Direct Selective Laser Sintering of Hexagonal Barium Titanate Ceramics

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Abstract

A direct selective laser sintering (SLS) process was combined with a laser preheating procedure to decrease the temperature gradient and thermal stress, which was demonstrated as a promising approach for additive manufacturing of $BaTiO_3$ ceramics. The phase compositions in $BaTiO_3$ ceramics fabricated by SLS were investigated by X-ray and neutron diffractions. The surface morphologies and cross-section microstructures were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A dense hexagonal h-$BaTiO_3$ layer was formed on the surface and extended to a depth of 500 μm, with a relative density of higher than 97% and absence of pores or microcracks. SLS resulted in the formation of the high-temperature phase, h-$BaTiO_3$, which was retained at room temperature possibly due to the high cooling rate. The grain boundaries of SLSed h-$BaTiO_3$ ceramics consist of a Ti-rich secondary phase. Compared with that of the pressureless sintered t-$BaTiO_3$ ceramics, the Vickers hardness of SLSed h-$BaTiO_3$ is 70% higher.

Keywords: barium titanate; selective laser sintering; additive manufacturing

1. Introduction

Barium titanate ($BaTiO_3$) is functional ceramics with attractive ferroelectric and piezoelectric properties[1, 2, 3], which enable their broad applications such as acoustic imaging, chip capacitors, and dynamic access memories[4, 5]. The phase transformation of $BaTiO_3$ occurs with the temperatures: rhombohedral to orthorhombic at ~-90 °C, orthorhombic to tetragonal at ~0 °C,

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tetragonal to cubic at ~120 ºC, and cubic to hexagonal at ~1460 ºC[6, 7, 8]. Among these five polymorphs, tetragonal (t-BaTiO₃) phase is used to prepare piezoelectric ceramics with high piezoelectric coefficients and dielectric constants ($d_{33} \sim 150\ to\ 500\ pC/N$, and $\varepsilon' \sim 3000\ to\ 6800$ at a frequency range from 0.1 to 10 kHz, 25 ºC) [9, 10, 11]. In contrast, hexagonal BaTiO₃ (h-BaTiO₃) is a high-temperature phase that is usually metastable at room temperature. Li *et al.* suggested that the hexagonal phase can be stabilized at room temperature via the substitution of Cr and Sb for Ti[12]. Regarding the dielectric properties, Akishige *et al.* reported that single-crystal h-BaTiO₃ grown from the molten phase had a low dielectric constant ($\varepsilon' < 2{,}200$ at 1 kHz)[13]. Later, Yu *et al.* synthesized h-BaTiO₃ crystals using a pressurized electrostatic levitation furnace, which exhibited a giant dielectric constant ($\varepsilon' \sim 10^5$ at 5 kHz) at room temperature, which may arise from the Maxwell-Wagner effect contributed by the interfacial boundaries consisting of crystal defects[14, 15]. Hashemizadeh et al. reported that the permittivity of h-BaTiO₃ ceramics may be affected by the concentration of defects[16].

Selective laser sintering (SLS), as an additive manufacturing technique, offers freedom to design and produce complex geometric build-parts without the use of molds[17, 18]. SLS fabricates dense parts by using a continuous-wave (CW) laser beam to sinter the material powders selectively and additively layer-by-layer to build 3-D objects. The SLS process for ceramic materials can be classified into two categories, i.e., the indirect and the direct SLS[19]. The indirect SLS method, which relies on the polymer binder to form the complex shape ceramic/composite parts, has been widely applied in polymer-based ceramic composites[20, 21, 22]. For example, the polymer binders of ammonium polymethacrylate[23], hydrolyzed PVA[23], Polyamide 11[24], and polyvinyl butyral[25] have

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been used for the fabrication of BaTiO$_3$ ceramics. In these studies, a laser beam was employed to densify the polymer matrix rather than directly interact with BaTiO$_3$ powders. The indirect SLS process suffers from technical issues of significant heterogeneity, low density, and poor mechanical properties related to the use of polymer binders, which usually needs a post-heating treatment to improve the microstructures and mechanical properties of ceramics.

The direct SLS process is an alternative approach that eliminates the polymer binders, in which the laser beam directly irradiates and sinters ceramic powders. The major limiting factors in direct SLS process for ceramic materials are the rapid-changing thermal fields and high thermal gradients, which can generate residual stresses, pores, and crack propagation that can cause failures in the as-sintered ceramic parts[26, 27, 28]. To the best of our knowledge, there has been only one previous study by Basile *et al.* on the interaction between a Nd-YVO$_4$ laser and BaTiO$_3$ ceramic powders during the SLS process[29]. It was found that a laser power of 23 W can lead to a denser surface layer, while a high laser energy density of over 2-4 J/mm^2 can result in the formation of a mixture of h-BaTiO$_3$, orthorhombic Ba$_2$TiO$_4$, and an amorphous phase. However, only a low relative density (<50%) was achieved and the physical properties of the SLSed BaTiO$_3$ were not reported in that study.

To address the above-mentioned limitations in the direct SLS process, the SLS process was combined with a laser preheating procedure in this study. It is hypothesized that laser preheating can effectively decrease the temperature gradient and thermal stress, which may help reduce the formation of cracks and distortions in SLSed ceramics. BaTiO$_3$ ceramics were used as a model material to test this hypothesis. The phase compositions in the SLSed BaTiO$_3$ ceramics were

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investigated by X-ray diffraction (XRD) and neutron diffraction. The surface morphologies and cross-section microstructures were characterized by SEM and TEM. The Vickers hardness of SLSed $BaTiO_3$ ceramics were measured and compared with the pressureless sintered samples.

