SOL-GEL DEPOSITED THICK FILM BISMUTH TITANATE
BASED TRANSDUCER ACHIEVES OPERATION OVER 600 °C

Department of Engineering Science and Mechanics.
The Pennsylvania State University
University Park, Pa, 16802

ABSTRACT. Piezoelectric bismuth titanate based thick film transducers were deposited onto steel substrates using a sol-gel deposition method. The coated samples were microwave sintered at a temperature of 850 °C for 10 minutes. Samples had d33 values in the range of 10-18 pC/N with signal to noise ratios up to 64 dB on a 1.6 cm thick steel block at room temperature. The films tested proved to be capable of ultrasonic wave generation up to and over temperatures of 650 °C.

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INTRODUCTION

There are many practical scenarios in engineering that require real time system analysis and characterization but methods capable of doing so are often limited because of extreme operating conditions. Among the list of such extreme conditions are systems which demand operation at elevated temperatures, often including and exceeding temperatures of 500 °C. Ultrasonic non-destructive techniques using piezoelectric transducers are advantageous because they permit one to analyze multiple properties of systems quickly and reliably; however while monitoring at elevated temperatures such techniques are often restricted due to effects such as transducer depolarization or difficulty achieving mechanical coupling.

Bismuth titanate (Bi4Ti3O12) is a potential candidate for high temperature ultrasonics because of its relatively high Curie temperature and relatively strong piezoelectricity. In this paper thick film bismuth titanate based transducers are deposited onto stainless steel substrates using a sol-gel deposition technique. The sintering of the film was carried out using the newly emerging sintering method involving microwave energy at 2.45 GHz. The fabricated transducers have demonstrated operational capabilities to temperatures exceeding 650 °C.

EXPERIMENTAL

Bismuth titanate is a ferroelectric material discovered in 1949 by Aurivilius and has the so-called Aurivilius or bismuth layered perovskite structure. It is represented by
the general formula (Bi$_3$O$_2$)$_{2+}$($A_{n-1}B_nO_{3n+1}$)$^2$ (n=3 for bismuth titanate) [1-6]. Conventional preparation of bismuth titanate utilizes a mixed oxide technique in which Bi$_2$O$_3$ and TiO$_2$ are mixed in stoichiometric amounts, calcined and sintered [6-7]. Fabrication of thin film bismuth titanate can also be achieved through physical vapor deposition, chemical vapor deposition, metal organic chemical vapor deposition, and sol-gel methods [2],[8-10]. Kobayashi et. al [11-12] adapted the sol-gel technique for fabrication of thick film materials and is the basis for fabrication procedure explained later. The method is economical and relatively simple, and allows for direct application of the bismuth titanate to metallic substrates therefore eliminating the need for high temperature couplants/adhesive layers.

For the film preparation, bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O) was first dissolved in glacial acetic acid at 80$^\circ$C with constant stirring and then allowed to cool. A stoichiometric amount of titanium isopropoxide (Ti(OC$_3$H$_7$)$_4$) was then added resulting in a clear solution. The solution was then hydrolyzed with H$_2$O in a volumetric ratio of solution to water 2:1. Bismuth titanate powder was then added to the solution. Next a high intensity ultrasonic horn was used to mix the powder/solution mixture eliminating powder agglomerates and reducing average particle size. The mixture was sprayed onto a substrate using an air gun. After a thin later was sprayed the sample was placed onto a hot plate at 400 $^\circ$C to burn out residual organics. The spraying/heating process was repeated until the desired thickness is achieved.

Next in the procedure was sintering of the samples. First attempts using conventional heating processes often resulted in poor adhesion of the bismuth titanate or poor sensor quality. To overcome these setbacks, microwave processing techniques were employed. In microwave sintering of ferroelectric materials at 2.45 GHz the material is heated primarily through polarization/dipole rotation losses; resulting in a volumetric heating of the sample in contrast to interfacial heating experienced with conventional heating techniques [13]. Other works on microwave sintering of bismuth titanate compounds have reported that lower soak times and temperatures are required to achieve similar microstructures and percent theoretical densities of samples sintered using conventional heating techniques [14],[15].

The rate of microwave absorption per unit volume is generally expressed as:

$$P_a = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E_{ma}^2 + \mu_0 \mu''_{\text{eff}} H_{ma}^2$$

where $\varepsilon''_{\text{eff}}$ is the effective relative dielectric loss factor, $\omega$ is the frequency of microwaves used, and E is the internal electric field. The second term of (1) refers to the magnetic component of the microwave absorption and its effect in heating is often neglected for ferroelectric materials. Samples sintered using microwave heating have demonstrated superior adhesion and quality to those sintered using conventional heating techniques.

Fig. 1 schematically illustrates a microwave sintering system used. It is comprised of a microwave generator, circulator, waveguide and cavity. During sintering samples were placed inside a microwave transparent insulator made of fiberfrax. Alumina rods coated with carbon powder were used as susceptors to help heat the bismuth titanate at lower temperatures. Samples were sintered using microwaves at a frequency of 2.45 GHz in a multimode cavity in atmospheric conditions at temperatures of 875$^\circ$C with soak times of 10 minutes Generally the power required to maintain the sintering temperature is between 1-2 kW. Temperature measurements were made using an optical pyrometer.
FIGURE 1. Illustration of microwave sintering setup.

