

Fabrication and Properties of an Anisotropic TiO₂ Dielectric Composite

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Thermoplastic co-extrusion was employed to fabricate an anisotropic dielectric composite based on titanium dioxide with a microcellular architecture with 50 μm macropore channels aligned to create unidirectional porosity. The resulting channelled structure exhibits artificial anisotropic dielectric properties, with the dielectric relative permittivity being 9.6 transverse to the channels and 90 in the longitudinal direction.

I. Introduction

NATURAL dielectric anisotropy occurs in non-cubic single crystal dielectrics. Single-crystal TiO₂ in the rutile crystal structure is highly anisotropic, with a relative permittivity (ϵ_r) that varies from 170 (parallel to the *c*-axis) to 86 (perpendicular to *c*-axis),^{1,2} so it has a contrast ratio that is 1.98 in relative permittivity and 1.25 in dielectric loss tangent ($\tan\delta$). Polycrystalline titania has isotropic dielectric properties if it has a random orientation of grains, but can exhibit anisotropy if a degree of grain orientation is achieved. Anisotropy has been reported in polycrystalline titanates with grain orientation induced by directional dynamic ripening³ and in textured thin films.^{4,5}

Anisotropic dielectrics can be useful for resonators. Dielectric resonators are typically designed to operate at a given frequency via the excitation of a specific resonant mode. It is often desirable to have sufficient mode separation to prevent unwanted resonances. Different modes have different electric field distributions. Thus, an anisotropic dielectric could affect different modes by different amounts to enhance mode separation. This concept has been demonstrated previously using an arrangement of metal strips.^{6,7} Recently, Gong *et al.*⁸ reported on novel dielectric devices featuring dielectric ceramics with tailored and anisotropic dielectric permittivity. These were made from polycrystalline titania with random grain orientations. The dielectric permittivity variations were accomplished by controlled variations of porosity using sacrificial carbon to create pores of the desired size and shape.⁹ In this paper, we present the fabrication of a microcellular porous dielectric that offers a high degree of artificial dielectric anisotropy.

The design is illustrated in Fig. 1, showing a dielectric block with aligned cylindrical voids. Such a sample should exhibit anisotropic properties. An applied electric field parallel to the voids would see a high permittivity, while an electric field normal to the voids would see a low permittivity. We selected 37 vol% cylindrical voids to achieve high directional contrast.

To act as an effective medium, the size of the voids should be much smaller than the relevant wavelength. These materials are

designed for frequencies close to 6 GHz, where the wavelength in air is about 50 mm. In fully dense titania, the wavelength for 6 GHz microwaves is about 5 mm. Thus, we seek pores that are about 100 times smaller, or about 50 μm voids. As 50 μm voids are much larger than the grain size of sintered polycrystalline titania, they can be considered to be macropores. Macropores are preferred because they have a smaller pore area to pore volume ratio than do micropores. This reduces the dielectric loss caused by porosity.¹⁰ In addition, small pores are readily eliminated during sintering of titania, which undergoes significant grain growth during sintering.¹¹

To achieve a large number of 50 μm channel pores as a microcellular ceramic, we used the process of microfabrication by co-extrusion (MFCX). This process has been used previously^{12,13} to realize multi-material ceramics with features on this size scale. For this case, co-extrusion is carried out with a titania powder to define the cell walls, and extruded with carbon powder to define the pore channels. The carbon is a fugitive pore former that is removed by oxidation before sintering in air. The development of microcellular architecture involves three extrusion stages to achieve dimensional reduction. We will show that MFCX is a viable process to fabricate composite dielectric media with tailored dielectric properties that can be used as microwave resonators.

