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NEAR NET SHAPE FABRICATION OF PMN SCAFFOLDS

Aylin ŞAKAR-DELİORMANLI[1], Erdal ÇELİK[2], Mehmet POLAT[1]

[1] *Izmir Institute of Technology, Chemical Engineering Department, Urla, Izmir/Turkey*
[2] *Dokuz Eylul University, Metallurgy and Materials Engineering Department, Izmir/Turkey*

ABSTRACT

Solid free form fabrication techniques are commonly employed in near net shaping of ceramics especially in the manufacture of microelectronics. Lead magnesium niobate (PMN) is an important relaxor ferroelectric material with perovksite structure used in the production of these multilayer ceramic devices. In this study two dimensional PMN arrays and three dimensional periodic structures were produced by robocasting which is a direct writing technique. Aqueous colloidal gels have been formulated for use as ink in solid freeform fabrication process. Results showed that complex PMN shapes having rod size down to 100 μm can be successfully produced by robocasting process to be used in microelectronic applications.

Keywords: Shaping, Near Net Shape Fabrication, Robocasting, Perovskites, PMN

1. INTRODUCTION

Lead magnesium niobate is an important electrostrictive, relaxor ferroelectric material with perovskite structure and commonly employed in the production of multilayer ceramic capacitors, actuators, transducers, and motors [1-4]. Electrostrictive actuator is a category of transducers. In actuators it is desirable to enhance the displacement while maintaining the load bearing capability [5]. This can be achieved by manipulating the geometry of simple shape actuators into more complex geometries [6, 7]. Solid free form fabrication (SFF) techniques are able to produce 2-D or 3-D complex periodic structures to use in these application areas [8-16]. Such techniques use computer-controlled robotics to build three-dimensional components layer-by-layer [9, 12].

Robocasting is a free form fabrication technique and uses robotics to control layer wise deposition of ceramic slurries for near net shape processing [13]. The technique utilizes highly concentrated ceramic slurries with a small amount of organic binders [13, 14]. This direct write assembly technique is capable of producing 3D periodic structures consisting rods with different geometrical shapes such as cylindrical, square, hexagonal [15]. It has been utilized for the fabrication of periodic lattices of rods; for piezocomposites [16], 3D microvascular networks and multi-material composites [17-19].

Previously, Lewis and co-workers and Cesarano et al. conducted detailed research on the robocasting of alumina [13, 20], barium titanate [21, 22] and lead zirconate titanate [23] powders and produced different geometries to be used in different applications [24]. The aim of this study is to produce 2D arrays and 3D periodic PMN lattices to use in microelectronic devices and investigate their sintering behavior and microstructural evolution.

2. EXPERIMENTAL

2.1. Materials

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ was provided by Praxair Specialty Ceramics, Woodinville, WA, USA. Powder purity is 99.9% as reported by the manufacturer. Bulk density of the powder is measured to be 7.967 g/cm^3. Particle size, d_{50} of the powder was around 2.0 μm. Stable colloidal suspensions were prepared by adding pol(yacrylic acid) to the system and gelation was induced by adding poly(ethylene imine) PEI. Detailed description of the PMN ink design was reported in our previous study [25].

2.2. Method

Periodic lattices were assembled using a robotic deposition apparatus (JL2000, Robocasting Enterprises, Inc., Albuquerque, NM). Figure 1-a shows the picture of the robocaster that is used in the study and Fig.1-b demonstrates the direct writing operation. The deposition was performed at a volumetric flow rate of 7.5 mm/s. A constant pressure (between 10 – 100 psia) was applied to induce the ink flow through the nozzle. The deposition process was carried out under a non-wetting oil to prevent drying during assembly. Samples were dried at room temperature for 24 hours and at 80 ºC for over night.

For the sintering of 3D periodic lattices following heating procedure were applied: The binder was burned out by heating the samples at 1 ºC/min to 350 °C, 1 h dwell at 350 °C and 3°C/min to various temperatures ranging from 1000 to 1300 °C. During heat treatment, alumina crucible system with cover was used in order to prevent the lead loss from the samples. To provide a lead rich atmosphere, lead zirconate ($PbZrO_3$) powder bed was used inside the crucible.

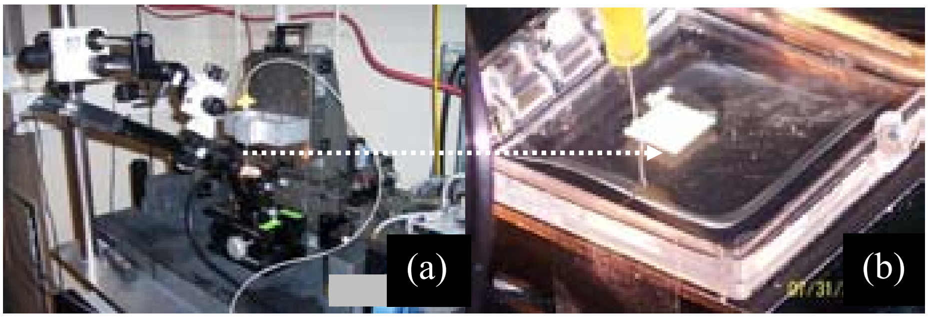

Figure 1 . a) Pictures of the robocasting assembly -deposition module with camera, b) Picture showing the printing process using 100 μm tip, Feature size 5mm.

