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Determination of the polymerization depths of lead-free piezoceramic pastes for UV 3D printing

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In present study, the polymerization depths for the implementation of the laser stereolithography process in the system (oligomer - piezoceramics) on the wavelengths of 445−465 nm UV range were determined in the original BTO, KNN and NBT lead-free piezoceramic pastes. It was shown that powder pastes, which provide a polymerization depth more than 150 μm, are promising for using in 3D printing. Such depth was chosen to guarantee a sufficient overlap of neighboring layers during polymerization, at the laser beam velocity speed from 1 m/s and the distance between the laser paths of 50 μm. For NBT pastes, successful photo polymerization was carried out for the first time, and for KNN paste the process performance was significantly increased.

Keywords: lead-free piezoceramics, stereolitography (SLA) - based ceramics 3D printing, UV- curing and bandwidths

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1. Introduction

Stereolithography-based ceramic 3D printing (SLA-BC) is a well-known technique for producing high-quality complex-shaped ceramic parts [1,2]. Fabrication systems Ceramaker (SLA process, France) and Lithoz (Digital Light Processing i.e. DLP, Austria) recommend for their customers mainly oxide structural ceramic pastes based on Al_2O_3 or ZrO_2, as well as hydroxyapatite for medical applications [3,4]. Previously, we proposed to use piezoceramics in the technological chain of the SLA-BC process. This paves the way for the design and production of functional micro-electromechanical systems (MEMS) of any complex shape such as sensors, actuators, sensors or other medical smart devices [5,6].

PZT ceramics based on lead titanate-zirconate Pb (Zr,Ti)O_3 has high piezoelectric properties [2]. However, the lead content ($\sim$ 60 mass%) causes environmental problems at all stages of the life cycle of PZT devices. in the EU since 2003 to protect the environment from lead pollution, its use is prohibited by law. Alternatively, piezoceramics based on $BaTiO_3$ (BTO), $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) can be recommended and show high potential in place of the widely used PZT ceramic [5].

In this work, the problems of photopolymerization of stereolithographic lead-free ceramic pastes for use in SLA-BC 3D printing are studied. These problems are traditionally associated with a large difference in refractive indices between the ceramic powder and the organic oligomeric binder [7]. In the spectral region 350−410 nm, typical for SLA/DLP systems, BTO-based piezoceramic materials have a high refractive index (2.65−2.81), in comparison with recommended manufacturers of technical ceramics, such as Al_2O_3 (1.79−1.8), or ZrO_2 yttrium stabilized (2.22−2.26). It is known from the literature [5,8] that for BTO ceramics the optimal bandwidth is 465 nm, for NBT is 640−670 nm, and for KNN the favorable range is > 460 nm. Previously,successful polymerization was shown in the $\sim$ 465 nm band for BTO in [8]. Therefore, we have now studied the optical properties and optimized the photopolymerization regimes for the BTO, NBT, and KNN piezoceramic powders prepared by us.

2. Materials and equipment

The initial materials for the synthesis of BTO, NBT, and KNN ceramics were purchased from Russian suppliers. The synthesized ceramic powders were milled in a Pulverisette 6 planetary mill (Fritch, Germany) for 0 to 3 hours in the presence of 3 mm zirconium beads and isopropyl alcohol. Then, the powders were dried in an oven at 70°C for 3 hours to remove residual isopropyl alcohol. 7 batches of powders were made: („as is“, milling for 15, 30, 45, 60, 120 and 180 min). The particle size distribution of the crushed powder and the specific surface area were determined by laser diffraction on a Nanotec Analyzette 22 Particle size analyzer (by Fritsch GmbH, Germany). The grain sizes of ceramic phases (compounds) and their morphology were studied using JSM-6390LA scanning electron microscope (SEM) (by Jeol Ltd, Japan) [7,8].

A total of 137 series of ceramic pastes (polymer-ceramic compositions) were prepared from the BTO, KNN and NBT powders synthesized by us. The original pastes were developed by us based on acrylate monomers, with