II. Materials and Fabrication

The TiO₂ was a commercial powder consisting of 99.8% pure titanium dioxide powder (203-4, Ferro Electronic Materials, Penn Yan, NY) with a particle size of 1.2 μm. It is compounded in a thermoplastic binder at a powder solids loading of 54.1 vol% titania. This corresponds to an 83.4 wt% titania. The thermoplastic binder was a blend of 42.2 wt% poly (ethylene-co-ethyl acrylate) (EEA 6182, Union Carbide, Danbury, CT), 46.7 wt% poly (isobutyl methacrylate) (Acryloid B 67, Rohm and Haas, Philadelphia, PA), 8.2 wt% polyethylene glycol (PEG 1000, Fisher Scientific, Pittsburgh, PA), 1.7 wt% heavy mineral oil (Witco Corp., Petrolia, PA), and 1.3 wt% stearic acid (Crompton #3773B DW, Chemtura Corporation, Middlebury, CT). The nature of this thermoplastic binder has been reported in detail by Knapp and Halloran.¹⁴ The thermoplastic was melted in a high-shear mixer at 120°C, and compounded with the titania powder to create a homogeneous mixture. The mixing was conducted in a torque rheometer (Plasti-corder PL2100, C.W. Brabender, South Hackensack, NY), so that the rheology could be measured. The fugitive material was a high-purity carbon powder with an average particle size of 5.6 μm (Asbury 4023, Asbury Graphite Mills Inc., Asbury, NJ). The carbon powder was compounded in the same thermoplastic at 54 vol% solids in the torque rheometer, and rheology was adjusted by minor additions of mineral oil until it matched the titania compound. These loaded thermoplastic compounds were warm molded at 125°C and 12 MPa in a die to make two 25.4 mm diameter rods: a white rod of the titania thermoplastic and a black rod of the carbon thermoplastic.

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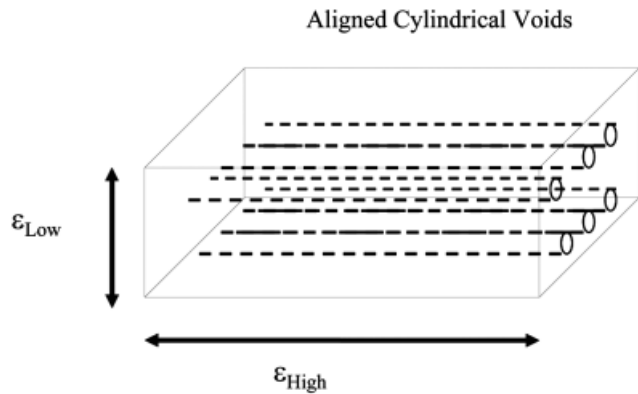


Fig. 1. Design of an artificially anisotropic dielectric with longitudinally aligned cylindrical voids. Relative permittivity is high in the longitudinal direction, and low in the transverse direction.

The three-stage extrusion process of MFCX is illustrated in Fig. 2. For the first stage, the white (TiO₂) rod and the black (carbon) rods are separately extruded using a heated piston extruder (Bradford University Research, Bradford, UK) with a 3.25 mm diameter die to produce white and black filaments 3.25 mm in diameter. Extrusion is performed at 115°C using a feed rate of 3 mm/s. These small filaments are bundled to fabricate a master feed rod. The master feed rod is formed by surrounding seven carbon filaments by 12 TiO₂ filaments so that 7/19 or 36.8% consists of sacrificial carbon material. This bundle is warm molded into a cylindrical rod to form the core of the master feed rod. These master feed rods are extruded in a second stage through a reduction die to achieve 3.25 mm diameter filaments that have a core-shell geometry with a carbon core surrounded by a titania shell. These core-shell filaments are bundled once again by warm molding a final feed rod from 38 core-shell filaments. In the final stage, this feed rod is co-extruded through a 1 mm diameter die to yield final co-extruded filaments containing 38 axially aligned carbon channels in a titania matrix. The carbon channels become the aligned pores, with the titania matrix becoming the solid cell walls.