Digital images of the 3D structures were taken by a Digital Camera (Kodak Easy Share Z650). Optical images of the samples were obtained using a Stereo Microscope (Nikon, SMZ 2T, Light 2) with a camera. Microstructures of the samples were observed using a scanning electron microscope, (Philips, XL-30S FEG).

3. RESULTS AND DISCUSSION

3.1. Robocasting

In the study the PMN inks was robotically deposited onto a moving *x*-*y* stage yielding a 2-D pattern. After a given layer was generated, the stage was increased in the *z*-direction and a second layer was deposited. This process was repeated until the desired 3-D structure was created. Depositions down to 100 μm were successfully performed. Figure 2 show the 3D lattices produced by robocasting method. The pictures were taken just after deposition step therefore the structures are still in oil reservoir. The radial lattice in Figure 2 has a cylindrical symmetry where the top layer is an array of radial lines and the underlying layer is a series of concentric rings. The rings appeared to maintain the arc shape during deposition.

Figure 2. Radial PMN structures produced by robocasting.

3.2. Optical Microscope Images and Microstructral Characterization

Two dimensional arrays and three dimensional assemblies consisting of a continuous spiral pattern and a parallel array of rods were produced by robotic deposition using 100 µm tips, as shown in Figure 3-a and b. Similarly, pictures of three dimensional lattices are shown in the same figure (Fig 3, c-f). Structures produced by PMN inks which contain adequate amount of PEI kept their shape during deposition. Results showed that it was possible to create well shaped, uniform lattices having rod sizes in the range of 100 µm to 500 µm using PMN ink in the presence of 0.04 to 0.06 mg/m^2 PEI. At a PEI concentration of 0.08 mg/m^2 the yield stress of the PMN ink was too high therefore, at this concentration the flow properties of the ink was poor. Above this value some difficulties were observed in shape retention due to decrease in destabilization of PMN inks [25].

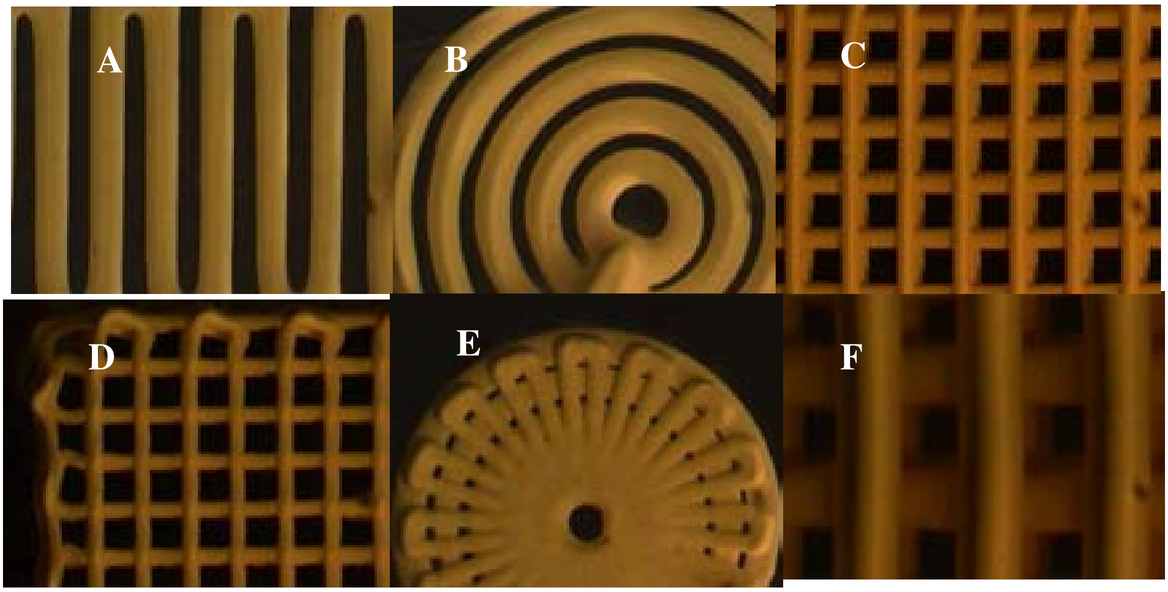

Figure 3. Pictures of two dimensional PMN arrays and three dimensional structures produced by robocasting a) linear array, D: 100 µm b) radial array D: 100 µm c) square lattice, D: 200 µm d) square lattice, D: 100 µm e) radial structure, D: 200 µm f) square lattice, D: 500 µm.

