ELECTRICAL AND OPTICAL PROPERTIES OF PZT THICK FILMS IN HIGH TEMPERATURE FLEXIBLE ULTRASONIC TRANSDUCERS FOR STRUCTURAL HEALTH MONITORING AND NDT

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ABSTRACT

Lead-zirconate-titanate composite films (PZT-c) deposited by the sol-gel spray technique on metal membrane for the fabrication of flexible ultrasonic transducers (FUTs) and developed for structural health monitoring (SHM) and non-destructive testing (NDT) applications was found to be absorbent in the ultraviolet light spectrum with its absorbance edge at approximately 400 nm in its as-deposited wet state. The absorbance edge was observed to shift to higher wavelengths with each 10-minute heat treatment performed at 350, 450, 550°C. After the heat treatment at 550°C, the absorbance edge had shifted to 470 nm. The composite film was also found to be photoconductive when illuminated with a xenon locked-in source and measured with a four-point probe technique. A capacitance measurement performed during heat treatment from room temperature to 350°C under dark and illuminated UV conditions showed a change in charging effect with illumination.

Keywords: Flexible ultrasonic transducer, High temperature, Photoconductive sol-gel composite film, UV absorbent, Structural health monitoring
INTRODUCTION

The development of thin and thick composite ceramic films has been of significant interest for applications in high temperature (HT) ultrasonic non-destructive testing (NDT) [1, 2] or structural health monitoring (SHM) [3, 4] in industrial settings using ultrasonic transducers (UTs) and techniques. This has been of particular interest to the energy and industrial sectors as broad frequency bandwidth UTs are desired to achieve high spatial resolution for pipe thickness measurements or defect size inspections [5-6]. Typical HT broadband frequency bandwidth UTs may be bulky and non-flexible since they generally require a backing to serve as an ultrasonic damper. They may be bonded onto a delay line [1], which renders it equally bulky. Alternative ways to fabricate HTUTs that are non-bulky and conformable to pipes have been demonstrated by the sol-gel spray method [7,8] using various sol-gel materials such as PZT and Bizmuth Titanate (BiT) [9, 10].

Commercially available FUTs made from piezoelectric polymers such as polyvinylidene fluoride (PVDF) [11] and piezoelectric ceramic/polymer composites [11, 12] include polymer, which prevents the use of such flexible UTs at elevated temperatures. Operating frequencies were normally higher than 30 MHz and these may not be suitable for NDT and SHM of thick and highly attenuating materials. The sol-gel spray method used in this lab for the development of FUTs is commercially attractive due to its ability to be deposited as thick films.

The potential of such sol-gel composite films for such applications is high due in part to the high piezoelectric efficiency of such films that have been proven to be comparable to commercially available ultrasonic transducers [9,13] and due to its inherent flexibility and porosity rendering them conformable to different curvatures [9]. The fabrication of the FUT consists of sol-gel based sensor fabrication process [7] and may be done in 6 steps [9]. High volume production of such non-bulky, flexible HTUTs may be aided by the development of efficient methods of fabrication to reduce time, energy and costs. The use of intrinsic illumination to assist in the curing or firing of the PZT and BiT composite (PZT-c, BiT-c) films consisting of sol-gel PZT and used for such HT FUT fabrication is possible as sol-gel PZT has shown to exhibit enhanced ferroelectricity with UV exposure [14-16].

The objective of this investigation was to study the effect of UV on such sol-gel sprayed composite films used to fabricate HT FUTs. The goal was to characterize some photo-induced effects of film that were prepared and treated by the same steps as those used in the fabrication of HT FUTs in this lab. PZT-c films were sprayed with an air gun and were either heat treated in air inside a furnace at different temperatures, up to 650°C or air dried prior to measurement. HT FUTs fabricated have shown flexibility similar to PVDF FUTs [9, 19] and may operate at up to at least 150°C if fabricated with PZT-c [9] and 450°C with BiT-c [9, 10]. The study conducted in this investigation made use of the PZT-c films as the Curie temperature was lower than BiT-c films and therefore more amenable to conduct the temperature dependent measurements described.

EXPERIMENTAL PROCEDURES

Absorbance measurements were taken with a Thermo Scientific spectrometer on PZT-c sprayed onto a quartz slide that had been 1) dried for 10 minutes in an oven at 100°C and then treated at 350, 450, 550 and then 650 °C for 10 minutes each. A second set of absorbance measurements were taken with a Thermo Scientific spectrometer on PZT-c sprayed onto a quartz slide that had been 1) dried for 10 minutes in an oven at 100°C and then treated at 350, 450, 550 and then 650 °C for 10 minutes each. A second set of absorbance
measurements were taken for PZT-c sprayed onto another quartz slide after it had been 1) air dried for several hours and then 2) exposed to high intensity UV light for several minutes by a Thor Labs CS410 high intensity UV curing gun (peak wavelength of 365 nm). A third set of absorbance measurements were taken for PZT-c film sprayed onto 5 different glass slides, each treated under separate conditions, either air drying or drying at 100°C and then firing at either 350, 450, 550 or 650 °C.