To fabricate the anisotropic material, we mold a rectangular block from the co-extruded filaments. The 1 mm filaments are cut into 47 mm length, and about 250 pieces are aligned in a 44 mm × 47 mm rectangular die. The die and fibers are heated to 135°C for 1 h. The fibers are assembled and consolidated into a solid block by applying a pressure of 20 MPa for 15 min. The final green block is 4.47 mm thick. A 13 mm × 13 mm square is cut from the green block. Green bodies are placed on a bed of

sintered TiO₂ inside an alumina crucible. Binder removal is performed in flowing air using a 3-day heating schedule. Binder removal is completed at 520°C and carbon removal is completed at 640°C. After binder removal, the sample is fired at 1300°C (2 h) in air using a heating and cooling rate of 10°C/min. This sintering temperature produced cell walls with a relative density of 90% of theoretical, which is preferred for low dielectric loss in sintered titania.¹⁵

Micro-computed tomography (Micro-CT) images were taken to verify non-destructively the internal structure of the anisotropic dielectric. Images were obtained with 15 μm voxel resolution using GEMS Microview software (MS-130 Micro-CT, GE Medical Systems, Toronto, Canada).

III. Results and Discussion

(1) Fabrication Results

An optical micrograph of the as-molded green body is shown in Fig. 3. This shows the cut end of the green block, showing remnants of the previously round 1 mm co-extruded filaments. These have been distorted by plastic flow during the consolidation to form irregular polygons. The 38 carbon filaments are visible within each of the polygon, with significant distortion of those carbon filaments near the edges of the polygons.

The structure after sintering is shown in Fig. 4. On the left is a scanning electron micrograph at approximately the same magnification as the previous optical micrograph of the green structure. The microcellular architecture is obvious, with irregular polygonal domains consisting of aligned pore channels surrounded by sintered titania cell walls. Linear shrinkage during sintering was about 17%. The aligned channel pores were typically 50 μm, but some smaller channel pores were present due to co-extrusion flaws and distortions during molding. Direct counting of domains and pores gave an areal density of the polygonal domains of about 200 cm⁻², with an areal density of the pore channels at about 7400 cm⁻². On the right of Fig. 4, there is a higher magnification view of the sintered titania cell wall. The average grain size of the polycrystalline titania was 5.6 μm, with about 10% residual porosity within the cell walls present as 1–2 μm diameter micropores. The relative density for the anisotropic dielectric measured by the Archimedes method showed an overall porosity of 47%. This corresponds to 10 vol% residual micropores in the cell walls and 37 vol% aligned macropores.

Figure 5 shows the three-dimensional image of the anisotropic pores, shown as a vertical section superimposed on a horizontal section. Dense regions are shown as bright white and less dense regions are shown as dark gray/black. It corresponds very well to the structure observed via SEM in Fig. 4 and in agree-

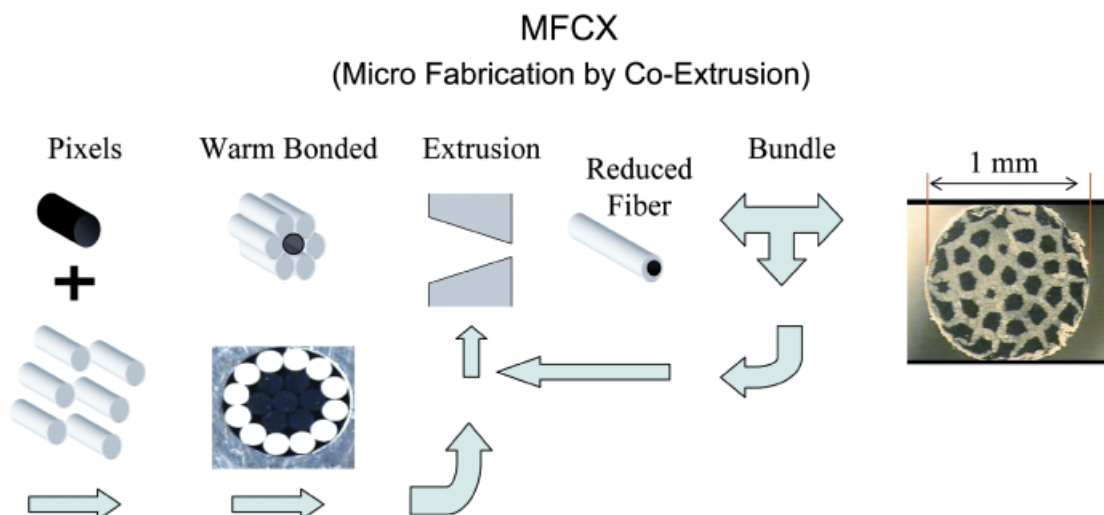


Fig. 2. Process diagram for Micro Fabrication by Co-Extrusion (© 2005 IEEE, Gong *et al.*⁸).

