control but great energy density. A 50×2 mm thick (20 layers) stripe-shaped sample was 3D-printed with no visible in-layer defects, except the overall roughness of the shape occurred due to the large size of the laser beam (Figure 5a). The laser was then masked with the metal plate, and a rectangular $10 \times 10 \times 5$ mm sample was 3D-printed using 50 layers (Figure 5b). The sample showed no signs of delamination or in-layer defects.

Figure 5. The 3D-printed BT greenbody samples, produced using a 465 nm industrial laser: (a) a $50 \times 2 \times 2$ mm sample, composed of 20 layers and 3D-printed with the unmasked laser, and (b) a $10 \times 10 \times 5$ mm rectangular sample, composed of 50 layers and 3D-printed using the masked laser.

4. Discussion

The problems with photopolymerization of stereolithography-enabled BT pastes and suspensions are often attributed to the large difference in refractive indices of the ceramic powder and the organic binder used in pastes and suspensions [1,4,10]. In this study, we demonstrated that the powder and the organic binder with a large mismatch in the refractive indices could be efficiently used for 3D printing by merely changing the spectral range of photopolymerization. In particular, the change from 355/405 nm (as in standard SLA/DLP technologies) to 465 nm improved the photopolymerization tenfold.

The scattering coefficient of BT (Figure 6a) was computed for the range 400–800 nm per equation $n^2 = 1 + 4.187\lambda^2 / (\lambda^2 - 0.223^2)$, following [11]. An extrapolation was made to the range of 300–400 nm to estimate an approximate value of the refractive index at 355 nm. The spectral absorption data for BT powder presented in [12] for the range of 350–800 nm were recomputed with equation $T = 10^{-A}$ to obtain the light transmission spectra (Figure 6b). On the basis of the light transmission data, we found that BT ceramics absorbed almost 70% of light at 355 nm (a typical wavelength for laser-based commercial

SLA 3D-printers), 14% of light at 405 nm (a typical wavelength for commercial DLP 3D-printers), and only 4% of light at 465 nm. The latter spectral range is not typical for photopolymerization-based 3D-printing.

Figure 6. (a) Refractive index of BT, extrapolated from [11], and (b) light transmission spectra of BT, recomputed from [12].

The refractive index of BT material reduced in the range of 355–465 nm from 2.81 to 2.54. Despite the gradual reduction, the BT refractive index at 465 nm was still much greater than the worst-case scenario for some SLA-enabled technical ceramics (i.e., refractive index = 2.26 for ZrO_2 or yttrium stabilized zirconia) that require thin 25 μm layers for efficient 3D printing. An additional factor that affects the polymerization efficiency is the small size (hundreds of micrometers) of the powder particles used for paste preparation. Such small particles augment light scattering, decreasing the photopolymerization depth. However, as demonstrated in this study, highly loaded BT pastes polymerize to the thicknesses in excess of 100 μm when the refractive index is still quite high and powder particles are small. Thus, the low light absorption of BT at 465 nm is considered to be a more important factor of successful 3D printing than the slight reduction in the refractive index. Thus, the powdered materials have to undergo a comprehensive optical testing prior to their usage as solid fillers in SLA-ready ceramic pastes. Attention must be paid to not only the refractive index of the powder, but also to its reflection, absorption, and transmission characteristics as functions of wavelength. The best spectral region could be selected for the efficient SLA application for selected materials, subject to the accessibility of the corresponding light source, photoinitiators, and reactive organic components (monomers/oligomers).

We demonstrated that BT exhibits high light absorption in the spectral range of 350–400 nm, which led to adverse effects when conventional SLA/DLP 3D printers were used. The shift to the spectral region of low light absorption, while BT's refractive index remained high, resulted in successful 3D printing of piezoceramic greenbody samples. Due to the low light absorption of BT in this spectral region, the 3D printing went smoothly, routinely reaching >100 μm layer thickness and showing no in-layer defects. The study showed that BT ceramics could be safely 3D-printed using SLA-based technology when the correct wavelength of light is selected for photopolymerization. The further improvement of the SLA-based 3D-printing setup would allow for testing the effects of laser interaction with piezoceramic materials and manufacturing of complexly shaped items made of BT and other types of piezoceramics, opening new possibilities for piezoceramic applications.

5. Conclusions

In the presented study, a laser-based stereolithography technique was implemented, using an 465 nm industrial laser not typical for SLA technology to study the behavior of BT-based ceramic pastes in the process of photopolymerization. A series of tests was conducted concerning different process parameters. The achieved polymerization thickness was 10 times greater than provided by the previously existing technology. The BT powder loading in the ceramic paste was kept at the high 55 vol % level. The spectral change in SLA processing from 355/405 nm to 465 nm significantly improved the efficiency of the 3D-printing behavior of BT ceramics.

The low light absorption of BT at wavelengths greater than 400 nm is a favorable factor for ceramic paste photopolymerization. Thus, a comprehensive study of the material's optical characteristics is often needed to formulate an efficient recipe for stereolithography-based 3D printing. Further research would be focused on the improvement of the experimental setup with a galvano-scanner unit instead of a robotic arm to increase the laser marking speed from 10 to 1000 mm/s and with additional optics to focus a laser beam to a small spot. Such an upgrade would allow for the usage of focused unmasked laser beam at large marking speeds to quickly 3D-print piezoceramic items with a good resolution. The parametric studies of polymerization process (including polymerized dots, lines, layers, and multi-layered structures) will be conducted in detail. Samples' microstructure will be studied, and thermal processing effects will be considered.

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