Photoconductivity of the PZT-c film was measured by the 4-point-probe technique under dark and illuminated conditions, the latter of which was performed with a Newport 150W Ozone Free Xe Lamp, with optical chopper and lock-in amplifier. A first measurement was taken for one PZT-c that had been sprayed and air dried for several hours. A second measurement was taken for a second PZT-c that had been dried at 95 °C for 10 minutes and then fired at 650 °C for 10 minutes.

Temperature dependent capacitance measurements were performed with an Agilent 4294A impedance analyzer during heat treatment of a sample on a hot plate from room temperature to 360 °C. The temperature was monitored with a thermocouple and the measurement was conducted for PZT-c sprayed on a 25 µm stainless steel membrane with a 3.5 mm diameter transparent indium tin oxide (ITO) top electrode. As it is the case for FUTs fabricated in this lab, the steel membrane acted as the bottom electrode. The PZT-c films had been dried for 10 minutes at 95°C and fired at 650°C for 10 minutes. The temperature dependent capacitance measurement was then measured under dark and illuminated conditions with a 200W Newport Hg lamp. The resistivity of the ITO top electrode was measured prior to experiments to be 17 Ω/□. All heat treatments in this study were performed in air and inside a furnace.

**OPTICAL PROPERTIES IN SOL-GEL PZT-C FILM USED TO FABRICATE HT FUT**

Absorbance measurements on sol-gel PZT-c film

A first absorbance measurement was taken from PZT-c sprayed onto one quartz slide, which was first dried at 100°C for 10 minutes and then heat treated in a furnace before each measurement. Heat treatments were performed at 350, 450, 550 and 650°C for 10 minutes each.

The result is presented in Fig. 1 (a) and shows the absorbance of the PZT-c film to UV with the absorbance edge shifting to longer wavelengths with each higher temperature treatment until up to 550 °C and then a slight shift to lower wavelength after 10 minutes of treatment at 650°C. The absorbance edge was estimated from Fig. 1 (a) to be at around 400 nm after being air dried. It increases gradually to about 470 nm after a heat treatment of 550°C then decreases back slightly after 10 minutes at 650°C.

Fig. 1 (b) shows the result of PZT-c sprayed onto another quartz slide and tested after it had been sprayed and air dried at room temperature for several hours. Fig. 1 (b) also shows the absorbance of this same film after repeated cycles of exposure to UV from a Thor Labs Curing Gun with one cycle being a duration of approximately 1 minute. The absorbance curve after 3 cycles of exposure is shown in red, exposure after 10 cycles in green and on the second day, after an additional 10 cycles and then 5 minutes under a 6W, 365 nm single wavelength UV source by UVP is shown in blue.

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Fig. 1  Absorbance measurements performed on (a) a first sample of PZT-c sprayed on a quartz slide and subjected to heat treatments at 350, 450, 550 and then 650°C and (b) a second PZT-c sample sprayed on a quartz slide and repeatedly exposed to UV light.

The results in Fig. 1 demonstrate that the PZT-c film used in the fabrication of HT FUT in this lab is UV absorbent and that it remains absorbent after being either air dried at room temperature or dried and then heat treated at 350, 450, 550 or 650°C.

Fig. 2  Absorbance measurements performed on five individual samples of PZT-c films sprayed on glass slides subjected to heat treatments at 350, 450, 550, and 650°C and normalized to individual film thickness.

Fig 2 shows the results of measurements taken on PZT-c sprayed onto separate glass slides that had been dried for 10 minutes at 100°C and then individually treated at either 350, 450, 550 or 650°C. The absorbance values are normalized to individual film thicknesses with background absorbance removed. The absorbance edge is observed at a longer wavelength for films treated at
higher temperatures until 550 °C. For the film treated at 650°C, the absorbance edge was observed to be at a slightly shorter wavelength from that which was treated at 550°C.

Estimated bandgap values were extracted from a plotted graph of $\alpha^2$ vs $h\nu$ ($\alpha$ is the coefficient, $h\nu$ is the incident photon energy) and are shown in Fig. 3, the values of which were calculated from the absorbance spectrum obtained and shown in Fig. 2. PZT-c which had been dried at 100°C and fired at 350°C had an estimated bandgap of 3.1 eV, 2.8 eV for 450°C, 2.5 eV for 550°C and 2.8 eV for 650°C.