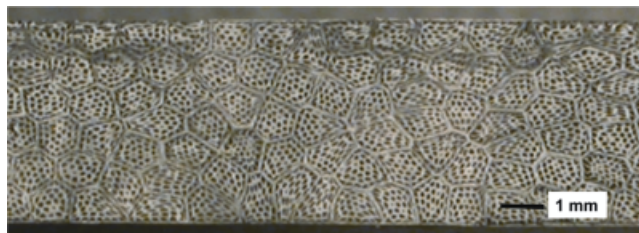


Fig. 3. Edge view of the green body formed after warm fiber consolidation.

ment with the tailored microarchitecture. However, this slice is observed much deeper in the sample. The near-parallel streaking in the Z-direction (parallel to the filament direction) indicates very good pore alignment. Analysis of the complete micro-CT data shows some fiber twisting and out-of-plane movement of a given pore channel, but the overall pore alignment from sample end to end is rather good for the bulk of the specimen. Note, however, the relatively poor alignment near the back of the sample, where die wall friction during pressing distorted filament alignment.

(2) Dielectric Properties

The dielectric characterization has been reported in more detail elsewhere.⁸ A low-frequency (30 MHz) capacitance measurement (Agilent 4263B LCR meter, Palo Alto, CA) was conducted to extract the effective dielectric constant in different directions before high-frequency resonance. The effective dielectric constant along the channel direction was 89. The effective dielectric constant perpendicular to the channels was 12. These low-frequency values will be shown to be close to, but not exactly the same as, the high-frequency values extracted by simulation (Ansoft High Frequency Structure Simulator—HFSS, Ansoft Corp., Pittsburgh, PA) of cavity resonance, which may be due to some imperfection of the alignment of channels.

For the cavity resonance experiments, the sample was placed inside a rectangular waveguide cavity and measured in two orientations. Measurements were performed using a two-port transmission configuration. The cavity was undercoupled during calibration and sample measurements. Conductive losses of the cavity were characterized by measuring and simulating the empty cavity and were accounted for in the sample simulations.

The first orientation is the 0° orientation, which has the channels aligned with the long side of the cavity, and the second orientation is 90°, which has the channels aligned with the short side of the cavity. The first transmission peaks for both orientations were identified with the TE₁₁₀ cavity mode, which are only affected by the permittivity perpendicular to the channels. These occurred at 5.43 GHz for the 0° orientation and 5.44 GHz for the 90° orientation. The unloaded quality factors Q_U for these

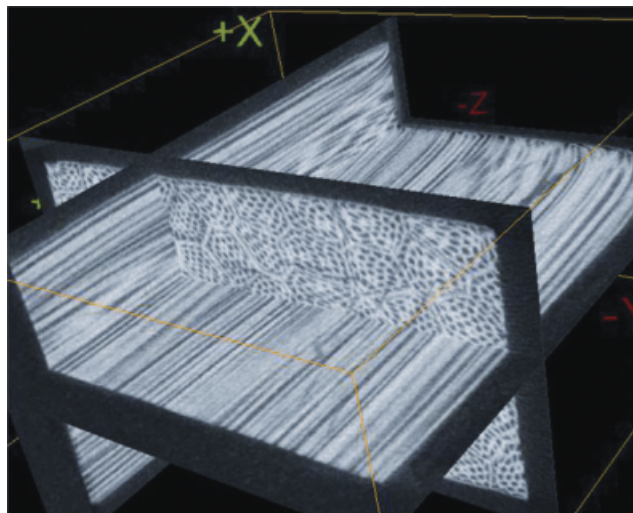


Fig. 5. Micro-CT image of the TiO₂ anisotropic material showing the aligned pore structure.

resonances were 2798 for 0° orientation and 2879 for 90° orientation. Using HFSS simulation, the permittivity in the transverse direction (perpendicular to the pore channels) was determined to be 9.6. The effective loss tangent in the transverse direction was determined from matching Q_U to be 1×10^{-4} .