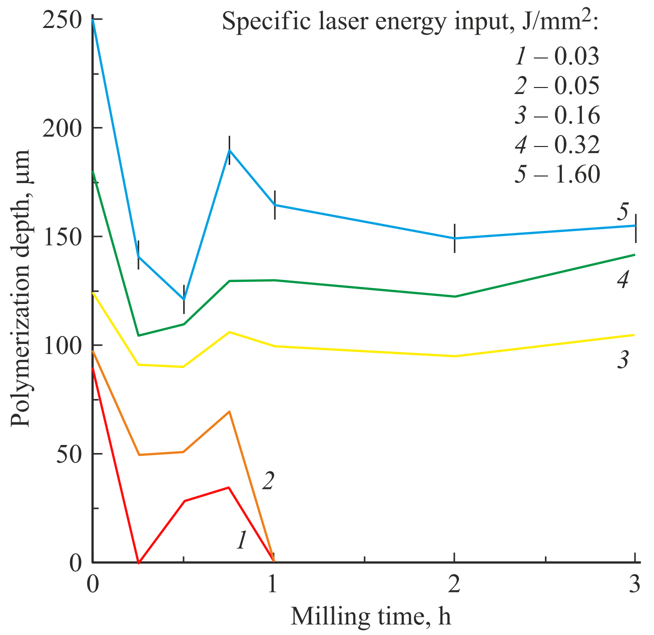

Figure 1. Depth of photopolymerization of BTO paste samples filled with powder with different grinding times, depending on the specific laser energy deposition.

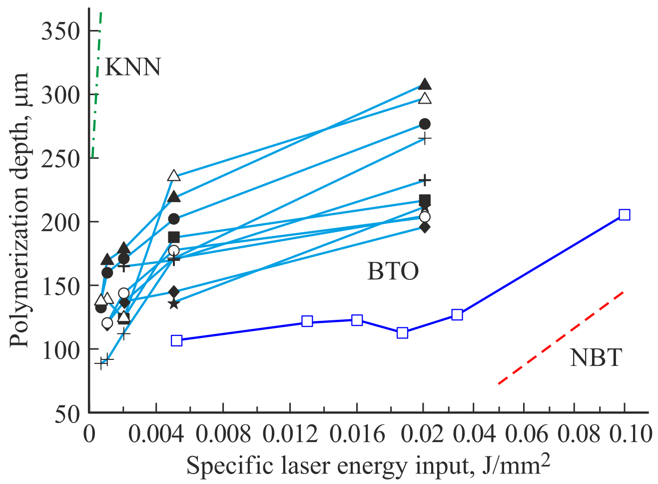

Figure 2. Minimum depths of polymerization of photopolymer-ceramic compositions based on synthesized lead-free piezoceramic powders KNN, BTO and NBT, depending on the specific laser energy deposition. Series of curves with triangles (▲, △) corresponds to pastes with powders BTO10 and BTO17.

a photoinitiator sensitive to UV radiation in the range of 440–470 nm (expandable to 650 nm), and plasticizing additives, including polyethylene glycol and/or dibutyl phosphate. Dysperbyk-111 and/or Disperbyk-180 (Chemie-BYK, Germany) were used as dispersants for ceramic powders. The filling of pastes with BTO, NBT and KNN ceramic powders ranged from 10 vol.% for the first tests, which were first tested for all compositions of components, to typical paste values recommended in 3D printing — 50–52 vol.%. On some pastes, we managed to achieve filling values of $\sim$ 52–58 vol.% with ceramic powder.

Studies have shown that filling the paste with powder can be carried out up to large values, but only in a certain range of filling values does the paste retain sufficient fluidity and the ability to be mechanically distributed on the 3D printing platform. The ratios given above (oligomer–piezoceramic), at the obtained values of powder filling, retained the ability to move under mechanical action. The fluidity control of the paste and its response to mechanical shear were evaluated visually and experimentally by its viscosity. The viscosity of the original oligomer measured by us was $\sim$ 80ṁPa·s (Brookfield DV2T viscometer). When ceramics were added, it increased to 10^8–10^4 mPa·s at shear rates $\sim$ 0.1–100 s^{-1}.

The measurements were carried out on a modular compact rheometer MCR 92 (Anton Paar GmbH, Austria) using a temperature-controlled measuring cell of the plane-to-plane type in the frequency oscillation mode. The developed (oligomer–piezoceramic) pastes showed the values of dynamic viscosity and viscoplastic shear moduli by several orders of magnitude lower compared to the commercial paste based on Al_2O_3. This means that the process of creating volumetric products will be difficult in terms of productivity. Therefore, we will continue to conduct rheological studies to fully optimize the composition and behavior of the paste during printing.