After sintering the samples were poled using the corona poling method. In this method samples are heated on a grounded metallic hotplate to 200$^\circ$ C. An array of metal needles is brought close to the sample surface. High voltage is applied to the needles until discharge is observed (usually between 10-20 kV). The voltage applied is maintained at 200$^\circ$ C for 10 minutes then the sample is allowed to cool down while the voltage remains applied. After corona poling gold electrodes were sputtered onto the sample. Samples are then poled again in a silicone oil bath at a temperature of 150$^\circ$ C for 10 minutes.

SENSOR PERFORMANCE AND CHARACTERIZATION

Fig. 2 shows SEM images taken of one sample at different locations. The samples appear to have a relatively high porosity. The density is estimated visually to be around 60%. It is also interesting that the sample microstructure varies greatly from one region to the next. This is thought to be because of non-uniform nature of powder/solution mixture.

In some tested samples signal to noise ratios as high as 65 dB were observed. The time and frequency domains of one such signal is shown in Fig. 3. In this case the

FIGURE 2. SEM images of sintered samples at different locations on the sample. Length scales: (a) 1 $\mu$m, (b) 100 nm and (c) and (d) at 2 $\mu$m.
substrate was a 1.6 cm rectangular block of steel. The voltage spike was 400 V. Signal gain was 60 dB and the signals were filtered using a band pass filter that allowed frequencies between 1-10 MHz.

To test the samples response at elevated temperatures an experiment was setup such that the bismuth titanate operated in pulse-echo mode while inside an oven. The temperature was raised until an ultrasonic response was no longer detected. Since solder cannot be used at very high temperatures the experimental setup shown in Fig. 4 was devised. The bismuth titanate/steel substrate was sandwiched between two bars of steel. One steel bar was coated with a high temperature epoxy and the positive wire lead ran between the electrode on the bismuth titanate and the epoxy layer. The second steel bar was grounded and would be in contact with the steel substrate. Tight contact was achieved by running nuts and bolts through both steel bars and tightening them. This setup was designed such that as the apparatus would heat, the nuts and bolts would expand, preventing loss of electrical contact from thermal expansion. The apparatus was placed inside the oven with uninsulated wire leads running out of opposite ends of the oven. An omega K-type thermocouple with an Omega HH81 digital readout was used to measure temperature inside the oven. The heating rate recorded inside the oven was, on average, 1.5 °C/min.
FIGURE 4. Illustration of high temperature experimental setup.

The sample tested had a 1.35 cm thick steel substrate with a gold electrode area of 3.4 cm². A 100 V tone burst with a frequency of 3.1 MHz and a pulse width of 0.82 µs was used to excite the bismuth titanate. The received signal was filtered using a band pass filter allowing 1-5 MHz with a gain of 60 dB. The signal recorded at room temperature is shown in Fig. 5. In this case the signal contains a much higher noise floor which is assumed to occur because the length of wires used (about 1.5 m). Fig. 5 and Fig. 6 show comparisons of the first back wall reflection obtained at various temperatures. The frequency domains of the signals were plotted but changed little with temperature, as was expected since tone-burst excitation was being used. These plots have been omitted for brevity.

From the echographs it is seen that signal degradation did not seem to occur until around temperatures of about 450° C, at which point signal amplitude began to decay rapidly as a function of increasing temperature and by 680° C, just shy of the reported Curie temperature for Bi₄Ti₅O₁², the signal was lost completely. Signal arrival time lengthened as temperature increased. The primary mechanism for this is believed to be the reduction of the acoustic velocity in the materials as temperature increases (increased travel path because of thermal expansion is assumed to be small due to the nature of the experimental setup described earlier).

It was unexpected that the material was capable of ultrasonic wave generation so close to its reported Curie temperature. It was originally anticipated that efficiency would decrease more at lower temperatures and by about 550° C the material would no longer have been capable of sending/receiving ultrasonic signals. To test if the sample could maintain operation at such high temperatures, the sample was repoled and the experiment was repeated, this time however the sample was heated to a temperature of 600° C and held for an extended period of time.

The sample maintained its functionality at this temperature for over an hour with minimal amplitude loss, confirming that operation at this temperature is indeed viable. The temperature was then raised to 625 °C. After 3 hours at this temperature a signal remained with only slight amplitude loss over time. These waveforms are shown in Fig. 7.

Why the transducer has been able to achieve operation up until this temperature is yet to be understood. It may be possible that transduction efficiency of bismuth titanate remains relatively high until just short of its Curie temperature. It was also learned after the experiment was performed that the high temperature epoxy used to keep the positive lead in contact with the electrodes contains magnesium oxide and mono magnesium phosphate.
FIGURE 5. Comparison of signals obtained at (a) 23 – 200 °C, (b) 200-400 °C and (c) 550-650 °C, and (d) 650 – 681 °C.

FIGURE 6. Comparison of signals obtained over the entire tested temperature range.
Magnesium is known as an acceptor dopant of bismuth titanate. It may be possible that some magnesium may have integrated itself into the crystal structure of the bismuth titanate, increasing its Curie temperature. Later attempts at repoling the sample proved to be difficult. This would support the suggestion that possible magnesium doping may have occurred since this would have increased the materials conductivity.

CONCLUDING REMARKS

Thick film bismuth titanate based transducers were successfully deposited onto steel substrates using a microwave sintering technique. Samples with SNR values up to 65 dB have been achieved and samples have demonstrated operation capabilities up and over 650° C. Such a high operating temperature may have been achieved through unintentional magnesium doping of the material. Further elemental analysis of the sample is required to determine if this is indeed the case.

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