Other additive manufacturing (AM) processes of ceramics, such as binder jetting[30] or stereolithography[31], apply polymer binders or resins in the green body of ceramic powders. Although the post heat treatment can remove the polymers, the density and precision of the final ceramic parts will degrade. Compared to them, the main advantages of this novel direct SLS process are: 1) highly dense ($\geqslant 99\%$ relative density) and continuous ceramic layers can be fabricated with the aid of a laser preheating procedure that reduces the temperature gradient and thermal stress; 2) the polymer binder is eliminated; 3) the direct SLS process has short process time (seconds), precise control, flexibility, and no contamination; and (4) the SLSed ceramics have extraordinary microstructures and mechanical properties.

2. Experimental Procedure

Tetragonal $BaTiO_3$ (t-$BaTiO_3$) powders with an average particle size of 50-70 nm and a purity of >99% were purchased from Alfa Aesar. The powders were pressed to a rectangle plate of $10\times10\times3$ mm^3 under a uniaxial pressure of 15 MPa at room temperature. After cold pressing, the powder compacts achieved a relative density of $33\pm1\%$.

A schematic illustration of the experimental set-up was shown in **Fig. 1**, which includes a CW CO_2 laser, a vacuum chamber, an X-Y translation stage, and a PC controller, and a pyrometer. The CO_2 laser (Firestar series V40, Synrad, Mukilteo, WA) has a wavelength of 10.64 μm, a maximum

output power of 40 W, and a beam diameter of 2.5 mm. According to a FTIR study by Bacha et al., the absorbance of $BaTiO_3$ nanoparticles (a mixture of 65% t-$BaTiO_3$ and 35% c-$BaTiO_3$ with a particle size of 67-73 nm) is around 20% at the wavelength of 10.64 μm[32, 33]. The $BaTiO_3$ powder compact was placed onto a stainless steel holder inside a vacuum chamber, which was pumped to a vacuum of ~10 Pa. An X-Y translation stage (Thorlabs, Newton, NJ) was used to control the positions of the samples, enabling the scan of laser beam in a large area. The temperature was measured at the laser spot using a single-color pyrometer (Endurance E1MHF1L00, Fluke, Everett, WA) that can measure temperatures in a range of 500 to 3000 ºC.

The $BaTiO_3$ powder compact was first pre-heated using a laser power density of 2.5 W/mm^2, a beam diameter of 2.5 mm, and a scanning rate of 60 mm/min. The maximum and average temperatures of the laser spot on the sample surface during the pre-heating process were 1061 and 998 ºC, respectively. After the preheating procedure, the laser power density was raised to 4.7 W/mm^2 immediately. The direct SLS process of $BaTiO_3$ powder compact was performed by scanning the laser beam in the preheated area with a scanning rate of 30 mm/min. The overlap ratio of the laser beam was 50% during both the laser preheating and sintering processes. The total exposure time to laser beam is 15 s (5 s during the pre-heating procedure and 10 s during the SLS process). For comparison, the $BaTiO_3$ powder compacts were pressureless sintered at 1000, 1200, and 1400 ºC, respectively, in a bench-top muffle furnace (KSL-1700X-KA, MTI, Richmond, CA) in air. The sample was heated to the set temperature (1000, 1200, or 1400 ºC) with a dwell time of 30 min, with a heating and cooling rate of 10 ºC/min.

The phase compositions of SLSed $BaTiO_3$ sample was analyzed by X-ray diffraction on a

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diffractometer (Smartlab, Rigaku, Tokyo, Japan) using the Cu Kα radiation operated at 44 kV/40 mA. A step size of 0.03º was used over the 2θ range of 15º to 90º. The International Centre for Diffraction Data (ICDD) used are: h-BaTiO$_3$ (JCPDS#: 34-0129) and t-BaTiO$_3$ (JCPDS#: 05-0626). The phase composition and lattice parameters of the SLSed BaTiO$_3$ was further analyzed using neutron diffraction at VULCAN at the Spallation Neutron Source, Oak Ridge National Laboratory[34, 35]. The SLSed layer was ground into powders and loaded in a vanadium can. Neutron diffraction patterns were collected with a center wavelength at 2.0 Å, which allows a measurable d-spacing from 0.5 to 2.4 Å. Rietveld refinement of the neutron diffraction pattern were performed using the General Structure Analysis System (GSAS) through the EXPGUI interface[36, 37].

The surface morphology and cross-sectional microstructures of SLSed BaTiO$_3$ were observed by SEM in two electron microscopes (Nova NanoSEM^{TM} 450 and Helios Nanolab 660, FEI, Hillsboro, OR) using the secondary electron imaging mode. The cross-sectional TEM specimens were extracted from specific locations and milled to electron transparency using with Ga ions in a focus ion beam (FIB) workstation (FEI Helios Nanolab 660, FEI). TEM characterizations were carried out using a S/TEM system (FEI Tecnai Osiris S/TEM, FEI) operated at 200 kV. The chemical element analysis were conducted by energy-dispersive spectrometry (EDS) using point, line-scan, and mapping modes in both SEM and TEM.

The relative density of SLSed ceramics was measured by the Archimedes method in water, which was designated as ρ_{arch}. Due to the non-uniform distribution of porosity along the depth, SEM images of the porosity was used to determine the local relative density, which was marked as ρ_{img}. Because of the high porosity of the pressureless sintered BaTiO$_3$ samples at 1200 ºC, their

densities were not measured by the Archimedes method but by the ratio of mass to volume. The dimensions of the pressureless sintered cubes were measured by a micrometer caliper. The Vickers microhardness test was conducted using a Knoop and Vickers tester (Tukon 2500, Wilson, Norwood, MA) on the polished surface and cross-section, with an indentation load of 0.25, 0.5, 1, 2, and 3 N for a dwell time of 10 sec. Vickers hardness for each load was determined from at least 14 individual Vickers indentations. Specimens for the dielectric constant measurement were fabricated by SLS to a dimension of $17 \times 15 \times 1$ mm^3, which were coated with a gold film and connected by a silver paste before the test. The dielectric constant measurement was conducted in a Keithley 4200A SCS-Parameter Analyzer in a frequency range of 1 kHz–10 MHz at 25 ºC.

