High Temperature Piezoelectrics - A Comparison

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Abstract
The ability to apply typical ultrasonic techniques in high temperature environments is desired for the monitoring of process variables, such as the viscosity of melts. They are also suitable for maintaining the structure and material integrities in harsh environments, for example, turbine blades, combustion engines and nuclear reactors. The commercial piezoelectric material PZT possesses a Curie temperature of about 350°C, but has a maximum recommended operation temperature of 150-250°C. In this work, three high temperature piezoelectric crystals, YCa₄O(BO₃)₃, LiNbO₃ and AlN, were studied for use in ultrasonic transducers under continuous operation for 55 hours at 550°C. The oxidation of AlN, known to occur at these temperatures, had no significant effect on the ultrasonic transduction efficiency, but the difficulty to achieve high quality AlN single crystals limits their applications greatly. YCOB was found to be capable of efficient ultrasonic transduction to about 1000°C.

Keywords: High temperature, piezoelectric transducer, Lithium niobate, Aluminium nitride (AlN), YCa₄O(BO₃)₃ (YCOB)

1. Introduction

Ultrasonic techniques have been widely applied for non-destructive evaluation (NDE) of material properties and structural integrity [1]. The ability to apply typical ultrasonic techniques in high temperature environments is desired for the monitoring of process variables, such as viscosity of melts. They are also suitable for maintaining the structural and material integrity in harsh environments, for example, turbine blades, combustion engines and nuclear reactors [2-5].

High temperature piezoelectric materials have been surveyed previously [6]. For example, the commercial piezoelectric material Lead Zirconate Titanate (PZT) possesses a Curie temperature of about 350°C, but has a maximum recommended operation temperature of 150°C – 250°C [6-7]. As a result, buffer rods and ultrasonic guided waves have been utilized to keep the piezoelectric materials out of the high temperature region for extended periods of time [8-9]. A guided wave system includes several restrictions such as dispersive behavior limiting bandwidth, sensor size, cumulative attenuation losses over the waveguide propagation length, and losses due to material discontinuities along the ultrasonic propagation path.

The limitations imposed by this methodology have been one of the many driving forces leading the development of new piezoelectric materials with operational temperatures exceeding 350°C. The relatively new high temperature capable materials include high Curie temperature ferroelectric materials and non-ferroelectric single crystals. Additionally, if the intended operating frequency is low (below 1 MHz), electrical resistivity becomes problematic at high temperatures [6, 10].

2. Background

Previous reports have shown numerous piezoelectric materials to be capable of operating as ultrasonic transducers up to 1000°C. However, the longevity of these materials under such conditions has been compromised.
2.1 Aluminium nitride

The group III-V material Aluminum Nitride (AlN) belongs to the Wurtzite structure, point group 6mm, and is not ferroelectric. No phase transitions exist aside from the melting point at 2800°C. The resistivity of high quality crystalline samples is on the order of 10 MΩ cm at 200°C [11, 12]. The dielectric constant is 8.5, and the piezoelectric strain constant has been estimated, for thin films, to be 5 pC/N [13, 14]. Oriented thin films of AlN have been utilized for high temperature transducers up to 1000°C with satisfactory results on at least two separate occasions and in a gamma radiation environment [15-17]. Bulk single crystal materials have received less attention because of the difficulty of growing high quality single crystal wafers; nonetheless, bulk single crystal AlN has been used for ultrasonic transducers up to 1000°C, and in an operating nuclear reactor core [18, 19]. AlN bulk single crystals show a very wide range of crystal quality, with electrical resistivity being strongly correlated with a crystal’s ability to operate as a pulse-echo transducer at elevated temperatures. The AlN sample reported in this work was selected from a collection based on its measured resistivity in excess of 10 MΩ cm at 400°C, and a measured coupling coefficient of 0.2.

2.2 Lithium Niobate

Lithium niobate has also been extensively studied for high temperature transducer applications and is a ferroelectric material with a Curie temperature in excess of 1000°C, depending on the stoichiometry [20]. Lithium niobate displays the 3m crystal symmetry with the corundum structure [6]. The 36° rotated Y-cut is quite sensitive in the longitudinal mode of vibration with a coupling coefficient of 0.48. However, lithium niobate is known to lose oxygen at elevated temperatures, particularly at low oxygen partial pressure [1, 21]. Given that hermetic packaging is commonly employed in high temperature electronics, oxygen loss may be particularly problematic. Furthermore, lithium niobate has been shown to decompose at 600°C, even in oxygen at atmospheric pressure [22]. However, the oxygen loss is an activated process and is not likely to have a discernible effect for short periods of time as shown, for example, by Svaasand, who treated his samples for 170 hours before observing their decomposition [22].