Whereas the PZT-c in Fig. 2 and Fig. 3 were heat treated individually for 10 minutes at either 350, 450, 550 or 650°C, the PZT-c in Fig 1 (a) was a single slide, heat treated at 350, 450, 550 and 650°C, for 10 minutes at each temperature for a total of 40 minutes in high temperature treatment. The absorbance edge trend where the edge increases until a temperature of 550°C and then decreases after 650 °C is observed in both cases. The band gap of the PZT-c film may be shrinking with the temperature level until 550°C and then widening slightly after 650°C.

**Photoconductivity measurements of sol-gel PZT-c**

The photoconductivity for PZT-c film that had been either 1) air dried or 2) dried for 5 minutes at 95°C and then fired at 650 °C were measured with a 4-point probe technique. The photoconductivity of PZT-c which had undergone 650°C heat treatment was 0.0205 $\Omega^{-1}$cm$^{-1}$. The voltage of the two PZT-c films under dark conditions and illuminated by the Xe lamp, optically chopped and locked-in, captured across two fingers separated by 0.2 mm is shown in Fig. 2. Fig. 2 (a) show the voltage under dark and illuminated conditions for the film that had been only air dried. Fig. 2 (b) shows the voltage level for the film that had been dried and fired at 650 °C. The result demonstrates that PZT-c film used in the fabrication of HT FUT, with an approximate thickness of 5-15µm was photoconductive after being sprayed and air dried as well as after being dried at 95°C and fired at 650°C i.e. after the final step in HT FUT fabrication.
photoconductivity for a 5 µm thick PZT-c film that had been dried and fired at 650°C was 0.0205 Ω⁻¹cm⁻¹.

Fig. 4: Voltage across two electrodes under dark and U.V. illuminated conditions of one PZT-c (a) that had been air dried and (b) that had been dried for 5 min at 100°C and fired for 5 min at 650°C

ELECTRICAL PROPERTY IN SOL-GEL PZT-C FILM USED TO FABRICATE HT FUT

Temperature dependent capacitance measurement of sol-gel PZT-c film

Fig. 5 (a) shows the setup used to measure the temperature dependence on capacitance under dark and UV illuminated conditions of a PZT-c sprayed onto a 25µm stainless steel membrane, the latter of which acts as the bottom electrode. The PZT-c film, with a thickness of 39 µm was dried at 95°C for 10 minutes and heat treated at 650°C for 10 minutes. A 3.5 diameter transparent indium tin oxide (ITO) top electrode was sputtered and acted as the top electrode. The capacitance was measured with a gradual increase in temperature (Forward) monitored by a thermocouple positioned over the stainless steel membrane, under dark conditions. The temperature was increased until the highest temperature allowed by the hot plate after which it was decreased back to room temperature during which time the capacitance was also measured (Back). The temperature was increased gradually again and the capacitance change was measured with UV illumination from the Newport 200W Hg lamp. After cooling back to room temperature, a second run with UV illumination was performed. The results are presented in Fig. 5 (b) and demonstrate that a repeatable capacitance peak shift of 100°C to lower temperatures was observed.
CONCLUSIONS

Sol-gel sprayed PZT-c films used to fabricate HT FUTs in this lab were observed to be UV absorbent between 200 - 450 nm. It was also observed that these films remained absorbent after undergoing the drying and firing steps in FUT fabrication, in other words after 10 minutes of drying at 100°C and 10 minutes of firing at 650°C.

For PZT-c film which was heat treated at 350, 450, 550 and then 650°C, the absorbance edge moved to a longer wavelength with each increase in firing temperature except until the 650°C step. For PZT-c film which had been individually heat treated at either 350, 450, 550 or 650°C, the absorbance edge was found to lie at a longer wavelength, the higher was the temperature except after 650°C. This trend was common for film sprayed on glass and quartz slides. The absorbance curves showed an estimated bandgap value for PZT-c films that had been dried at 100°C and fired at 650°C to be 2.8 eV.

PZT-c which had been sprayed and air dried as well as PZT-c which had been dried at 95°C and fired at 650°C both showed a photoconduction response to intrinsic illumination from a Xe lamp. The photoconductivity of a 5µm thick PZT-c film which had been dried at 95°C and fired at 650°C was 0.0205 Ω⁻¹ cm⁻¹.

An approximate 100°C shift to lower temperature of the temperature dependent capacitance peak was observed for a 39µm thick PZT-c film while being illuminated with a 200W Hg lamp. It is known that the temperature dependent capacitance peak is the location of ferroelectric and paraelectric phase transition. Therefore, the UV absorbent sol-gel sprayed PZT-c film, which was found here to be photoconductive and is used to fabricate HT FUTs in this lab experiences a 100°C shift in its Curie temperature. This gives a physical basis and incentive to use intrinsic illumination to lower the temperature at which such sol-gel sprayed PZT-c films are fired, the purpose of which would be to lower the cost in energy to fabricate the highly efficient and conformable HT FUTs developed in this lab.

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