3. Results and Discussion

Fig. 2A is a photograph of the SLSed BaTiO$_3$ sample, with a size of $8 \times 6 \times 1$ mm^3, showing its black color that turned from the white color of the BaTiO$_3$ powders. Similar black color was also observed during the reduction or plasma praying process of BaTiO$_3$ ceramics, which may be attributed to oxygen deficiency and/or the presence of Ti^{3+} ions[14, 38, 39, 40, 41]. It was observed that the SLSed BaTiO$_3$ sample sintered in the air environment was in white color, indicating that the black color of the SLSed BaTiO$_3$ sintered in the vacuum chamber may be attributed to oxygen deficiency generated in the vacuum environment. The precision of the as-sintered BaTiO$_3$ parts is ~1 mm, which may be improved to micrometers by smaller laser spot diameter, and the combination of post treatments such as milling, laser cutting and cleaning. It was observed that a laser preheating procedure before the SLS process decreased the temperature gradient and thermal

stress, resulting in a continuous and flat surface of BaTiO$_3$ ceramics. In contrast, BaTiO$_3$ samples fabricated by SLS without a laser preheating procedure generated a large number of cracks and pores, resulting in fragmentary pieces and debris.

XRD patterns of the BaTiO$_3$ raw powder, pressureless sintered BaTiO$_3$, and SLSed BaTiO$_3$ samples were compared in **Figs. 2B-1** to **2B-3**. The pressureless sintered BaTiO$_3$ specimens (Fig. 2B-2) have the tetragonal phase (space group: P4mm), which is the same as the raw powder (Fig. 2B-1). In contrast, the SLSed BaTiO$_3$ sample (Fig. 2B-3) has the hexagonal phase (space group: P6$_3$/mmc). From the XRD result, only h-BaTiO$_3$ was observed on the surface of SLSed BaTiO$_3$ layer. However, both h- and t-BaTiO$_3$ can be found from the neutron diffraction result. As the SLSed BaTiO$_3$ specimen was ground into powders for neutron diffraction analysis, some unsintered powders and partially sintered areas were also mixed into the ground powders, resulting in the presence of t-BaTiO$_3$ in the neutron diffraction result. The neutron diffraction data (**Fig. 2C**) was refined with GSAS [42], which shows that the powder is a mixture of h- and t-BaTiO$_3$ with mass percentage of 53.7% and 46.3%, respectively. The fitting result was satisfactory($_wR_p = 0.0480$, $R_p = 0.0360$, and $\chi^2 = 2.556$) with precisely refined atomic positions. The lattice parameters of h-BaTiO$_3$ [a=5.7229 (1) Å, c=13.9637(5) Å] and t-BaTiO$_3$ [a=3.9926(1) Å, c=4.0334(1) Å] derived from the neutron diffraction data were consistent with the literature. The oxygen vacancy in h-BaTiO$_3$ was determined as about 3 at.%, which may be caused by the vacuum environment[14]. The BaO-TiO$_2$ phase diagram suggest that BaTiO$_3$ transforms from cubic to hexagonal phase at 1460 °C [8, 43]. The temperature of the sample surface was measured to be 1367 to 1411 °C during the direct SLS process. Glaister and Recnik et al. reported that that the cubic-to-hexagonal phase

transformation occurs at 1330 °C in hydrogen atmosphere, and a high concentration of oxygen vacancies and Ti^{3+} ions may stabilize the hexagonal $BaTiO_3$ phase at room temperature[44, 45]. Similarly, the vacuum environment may reduce the cubic-to-hexagonal phase transformation temperature in $BaTiO_3$. In addition, the cubic-to-hexagonal phase transformation temperature may be also reduced in $BaTiO_3$ nanoparticles due to the high surface energy, as the starting powders had a fine particle size of 50-70 nm. Many literatures have reported that the tetragonal-to-cubic phase transformation temperature in $BaTiO_3$ shifts to lower temperatures with decreasing particle size, which can be attributed to the surface energy, stress, and/or softening of lattice vibration mode.[46, 47, 48] The presence of h-$BaTiO_3$ phase was also revealed by Basile *et al.*[29] during the investigation of the interaction of $BaTiO_3$ powder with an Nd-YVO_4 laser beam. The laser process resulted in a high cooling rate ($>10^2$ °C/s) during the direct SLS process[49, 50], which is the probable mechanism (i.e., quench) to retain the h-$BaTiO_3$ phase at room temperature.

The surface morphology of direct SLSed $BaTiO_3$ ceramics were characterized by SEM. After the laser preheating procedure (2.5 W/mm^2, 60 mm/min), the visual inspection indicated that the surface of the powder compact remained flat. However, it was observed that if the power density was higher than 2.5 W/mm^2, V-shape grooves, cracks, and melted powder balls started to form on the sample surface. During the direct SLS process, the laser beam (3.5-5.7 W/mm^2, 30 mm/min) re-scanned the preheated area. **Fig. 3A** shows that after direct SLS, a dense and flat surface was formed, along with the ridges and protuberant lines that may result from the scanning of the laser beam that induced rapid heating and cooling of the local areas. The enlarged view of the flat (**Fig. 3B**) and ridge area (**Fig. 3C**) indicate the absence of microcracks or pores. The relative density

(ρ_{arch}) of the SLSed surface layer was measured to be 98.7%. To reveal the grain boundary, thermal etching of the SLSed BaTiO$_3$ sample was carried out at 1200 °C for 30 min; the polished surface after thermal etching is shown in **Fig. 3D**. As a comparison, **Figs. 3E, 3F** and **3G** present the surface morphologies of BaTiO$_3$ ceramics pressureless sintered at 1000, 1200 and 1400 °C, respectively, for 0.5 hour. After pressureless sintering at 1000 °C, the powder compact showed very limited consolidation. Significant grain growth was observed after pressureless sintering at 1200 °C, and remarkable densification was observed when the temperature raised from 1200 to 1400 °C. The relative density increased from 60.3% at 1200 °C to 96.9% at 1400 °C, which was in the similar level with the SLSed BaTiO$_3$ ceramics. However, the pressureless sintered samples are all t-BaTiO$_3$, different from h-BaTiO$_3$ on the surface of SLSed samples. It is noted that the cooling rate during the pressureless sintering was 5-20 °C/min, which was much lower than that during the direct SLS process (10^2-10^{11} °C/s)[49, 50]. Thus, any h-BaTiO$_3$ phase formed in pressureless sintered sample at 1400 °C may have been transformed to t-BaTiO$_3$ during the slower cooling process.