2.3 ReCOB

Oxyborate crystals with general formula ReCa₄O(BO₃)₃ (Re = rare earth element, abbreviated as ReCOB) have been extensively studied for nonlinear optic applications, such as second and third harmonic generations [23]. The crystals can be readily grown from the melt using the Czochralski (CZ) pulling technique or the Bridgman technique at 1500°C [23]. Analogous to AlN crystals, no phase transitions occur in ReCOB crystals prior to their melting point, which is around 1400°C-1500°C, thus expanding the potential temperature usage range. Recently, oxyborate crystals have attracted attention for piezoelectric applications, due to their ultrahigh electrical resistivity at elevated temperatures. For example, YCa₄O(BO₃)₃ (YCOB) possesses a resistivity of 2×10⁸ Ω cm at 800°C [24]. The dielectric permittivity, piezoelectric strain constant, and electromechanical coupling factor of the XYlw - 15°/45° cut were found to be on the order of 11, 6.5 pC/N, and 0.12, respectively, with little variation in the range of room temperature to 950°C [25]. Additionally, this material has been successfully employed as a vibration sensor up to 1000°C [26].

In this work, three high temperature piezoelectric single crystals, AlN, Lithium niobate, and
Oxyborate crystals, were studied for use in ultrasonic transducers. Their behavior is presented in terms of waveforms, insertion loss and dielectric properties.

3. Experimental procedure

The three piezoelectric materials tested had a surface area of roughly 10 mm$^2$ and operated at a center frequency of 10 MHz. A spike pulser-receiver (Panametrics-5800) was utilized in conjunction with a 100 MHz digital oscilloscope (Tektronix 54104B). Three distinct experiments were performed. First, a long term in-situ test was performed at 550°C for more than 55 hours on all three piezoelectric materials with standard atmospheric conditions. The transducers were operated continuously and their performance was recorded. Second, the three piezoelectric materials were subjected to heat treatments at standard atmospheric conditions at 950°C for 24 hours and 1000°C for 48 hours with ultrasonic performance testing after each heat treatment. Lastly, the YCOB material was operated with an increase in temperature up to 950°C.

The test fixture utilized is shown in Figure 1.

![Figure 1. Experimental fixture and the fabricated high temperature ultrasonic transducer.](image)

For ultrasonic coupling the experiments utilized mechanical pressure provided by a wave spring (UNS S66286 wave spring) to compress the piezoelectric material onto the ultrasonic propagation medium. Trial and error revealed that the experiment could be repeated more than 20 times or carried out continuously for several days provided the temperature was kept below 560°C. This level of repeatability and longevity was achieved with the spring providing 150 psi of pressure by way of 1 mm of displacement. For higher temperatures (~950°C) a thicker Al foil and a pressure of 300 psi was needed. Of particular significance is the fact that this coupling method allows for thermal expansion of mismatched materials to be coupled; the AlN crystal with a thermal expansion coefficient of roughly 4 ppm/°C was coupled to Al with a thermal expansion coefficient of 24 ppm/°C.

4. Results

In the long term in situ test, the echo amplitude was recorded throughout a period of 55 hours with the transducers held at 550°C; the resulting amplitude evolution is provided in Figure 2. From Figure 2, it is apparent that minimal variation was observed for AlN and YCOB, while a slight variation was observed for the lithium niobate transducer. Additionally, the bandwidth and background noise were unchanged.

Beyond 55 hours all the transducers began to display a monotonic decrease in pulse-echo amplitude. This decrease is attributed to the carbon-carbon backing material which begins to lose considerable mass and volume. This loss of mass and volume reduces the coupling pressure and the area of electrical contact, which causes the reduction in the pulse echo amplitude. However, compressing a wad of Al foil under pressure and at a temperature of 550°C, results in a suitable backing material that does not lose mass or volume under these
test conditions. Therefore, in future work, this will be the backing of choice.

