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# Fabrication of BaTiO<sub>3</sub> dielectric films by direct ink-jet printing

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#### Abstract

Direct ink-jet printing can assemble ceramic powders into complex 3-D structures by deposited droplets of ceramic inks through a desktop and industrial printing. In this paper,  $BaTiO_3$  films were prepared using 8 vol.%  $BaTiO_3$  colloidal inks. The definition and uniformity of the  $BaTiO_3$  films were determined and adjusted successfully via the variation of the printer and image file resolutions. © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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#### 1. Introduction

A new method of computer-controlled droplet-deposition referred to as 'solid freeform fabrication' (SFF) has been investigated in recent years [1–4]. SFF techniques are tool-less manufacturing methods in which functional components are produced directly from a computer model. They can rapidly fabricate components with geometries that cannot be manufactured by other conventional methods. Direct ink-jet printing [5–15] is one of the most flexible SFF technologies. It is a special fabrication way where ceramic components are constructed from droplets of ceramic ink by an incremental building process.

Ink-jet printers generate and position droplets using one of two different mechanisms: continuous ink-jet printing and drop-on-demand printing. In continuous ink-jet printing, a stream of fluid is passed through a small orifice. The stream disperses into small droplets by Rayleigh instability; this activity is normally controlled by a small, superimposed mechanical oscillation. If an electric charge is imparted to the drops, these drops can subsequently be steered by applying an electrostatic field. Drops not required for printing are captured and recirculated into the reservoir. In the case of drop-on-demand ink-jet printing, the drops are only

formed when required and position control is achieved by mechanically positioning the print-head above the desired location before drop ejection. Both methods of ink-jet printing have been used successfully to build ceramic objects of submillimeter-scaled components and multimaterial devices [9,10]. Continuous ink-jet printer operates at much faster droplet generation rates than drop-on-demand printer; however, the need to use an electrically conducting fluid and the possibility of contamination during the recirculation process limits the ceramic applications. Hence, for this study, we have used a drop-on-demand printer of EPSON C20 model.

In direct ink-jet printing process, ceramic powder passes through the nozzle and so a well-dispersed suspension is required in which the deposition of agglomerates is forbidden. Thus production will cease in preference to the deposition of large particle or agglomeration of a size greater than or equal to the nozzle diameter. In this paper, an 8 vol.% BaTiO<sub>3</sub> colloidal ink has been prepared to fabricate an even and continuous BaTiO<sub>3</sub> film by ink-jet overprinting. The quality of the films were determined and improved successfully through the variation of the resolution of ink-jet printer and picture files.

# 2. Experimental

Ultrafine BaTiO<sub>3</sub> powders were prepared from the hydrothermal process with particle sizes of 100–200 nm, as revealed by SEM. The BaTiO<sub>3</sub> powder was dispersed in

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Table 1
The composition of BaTiO<sub>3</sub> ceramic ink

Composition	Grade and supplier	Content	Density (g cm <sup>-3</sup> )
BaTiO <sub>3</sub>	Synthesized by hydrothermal	8 vol.%	5.81
Polyacrylic acid	$M_{\rm w}=5000$	0.7 wt.% of BaTiO <sub>3</sub> powder	
Water	Deionized	92 vol.%	1.00

water with the addition of a molecular weight 5000 polyacrylic acid (PAA). The ink composition is given in Table 1 and allows the ceramic to be present at 8 vol.% after drying. The PAA was fully dissolved in deionized water before adding the ceramic powder, following adjust pH 12, subsequently suspensions was dispersed using an ultrasonic probe for 15 min.

The colloidal ceramic inks were poured into the ink reservoir of the ink-jet printer. The printer uses a piezoelectric actuator to eject a small quantity of ink from the reservoir immediately behind the print-head. This reservoir is replenished from a large reservoir held above the print-head. In order to use the printer to deposit ceramic films, we need only to replace the desktop printer ink with a suitably dispersed suspension of ultrafine ceramic particles.

#### 3. Results and discussion

Prior to each experimental run, the printer was flushed through with ceramic ink to remove any contamination from previous printing runs. Printing was carried out on a polyester membrane using 20 overprinted layers at a printer defined resolution of 360 dot-per-inch (dpi) to form a constant density film of dimensions  $5 \, \text{cm} \times 7 \, \text{cm}$ . Fig. 1 shows a printed film that was made by using the BaTiO<sub>3</sub> colloidal ink from a computer-generated picture file. The printed film is not perfect and a number of defects are evident: (1) a



Fig. 1. The photograph of ink-jet printed film at 360 dpi resolution using  $8\,\text{vol.}\%$  BaTiO<sub>3</sub> ceramic colloidal ink (printed area  $5\,\text{cm}\times7\,\text{cm}$ ).

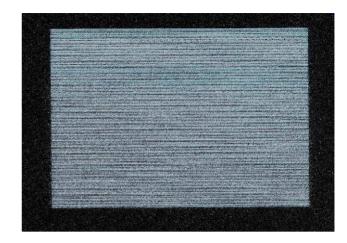


Fig. 2. The photograph of ink-jet printed film at  $720\,\text{dpi}$  resolution using  $8\,\text{vol.}\%$  BaTiO<sub>3</sub> ceramic colloidal ink (printed area  $5\,\text{cm}\times7\,\text{cm}$ ).

lack of definition and uniformity, particularly at the edge of printed regions; (2) a clear banding is visible.