Fig. 4A shows the cross-sectional microstructures of the SLSed BaTiO$_3$ ceramics, which can be divided into two typical regions divided by the red dot line. The top layer, from the surface to a depth of about 500 μm, exhibits a dense layer that is absence of pores or microcracks. The relative density in the top layer is higher than 97% (**Fig. 4B**). The bottom layer, below the depth of 500 μm, contains a large number of pores and cracks, with the relative density decreasing slowly with the depth to $76.7^{+2.8}_{-1.6}$ % at 900 μm. The complete densification in the top layer may be attributed to the laser preheating, which effectively reduced the temperature gradient of in the powder compacts, allowing for sintering of BaTiO$_3$ ceramics from the surface to surface to a depth of about

500 μm. The grain-size distribution of SLSed and pressureless sintered BaTiO$_3$ are compared in **Fig. 4C** and **4D**, respectively. The average grain size of the SLSed h-BaTiO$_3$ (120 μm) is larger than that of the pressureless sintered t-BaTiO$_3$ ceramics (70 μm). Although the measured maximum temperature range of the laser spot (1367-1411 °C) was close to the pressureless sintering temperature (1400 °C), the enhanced grain growth was achieved in BaTiO$_3$ by SLS for only 15 s. This enhanced grain growth may be attributed to: 1) laser-enhanced diffusion, which may result from the rapid heating and fast cooling rates that establish a non-equilibrium mass flow mechanism[51, 52]; 2) oxygen vacancies induced under the vacuum atmosphere, which may also enhance the diffusion rate[53, 54]; and 3) the underestimation of temperature in the laser spot. As the measured temperature (1367-1411 °C) is the average temperature of the laser spot, it could not show the temperature distribution in the laser beam, which has a Gaussian distribution of power energy. Thus, the maximum temperature in the center of laser spot may be higher than 1411 °C.

Fig. 5A shows the cross-sectional microstructures of the top dense layer in the SLSed BaTiO$_3$ ceramics, which reveal large grains with an average grain size of 120 μm. Most grains have a longer side that is nearly perpendicular to the surface, indicating the grain growth along the thermal conduction in the depth direction during the direct SLS process. An enlarged view of the grain structures shows the presence of a secondary phase (with a thickness of 200 to 3000 nm) along the grain boundaries (**Fig. 5B**). EDS mapping in SEM (inset in Fig. 5B) indicates that the grain boundary has a higher Ti concentration than the grain matrix. The secondary phase in the grain boundaries was further characterized by scanning transmission electron microscopy (STEM). **Fig. 5C** shows the high-angle annual dark-field (HAADF) image that indicates a low-Z phase at the

grain boundary. EDS mapping (inset of Fig. 5C) and line-scanning (**Fig. 5D**) analysis suggested that Ba, Ti, and O have a homogenous distribution and an atomic ratio of Ba: Ti: O =1: 1.1: 2.9 within the grains. In contrast, grain boundaries have a much higher concentration of Ti and slightly higher content of O, with an atomic ratio of Ba: Ti: O = 0.5: 1.5: 3, suggesting that Ti element was enriched in grain boundaries of SLSed h-BaTiO$_3$. The grain boundaries in the pressureless sintered BaTiO$_3$ samples were also characterized by EDS in SEM and TEM, which showed no evidence of element segregation. The exact mechanism for the element segregation in grain boundaries of SLSed BaTiO$_3$ ceramics remains to be elucidated, which may be related to the non-equilibrium conditions during direct SLS process, such as different diffusion or evaporation rates of Ba and Ti along the grain boundaries during laser irradiation.

Fig. 6A presents a bright-field TEM image in the top dense layer in SLSed BaTiO$_3$ ceramics, which show two BaTiO$_3$ grains, with a secondary phase locating at their grain boundary. To further characterize the crystal structures of the SLSed BaTiO$_3$ ceramics, HRTEM images with inverse fast Fourier transform (IFFT) images and selected area electron diffraction (SAED) patterns were presented in **Fig. 6B-6E**. The SAED patterns in the inset of Figs. 6B and 6E confirmed the hexagonal structure of BaTiO$_3$, which is consistent with the XRD and neutron diffraction results. In the HRTEM image in area 1 (**Fig. 6B**), the d-spacing of $(11\bar{2}0)$ plane was measured to be 2.862Å, which agrees with the value derived from the neutron diffraction (2.861 Å). The HRTEM image in area 2 is shown in **Fig. 6C**, which was tilted at a small angle (< 5º) to be located in the zone axis $[1\bar{1}00]$. The measured d-spacing of (0002) plane is 6.955 Å, slightly smaller than the value derived from the neutron diffraction result (6.981 Å). The simulated HRTEM image (inset

in Fig. 6D) suggests that the lattice fringes in the IFFT (**Fig. 6D**) are from Ba and Ti atoms.