The modes of polymerization of individual layers were tested on a laboratory bench SLA-BC, developed at Skolkovo Institute of Science and Technology, and equipped with an XY-galvanometer, with replaceable UV laser modules KLM-650-1000 (650 nm, 1000 mW, cw mode, OOO „FTI-Optronik“, Russian Federation), repetitively pulsed source DMLS445-3.5W (445 nm, 3.5 W, OOO „LaS“, Russian Federation) and laser LDM450-3-12 (465 nm , Purelogic R&D, Voronezh, Russian Federation). The shape of the spot in focus from the indicated sources had the form of an ellipsoid 0.8 $\times$ 0.9 mm, and a diaphragm was used to obtain a circle. The paste application and leveling system corresponded to the well-known technical solutions implemented on the 3D Ceramaker (France), manufacturing system. The power of laser radiation (LR) varied from the minimum to the maximum values ($\sim$ 1–0.9 mW) over the entire range of laser beam scanning speeds.

3. Results and discussion

Each type of prepared paste was used for experiments to determine the maximum depth of photopolymerization and for subsequent 3D printing of piezoceramic samples. Testing of the photopolymerization conditions was carried out at different LR scanning speeds. The depth of polymerization decreases with decreasing powder particle size (Fig. 1). Only powders milled for 15–45 min demonstrated photopolymerization even at high laser scanning speeds (up to 50 mm/s). The best photopolymerization depth ($>$ 100 μm) was observed for the powder milled for 45 min

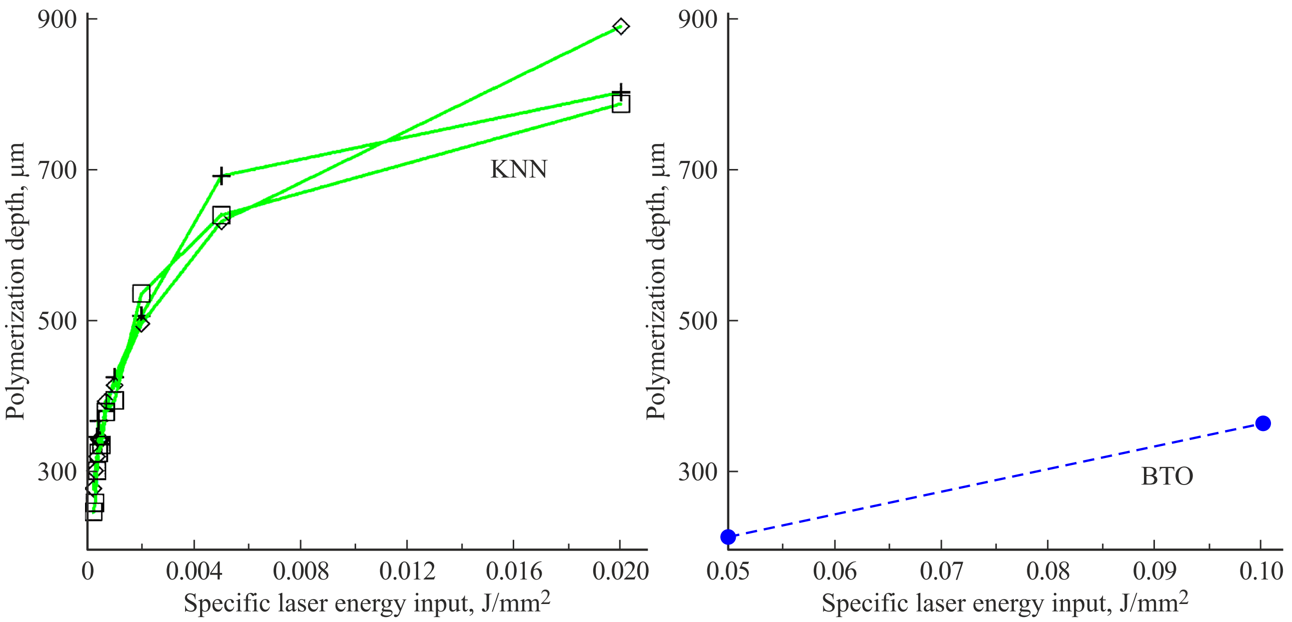

Figure 3. Maximum depths of polymerization of photopolymer-ceramic compositions based on synthesized lead-free piezoceramic powders KNN (left) and BTO (right), depending on the specific laser energy input.

at a laser scanning speed of 1–10 mm/s. Additional tests for BTO paste were made for a laser scanning speed of 3 mm/s. These tests showed a polymerization depth of 146 μm, which is suitable for polymerizing 100 μm thick paste monolayers in a 3D printing process. The thicknesses of the monolayers should be thick enough ($\sim 100\,\mu$m) to ensure high throughput of the process, and thin enough ($\sim 50\,\mu$m) to ensure the accuracy of the 3D printed products. We have recommended the following modes of 3D printing of thick samples: distance between passes 0.2 mm, laser scanning speed 3 mm/s, layer thickness 100 μm.