The second transmission peak for the 0° orientation was the lowest dielectric resonator (DR) mode, at 6.45 GHz with a Q_U of 1470. For the 90° orientation, the second peak was a higher DR mode at 7.11 GHz with Q_U of 1815. The effective dielectric properties in the longitudinal direction (parallel to the pore channels) were fit to a permittivity of 90 and a loss tangent of 9×10^{-4} . The simulated resonance based on these effective properties fit the measured frequencies within 2.4%.

In the case of random unoriented pores, a sample with similar total porosity would have an isotropic effective permittivity. Using the Bruggeman effective medium model, an isotropic sample with 37% or 47% total porosity would exhibit a relative permittivity of 51 and 39, respectively. This behavior has been characterized previously in TiO₂.⁹ Although the Bruggeman assumptions are not valid in the present case, it is useful to compare the random case with the oriented pores in the anisotropic sample to elucidate the importance of orientation. The pore alignment creates two directional effective permittivity values of 90 and 9.6—values much different from a randomly porous TiO₂ at the same pore fraction. The contrast ratio for this artificial anisotropic titania is $90/9.6 = 9.4$ for the relative permittivity and $10^{-3}/9 \times 10^{-4} = 9$ for the loss tangent.

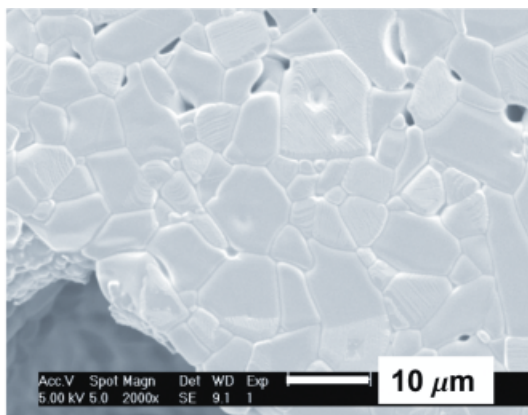
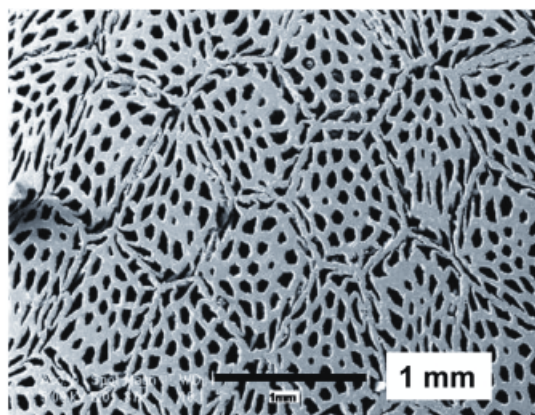


Fig. 4. (Left) SEM micrograph showing the pore structure (© 2005 IEEE, Gong et al.⁸) (Right) Microstructure of the dense walls.

Although we realized this design using thermoplastic co-extrusion, the major features could have been realized by conventional extrusion with a honeycomb die, with appropriate changes in design to account for differences in cell size and wall thickness. A fine-scale ceramic honeycomb (such as Celcor 900/2, Corning Inc., Corning, NY) offers cells in a size comparable with the polygon domains in the co-extruded materials described herein, without the finer scale 50 μm channel voids.

IV. Conclusion

Thermoplastic co-extrusion was used to fabricate an anisotropic dielectric composite based on titanium dioxide with microcellular architecture with 50 μm macropore channels aligned to create unidirectional porosity. The resulting channeled structure exhibits artificial anisotropic dielectric properties, with the dielectric permittivity being 9.6 transverse to the channels and 90 in the longitudinal direction. The contrast ratio in permittivity and loss tangent was greater than 9:1, demonstrating that artificially anisotropic dielectrics can be designed with high anisotropy.

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