A typical Vickers indentation at a load of 1 N is displayed in **Fig. 7A**. The Vickers microhardness on the surface of SLSed h-BaTiO$_3$ ceramics initially decreased with the applied load, and then asymptoted at 8.5 GPa with a higher loads of 2 to 3 N (**Fig. 7B**). The average microhardness values are almost the same from the surface to a depth of 800 μm (**Fig. 7C**). For comparison, the hardness of the pressureless sintered t-BaTiO$_3$ sample was 5.0±0.4 GPa. Despite that the average grain size of SLSed h-BaTiO$_3$ (120 μm) is larger than that of the pressureless sintered t-BaTiO$_3$ (70 μm), the hardness of the SLSed sample is 70% higher than the pressureless sintered t-BaTiO$_3$ sample. Ctibor et al[41] reported the hardness of a plasma sprayed BaTiO$_3$ coating, which was a mixture of h-BaTiO$_3$ (~24 wt.%), t-BaTiO$_3$ (~64 wt.%) and an amorphous phase coating, was 6.0±1.3 GPa measured by Vickers microhardness at a load of 1 N. The Vickers hardness (H_v) of ceramics can be correlated with elastic modulus (E) according to an empirical formula proposed by Jiang et al.[55]:

$$E = 16.48H_v \ , \tag{1}$$

The elastic modulus of h-BaTiO$_3$ and t-BaTiO$_3$ at room temperature is 153.3-258.1 GPa[56] and 91.8-98.9 GPa[57, 58], respectively. According to Equation 1, the Vickers hardness of h-BaTiO$_3$ and t-BaTiO$_3$ is predicted to be 9.30-15.55 GPa, and 5.57-6.00 GPa, respectively. These calculated values are in good agreement with the experimental results, while their slight difference may be related to extrinsic factors such as grain size and indentation size. The dielectric constant of SLSed BaTiO$_3$ was measured as 200~1800 at a frequency range from 10 kHz to 10 MHz, which is consistent with that of the single-crystal h-BaTiO$_3$ ($\varepsilon' < 2,200$ at 1 kHz)[13]. The measured dielectric

constant is significantly higher than that of $BaTiO_3$ ceramics fabricated by other methods including indirect SLS[24, 59], melt blending and cryogenic grinding[24], or hot pressing[60].

4. Conclusion

(1) The direct SLS process was combined with a laser preheating procedure to reduce the temperature gradient and thermal stress during laser sintering of $BaTiO_3$ ceramic powders.

(2) A fully dense h-$BaTiO_3$ layer can be formed on the surface and extended to a depth of 500 μm, with a relative density of higher than 97%, an average grain size of 120 μm, and absence of pores or microcracks.

(3) XRD, neutron diffraction, and TEM investigations confirmed the formation of a high-temperature phase, h-$BaTiO_3$, in the SLSed samples, which was retained at room temperature possibly due to the high cooling rate. A Ti-rich secondary phase was distributed at the grain boundaries of the SLSed h-$BaTiO_3$.

(4) Compared with the pressureless sintered t-$BaTiO_3$ ceramics, the hardness of the SLSed h-$BaTiO_3$ is 70% higher. The dielectric constant of SLSed h-$BaTiO_3$ was 200~1800 at 10 kHz to 10 MHz.

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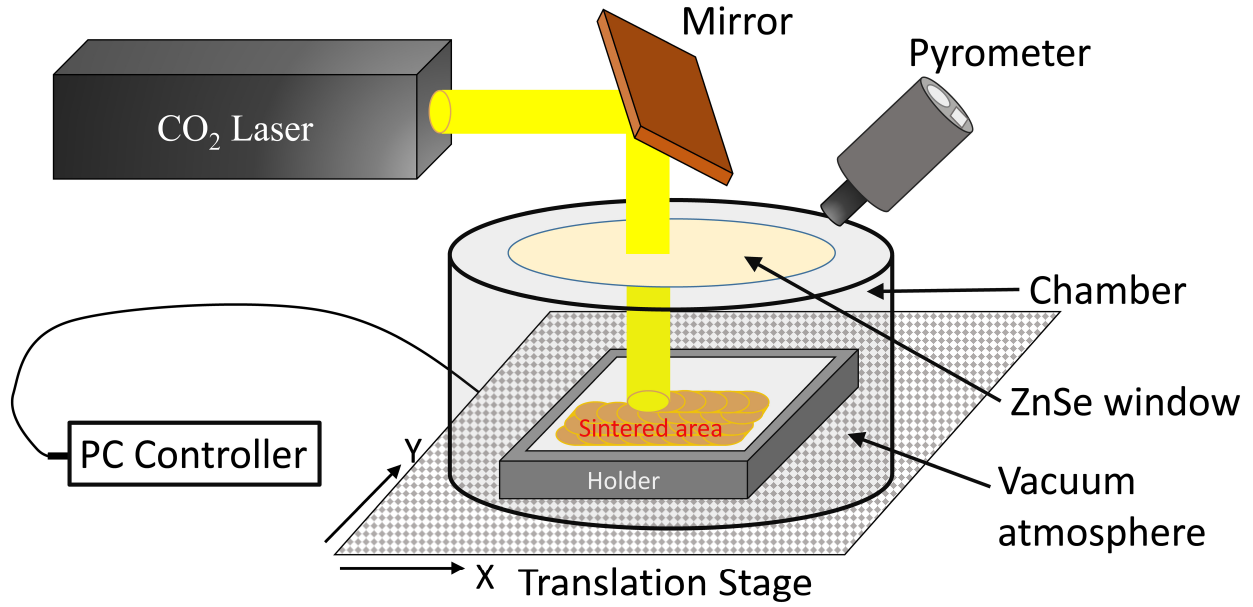
Figures:

Fig. 1 The schematic diagram of the experimental setup for laser preheating and direct SLS of BaTiO$_3$ ceramics in a vacuum atmosphere.
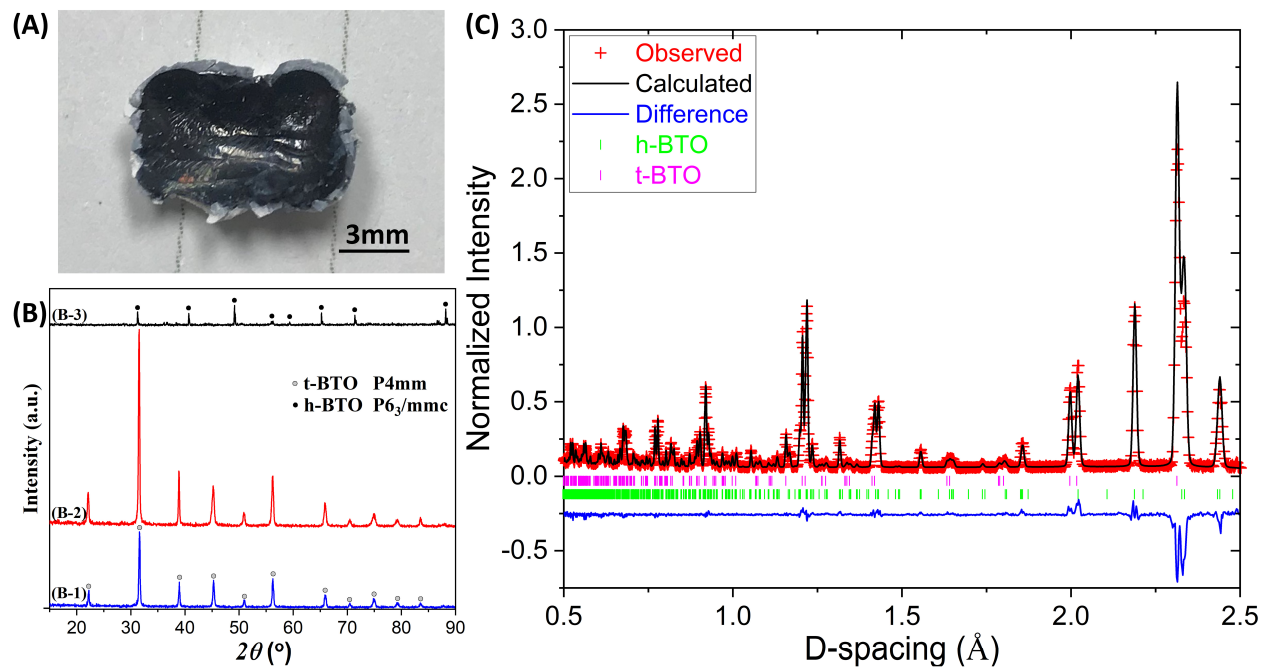
Fig. 2 (A) Photograph of a SLSed BaTiO₃ specimen. XRD of (B-1) BaTiO₃ raw powder, along with bulk BaTiO₃ specimens fabricated by (B-2) pressureless sintering at 1400 ℃ and (B-3) direct SLS; (C) Neutron diffraction with Rietveld refinement measured for powders ground from the SLSed specimen. BTO=BaTiO₃.
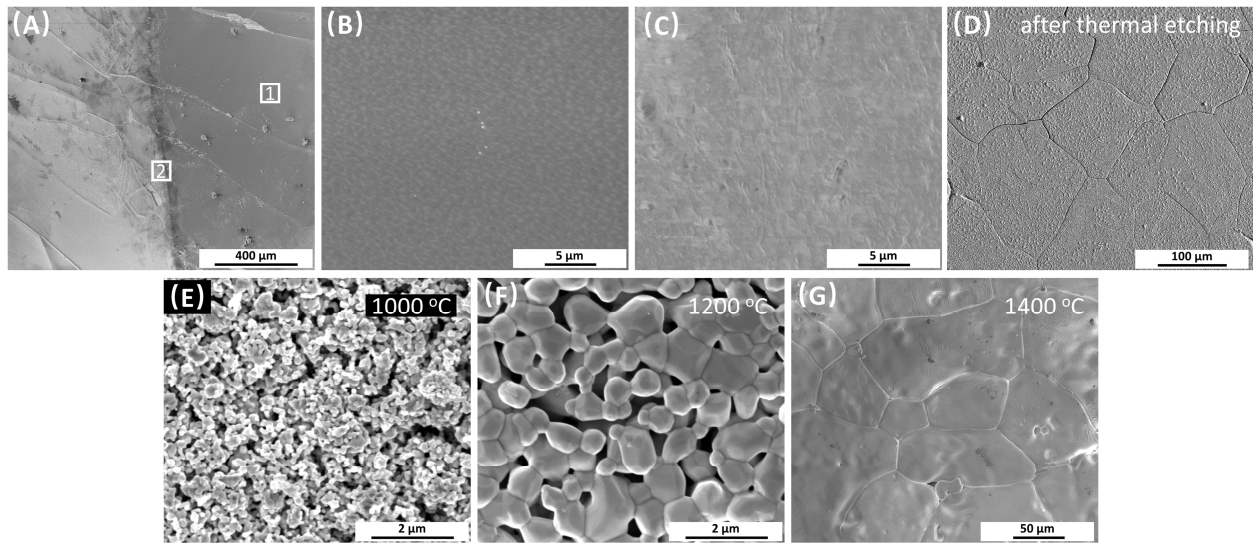
Fig. 3 Scanning electron microscopy (SEM) images of BaTiO₃ ceramics fabricated by direct SLS process: (A) the surface, (B) an enlarged view of the flat area ("1"), (C) an enlarged view of the ridge area ("2") , (D) the polished surface after thermal etching at 1200 °C for 30 min. SEM images of BaTiO₃ ceramics prepared by pressureless sintering at (E) 1000 °C, (F) 1200 °C, and (G) 1400 °C, respectively, for 0.5 hour.