An analysis of the results of milling and sifting on BTO fractions of piezoceramics showed that at laser energy inputs of 0.2–1.6 J/mm^2, the results of photopolymerization show stability. Millings from 30 to 60 min are sufficient and can be recommended for 3D printing

The laser specific energy deposition can be increased in two ways ::by decreasing the speed of the laser beam and decreasing the distance between the tracks from the laser. Since the speed of 50 mm/s is too low for 3D printing (typical values in technological settings are in the range of 1000 mm/s), the distance between tracks was reduced by 2 times, to 50 μm. In repeated tests, relatively hard square monolayers were obtained, retaining their shape when removed from the paste. The film thicknesses were 198–225 μm (see Fig. 1). The value of 50 μm was chosen as the optimal distance between the laser tracks.

To determine the optimal laser energy deposition for pastes based on BTO, KNN and NBT and to select the scanning speed of the laser beam, tests were performed on a series of new ceramic pastes prepared by us from the synthesized powders. Within the framework of the experiments, square regions (side 1×1 cm) were polymerized in a layer of ceramic paste deposited on the substrate (layer depth up to 1 mm). Polymerization was performed at different speeds of the laser beam: from 10 to 1500 mm/s. Next, the thicknesses of the polymerized monolayers were measured (Fig. 2, 3). Based on the results of these tests, (1) the synthesized powders, which reduce the photopolymerization of the ceramic paste, were screened out and (2) the optimal laser processing modes were selected.

Fig. 2 shows the minimum polymerization depths of BTO, KNN and NBT ceramic pastes at which success can be expected in 3D printing. The depth of 150 μm was chosen to provide sufficient overlap of adjacent layers during polymerization to avoid delamination of the product at layer thicknesses of 50 or 100 μm. For the BTO paste, the BTO10 and BTO17 powders were chosen (Fig. 2). On the whole, BTO piezoceramics showed average characteristics for the photopolymerization of ceramic pastes (solid curves in Fig. 2).

Among the pastes with KNN, the KNN6 powder was chosen, which showed good results in photopolymerization (Fig. 2, dash-dotted curve). For this KNN powder, the polymerization depth exceeded 300 μm, even at a laser beam speed of 4000–5000 mm/s.

For NBT powder, as noted earlier, photopolymerization and 3D printing studies should be carried out using a 650 nm laser, but at the time of our research, this laser module was not yet installed. In this regard, NBT photopolymerization tests were carried out with a photoinitiator operating at a wavelength of 440–470 nm. In this spectral range, NBT ceramics have a second local light absorption maximum. In particular, monolayers with a thickness of $80-120\,\mu$m were obtained at a laser beam speed of 20 mm/s, and even a thickness of $152\,\mu$m at a velocity of 10 mm/s (Fig. 2, dashed curve). The filling of the pastes with NBT powder of piezoceramics was ~ 50 vol.%. Thus, for the first time we managed to obtain a ceramic paste with NBT as a filler, however, the photopolymerization activity of such a paste requires additional optimization for its use in 3D printing.

Typical laser beam speeds for commercial pastes on commercial 3D printers are in the thousands of mm/s. For the pastes based on BTO and KNN studied in this work, values from 1000 to 5000 mm/s were achieved. Fig. 3 shows the successful results on the depth of polymerization of pastes based on KNN and BTO. We have obtained curing thicknesses up to $300\,\mu$m for BTO paste (dashed curve, Fig. 3), and up to $700-900\,\mu$m for three KNN based formulations. Obviously, such high polymerization depths were obtained with significant laser energy deposition. This can only be done at slow LR scanning speeds, which certainly seriously reduces the performance of the SLA-BC 3D printing process and requires additional work.

4. Conclusion

3D printing of lead-free piezoceramic samples (and monolayers) from BTO, KNN and NBT pastes was carried out after optimization of grinding modes and laser processing parameters at wavelengths of 445 and 465 nm. Paste compositions have been found that have shown the best results in polymerization experiments. We recommend LI scanning speed for BTO paste ~ 1000 mm/s. At the same time, laser energy depositions from 0.01 to 0.1 J/mm2 are already sufficient for reliable polymerization. Polymerization layer thicknesses of $50-100\,\mu$m are typical for commercial pastes and can be recommended for 3D printing of piezoceramics. For the first time, the speed of the laser beam was increased to 1500 mm/s for BTO-based pastes and up to 4000 mm/s for KNN-based pastes, which indicates a high efficient photopolymerization of such pastes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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