The pulse-echo performance of the three materials was then evaluated using thermal ratcheting tests. The piezoelectric crystals were heat treated in standard atmospheric conditions at 950°C for 24 hours and 1000°C for 48 hours. The ultrasonic pulse echo performance was evaluated at room temperature and at 500°C in the pristine state and for the two states of heat treatment. The performance was monitored in terms of the insertion loss defined by Equation 1 and shown in Figure 3.

\[
I.L. = 20 \log_{10} \left( \frac{V_{input}}{V_{output}} \right) - \text{Receiver Gain} \quad (1)
\]

The high temperature couplant used has a relatively short lifetime at 500°C. When the fixture was placed directly in the furnace at 500°C, as was done here, the signal first degrades and then improves steadily reaching the highest amplitude and bandwidth after roughly one hour. The couplant then begins to decompose and the signal is no longer apparent after three hours at 500°C.

It can be seen from Figure 3 that all three materials seemed to be unaffected by the heat treatment. In any event, the observed variation was less than the statistical spread obtained by
repeating each experiment four times. The entire fixture was disassembled and reassembled when repeating the experiments. The data obtained at 500°C corresponds to the peak amplitude throughout the curing and decomposing of the high temperature couplant.

The dielectric and piezoelectric properties of YCOB and LiNbO$_3$ where monitored for degradation when subjected to heating to 850°C for 120 hours in air. After the heat treatment, it was observed that YCOB had gone from slightly opaque white to yellow and the LiNbO$_3$ had developed pitting that was observable with the naked eye, similar to the results found by Svaasand [22]. The piezoelectric strain constant, measured with a d$_{33}$ meter, was found to be unchanged from its pristine value in both materials.

The in-situ tests up to 950°C were then performed on the YCOB transducer. The fixture was placed in an open tube furnace and heated at a rate of 10°C/min while ultrasonic waveforms were recorded. The waveforms obtained at room temperature, 300°C, 600°C and 950°C are given in Figure 3.

The waveforms revealed very satisfactory performance of the YCOB crystal based transducer up to 950°C. In fact, the signal improved, displaying an increase in amplitude and bandwidth. The most likely cause of signal improvement is the softening of the silver foil, allowing for improved coupling to the stainless steel propagation medium. The signal was maintained at 950°C for 5 minutes. The temperature was then further increased causing the silver coupling foil to melt, causing loss of signal due to short-circuiting.

5. Discussion & conclusion

In summary, the long-term in-situ test indicates that all three materials are suitable for operation at 550°C for at least 55 hours. Additionally, it was found that the carbon-carbon backing material is a limiting component. A solution based on a porous Al backing was found, but thorough testing on this backing needs to be completed. This backing material is easily created by compressing Al foil at 550°C under 150 psi for 5 hours.

The thermal ratcheting test revealed significant changes in the dielectric properties and only negligible changes in the ultrasonic performance of lithium niobate. Dielectric changes of the observed magnitude would be expected to have a noticeable effect on the ultrasonic performance. However, the heat treatments were not equivalent during the dielectric and ultrasonic testing as is clear from the above discussion. It is likely that the longer heat treatment caused a more pronounced change in the dielectric properties.

All three materials, YCOB, AlN and LiNbO$_3$, exhibited stability in ultrasonic performance through the heat treatment of 950°C for 24 hours and 1000°C for 48 hours. Any variations observed were less than the experimental error.

The YCOB crystal exhibited a much less pronounced change in dielectric properties after heat treatment. It is expected that YCOB is more stable at high temperatures than LiNbO$_3$ which is known to deplete its oxygen, particularly at low oxygen partial pressure.

The significant findings from this experiment include:

1. At atmospheric oxygen partial pressures, 48 hours of exposure to 950°C, or 24 hours exposure to 1000°C had no significant effect on the efficiency of ultrasonic
transduction of LiNbO$_3$, YCa$_4$O(BO$_3$)$_3$ and AlN.

2. The oxidation of AlN, known to occur at these temperatures, had no significant effect on the ultrasonic transduction efficiency, but the difficulty to achieve high quality AlN single crystals limits their applications greatly.

3. YCOB crystal was found to be capable of efficient ultrasonic transduction to about 1000°C.

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References