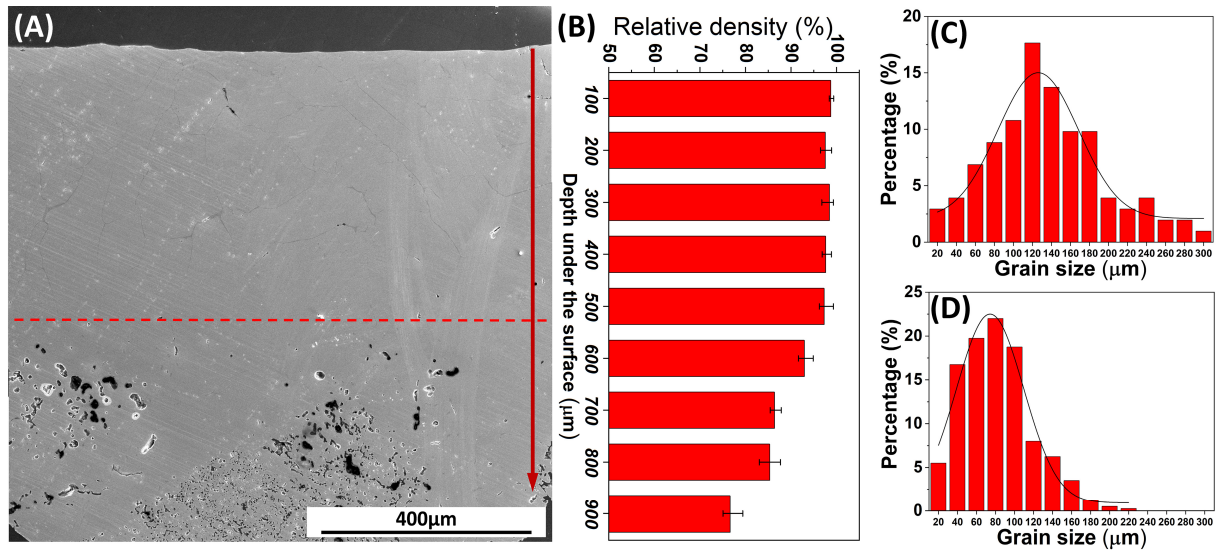
Fig. 4 (A) SEM image of the cross-sectional microstructures of the SLSed BaTiO₃. (B) Relative density as a function of depth from the surface. The grain-size distribution of (C) SLSed BaTiO₃ and (D) pressureless sintered BaTiO₃ (1400 °C for 0.5 hour).
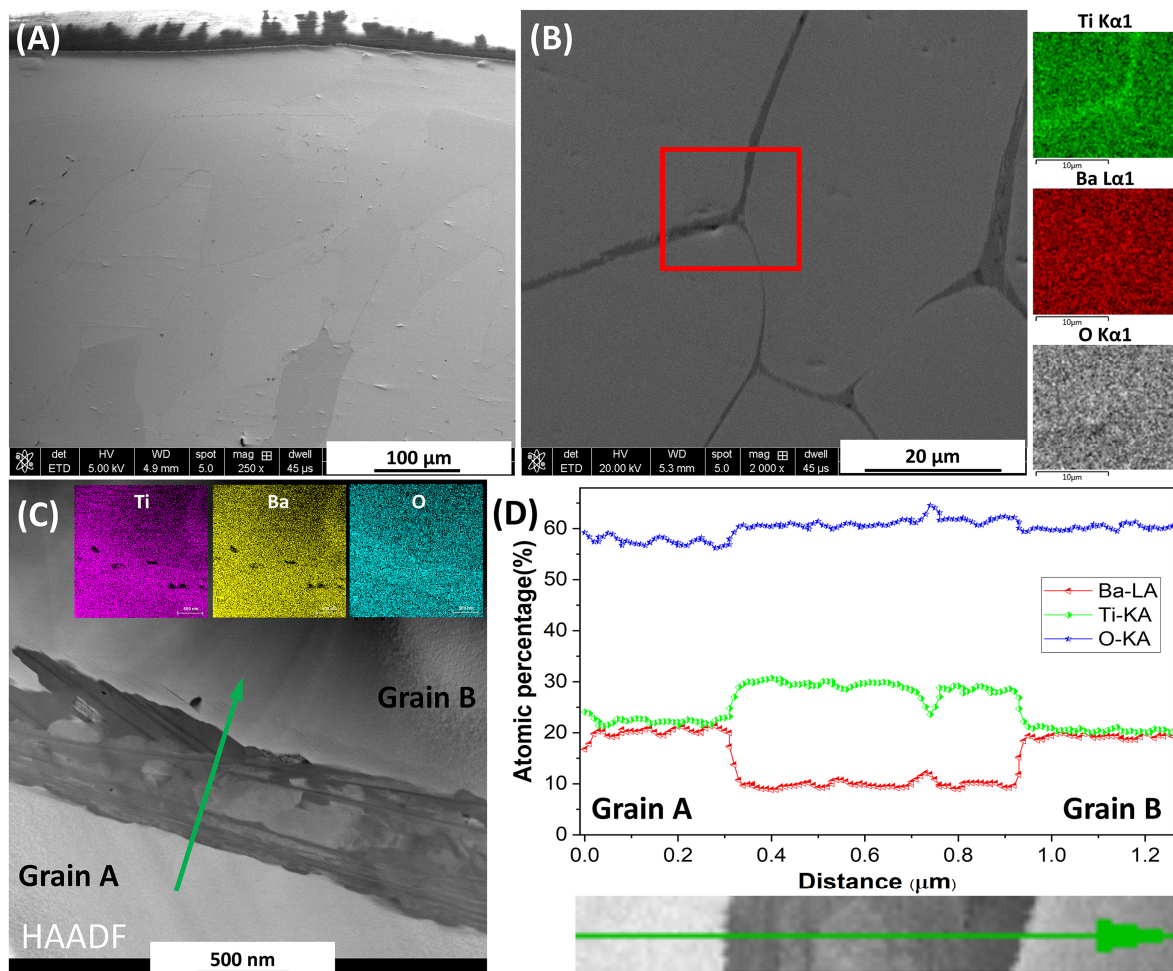
Fig.5 Cross-sectional microstructures of the top dense layer in the direct SLSed BaTiO₃ sample:
(A) low-magnification SEM image; (B) SEM image of an enlarged view of the grain boundaries,
combined with EDS mapping of Ti, Ba, and O elements in the area marked by a red frame; (C)
HAADF image of the grain boundary with the inset EDS mapping of Ti, Ba, and O elements; and
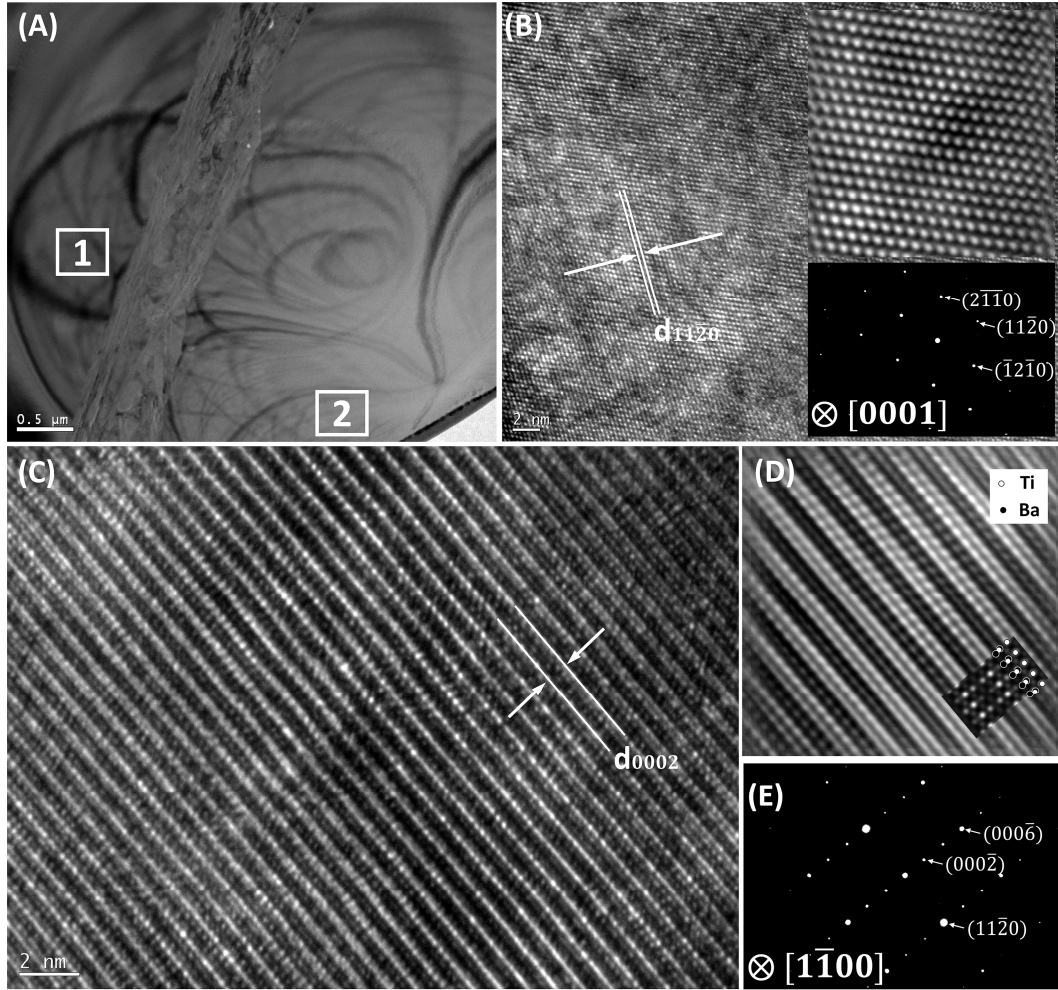(D) EDS line-scanning analysis of Ba, Ti, and O elements along the green arrow.