There are two defects related to printer resolution, which is the key to determine print quality. The higher printer resolution is, the larger coating ratio of droplet impact on the substrate surface is. There are two resolutions of EPSON C20 printer, 360 and 720 dpi. It is evident that print quality at 720 dpi resolution is better, but the drying time during the film overprinting process is a little longer.

Fig. 2 shows the photograph of multilayered films printed with a resolution of 720 dpi. Compared to Fig. 1, the definition and uniformity of BaTiO<sub>3</sub> films were improved. The droplets printed on the substrate surface dried quickly to have avoided liquid flowing. Thus, obvious horizontal strips are presented in Fig. 2, which was resulted from the lack of vertical resolution.

Besides, the resolution of image file can also influence the printing quality of the films. The higher quality films can be obtained by using a higher resolution image file (see Fig. 3).

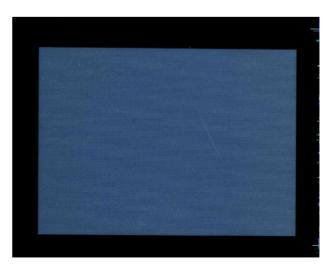
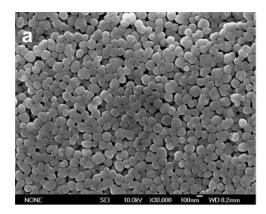


Fig. 3. The photograph of ceramic colloidal ink-jet printed film using higher resolution image file (printed area  $5\,\mathrm{cm} \times 7\,\mathrm{cm}$ ).



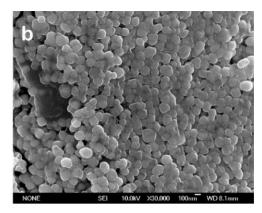


Fig. 4. SEM micrographs of printed BaTiO<sub>3</sub> films: (a) surface and (b) cross-section.

Compared to Figs. 1 and 2, the BaTiO<sub>3</sub> film prepared with high resolution of file and 720 dpi has high definition and uniformity as shown in Fig. 3. It is noticeable that obvious horizontal strips in films have been improved and eliminated.

Fig. 4(a) shows the surface micrograph of the BaTiO<sub>3</sub> film. The size of the particles is uniform and compacted densely. Fig. 4(b) shows the dense accumulation of ceramic particles in the cross-section of printed BaTiO<sub>3</sub> films by 20 layers of overprinting. The pores present in the surface were caused by evaporation of the solvent. The non-uniform pores were dependent on the solid content of ceramic inks. If the porosity and its distribution were optimized and eliminated before sintering, a dense film surface with an interior consisting of a regular array of uniform sized pores could be fabricated. Thus, it is necessary that the design of concentrated colloidal inks with suitable rheological properties is undertaking in our lab.

## 4. Conclusion

In this paper, we have successfully explored the feasibility of preparing a dilute aqueous colloidal ink of  $BaTiO_3$  ceramic nanoparticles with dispersant that can be deposited by ink-jet printing. The  $BaTiO_3$  ceramic films with a thickness of 1.5  $\mu$ m were fabricated by multilayer deposition. The low vapor pressure of water under ambient conditions limits the number and thickness of the possible overprinted layers. Thus, higher solid loading suspensions have been required in the ceramic colloidal inks.

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#### References

- [1] H.L. Marcus, J.J. Beaman, J.W. Barlow, Am. Ceram. Soc. Bull. 69 (6) (1990) 1030.
- [2] E. Sachs, M. Cima, P. Williams, J. Eng. Ind. 114 (1992) 481.
- [3] D. Kochan, Comput. Ind. 20 (1992) 133.
- [4] J. Cawley, P. Wei P, Z.E. Liu, Am. Ceram. Soc. Bull. 75 (5) (1996) 109.
- [5] P.F. Blazedell, J.R. Evans, M.J. Edirisinghe, J. Mater. Sci. Lett. 14 (1995) 1562.
- [6] P.F. Xiang, J.R. Evans, M.J. Edirisighe, Proc. Inst. Mech. Eng. B 211 (1997) 211.
- [7] W.D. Teng, M.J. Edirisinghe, J.R. Evans, J. Am. Ceram. Soc. 80 (2) (1997) 486
- [8] W.D. Teng, M.J. Edirisinghe, Br. Ceram. Trans. 97 (4) (1998) 169.
- [9] J.K. Seong, D.E. Mckean, J. Mater. Sci. Lett. 17 (1998) 141.
- [10] M. Mott, J.H. Song, R.G. Evans, J. Am. Ceram. Soc. 82 (7) (1999) 1653.
- [11] M. Mott, R.G. Evans, Mater. Sci. Eng. A 271 (1999) 344.
- [12] J.H. Song, M.J. Edirisinghe, R.G. Evans, J. Am. Ceram. Soc. 82 (12) (1999) 3374.
- [13] A. Atkinson, J. Doorbar, A. Hudd, J. Sol–Gel Sci. Technol. 8 (1997) 1093.
- [14] P. Blazdell, S. Kuroda, J. Am. Ceram. Soc. 84 (6) (2001) 1257.
- [15] M. Mott, R.G. Evans, J. Am. Ceram. Soc. 84 (2) (2001) 307.