Figure 4 shows the surface view and the cross section of the dried samples produced by robotic deposition. SEM micrographs reveal that samples contain some degree of porosity although they contain negligible amount of binder. It is clear that samples sintered at 1180 °C did not show any shape deformation during processing and kept their homogeneous structures. On the other hand micrographs shown in Figure 4-d demonstrates that samples sintered at 1300 °C have a heterogeneous microstructure and contain high amount of pyrochlore which is an undesired phase. The Figure 5 demonstrates the microstructures of the 3D PMN assemblies sintered at various temperatures. Accordingly, samples sintered at 1000 °C have very high degree of porosity. At 1150 °C a decrease was observed in porosity but samples still have relatively low density. On the other hand, sintering at 1180 °C produced a homogeneous and single phase structure having high densities and low porosity. However, above that temperature (e.g. 1250 °C) significant grain growth was observed. Abnormal grain growth in PMN with a broad distribution in grain sizes compromises the desired electrical properties.

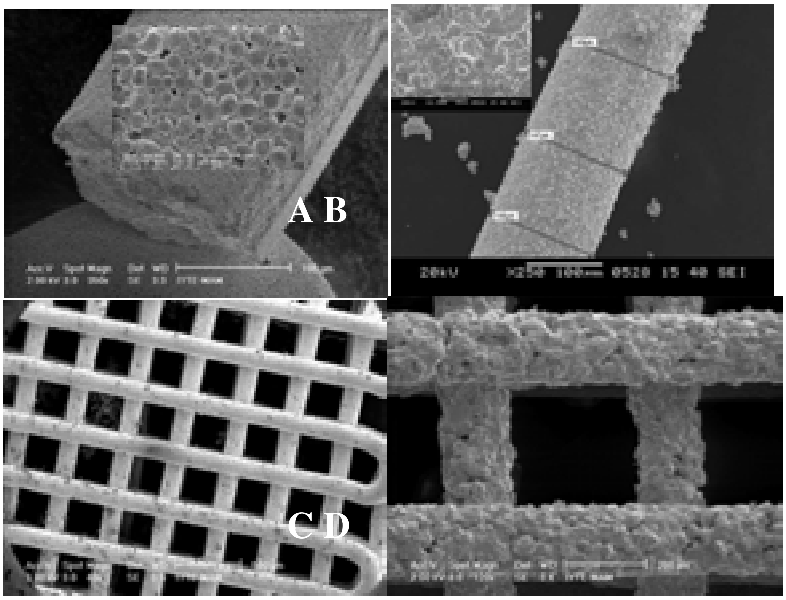

Figure 4. SEM micrographs of the structures produced by robotic deposition method a) green state b) after sintering at 1150 °C for 2 hours c) 1180 °C for 2 hours d) 1300 °C for 2 hours.

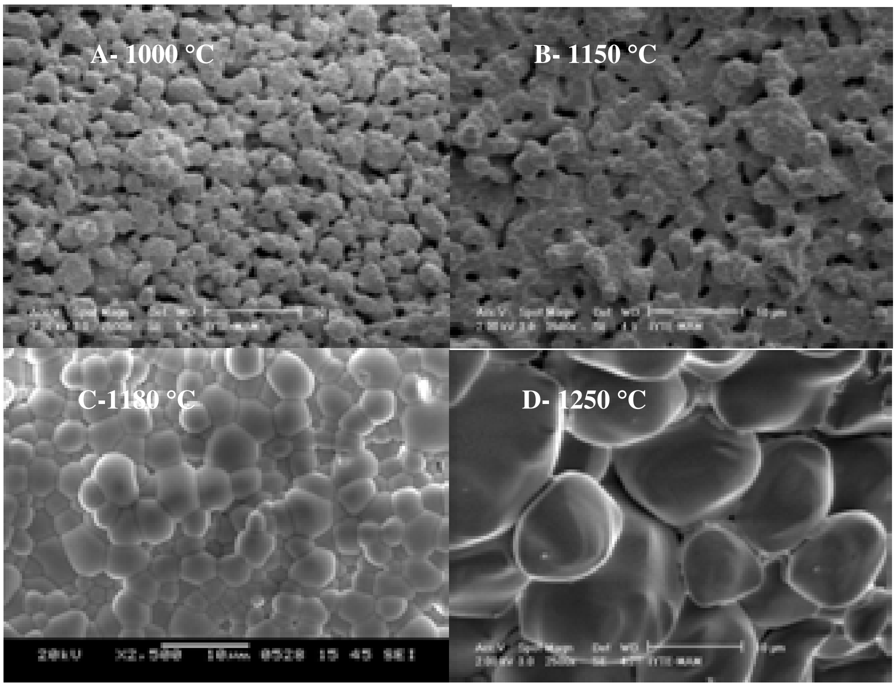

Figure 5. SEM micrographs of PMN samples showing the microstructural evolution as a function of sintering temperature, sintering time 2 hours, heating rate 10 °C/min.

4. CONCLUSIONS

In this study 3D PMN lattices and radial structures were successfully manufactured by robotic deposition method. Results showed that it is possible to produce complex PMN shapes having rod size between 100 µm to 500 µm by this technique. The 3D assemblies sintered at 1180 °C for 2 hours have low porosity, high density and homogeneous microstructures. For future studies our goal is to decrease the rod size and manufacture more complex geometries to be used in microelectronic device applications.

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