Fig. 6 TEM characterizations of the top dense layer in the direct SLSed BaTiO$_3$ ceramics: (A) bright-field TEM image of two BaTiO$_3$ grains and a second phase at the grain boundary; (B) HRTEM image of area 1 shows the lattice fringe of $(11\bar{2}0)$ planes, with the inset IFFT image and SAED pattern on the zone axis $[0001]$; (C) HRTEM image of area 2 shows the lattice fringe of (0002) planes; (D) IFFT image with the inset simulated HRTEM image; and (E) SAED pattern on the zone axis $[1\bar{1}00]$.
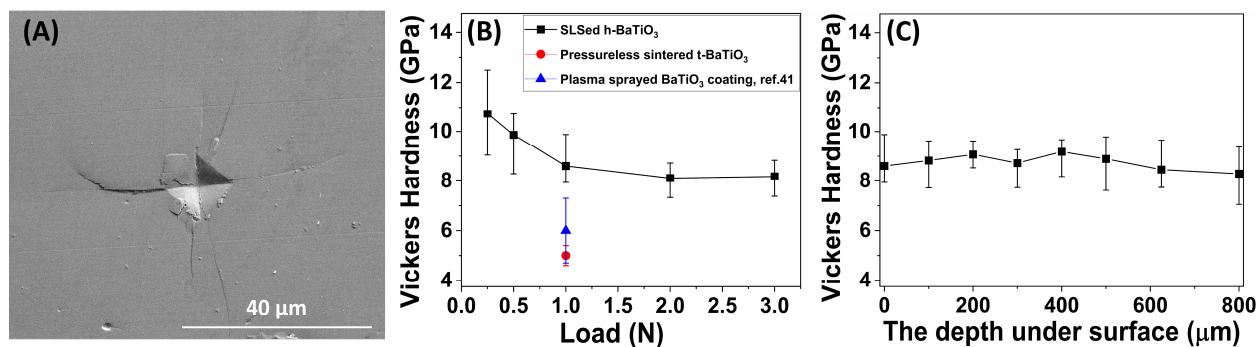
Fig.7 (A) SEM image of a typical Vickers indentation in the SLSed BaTiO₃ sample. Vickers microhardness as a function of (B) the load from 0.25 to 3 N on the surface; (C) the depth at a load of 1 N.