10.1109/ULTSYM.2015.0212

Sol-Gel Composite Materials for Continuous Monitoring at 600°C

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***Abstract*— Ultrasonic testing is mainly used because it can detect internal defects however, on-line monitoring for thermal power generation is difficult due to high temperatures such as 550°C. Sol-gel composite ultrasonic transducers can operate high temperatures and in the recent study, Mn-doped $CaBi_4Ti_4O_{15}$(CBT)/Pb(Zr,Ti)O_3(PZT) sol-gel composites has been developed for nondestructive testing above 500°C to improve sensitivity and signal-to-noise ratio (SNR) at high temperatures. Mn-domped CBT/PZT demonstrated comparable performance with $Bi_4Ti_3O_{12}$(BiT)/PZT at 500°C and it still showed ultrasonic response with reasonable SNR at 600°C even though BiT/PZT lost its ultrasonic response. From long-term monitoring test results to evaluate on-line monitoring capability, Mn-doped CBT/PZT was more suitable than BiT/PZT for long-term monitoring at 600°C.**

Keywords*— nondestructive testing; high-temperature; ultrasonic transuducer; sol-gel composite; long-term monitoring

I. INTRODUCTION

In recent Japan, development of high temperature has been desired for thermal plant nondestructive testing (NDT) applications. Because nuclear power plant operation has been stopped after Great East Japan Earthquake in 2010, thermal power plant has generated base power as well since 2011. Power generation by thermal power plant has become dominant role and currently they supplied up to ~90% of the total electrical power in Japan and thermal power generation dependency has been critical level. Therefore, the aging and overload of thermal power plants has become an issue and the development of next generation thermal power plant has been investigated. In order to maintain a stable supply and reliability of thermal power plant, periodical NDT has been carried out during shutdown. Ultrasonic NDT can detect internal defects or material deterioration without damage. In current situation, reduction of periodic inspection time and/or continuous monitoring is ideal in order to keep the power supply. However, ultrasonic NDT by conventional piezoelectric ultrasonic transducer is difficult. The reason includes operation temperature limit by Curie temperature of piezoelectric materials, deterioration of couplant and backing material at high temperature, weakness of single crystal against thermal shock. The pipe temperatures of current and next generation thermal power plants are 600℃ and 700℃, and there is no commercial transducer which can operate such high temperatures, therefore development of ultrasonic transducers which can continuously operate at least 600℃ is required.

High temperature ultrasonic transducers made by sol-gel composite method have been studied. Sol-gel composite material is made by ferroelectric powder and dielectric sol-gel solution. In past study, sol-gel composite fabricated from Pb(Ti,Zi)O_3 (PZT) powder and PZT sol-gel solution (PZT/PZT) and sol-gel composite composed of $Bi_4Ti_3O_{12}$ (BiT) powder and PZT sol-gel solution (BiT/PZT) had been developed. Both materials showed good sensitivity and signal-to-noise ratio (SNR), but they are not practical for thermal power plant applications because of low operation temperature limit. The practical operation temperatures of PZT/PZT and BiT/PZT were ~200℃ and ~500℃, respectively due to Curie temperature of ferroelectric powder. Sol-gel composite fabricated from high curie temperature $LiNbO_3$(LN) powder and PZT sol-gel solution(LN/PZT) was also developed and it could work at approximately 800℃, though sensitivity and SNR were not sufficient for real applications.

In order to improve the operation temperature, sensitivity and SNR, a new sol-gel composite, made by CaBi4Ti4O15 powder with approximately 800℃ Curie point and PZT sol-gel solution (CBT/PZT) has been developed in previous study. CBT/PZT showed ideal temperature stability up to 550℃, though sensitivity was low because of room temperature poling. SNR at high temperatures also deteriorated, probably because of electrical resistance deterioration. In order to improve the sensitivity and SNR of CBT/PZT, optimization of poling temperature and improvement of resistivity by Mn doping of CBT powder were attempt. Ultrasonic responses in pulse-echo mode of pure CBT/ PZT, Mn-doped CBT/PZT, BiT/PZT were measured and compared at various temperatures. As a result, the ultrasonic responses of pure CBT/PZT and BiT/PZT were deteriorated significantly at 550°C. For Mn-doped CBT/PZT poled at 400°C could be useful for high-temperature ultrasonic transducer applications, because of its reasonable sensitivity and reasonable SNR, though long-term durability was not evaluated yet. Furthermore, heating was performed by hot plate in the air and so the real temperature of the samples should be lower than the hot plate indication value and maximum operation temperature of the hot plate was limited to 550°C. In this study, maximum operation temperature investigation, thermal cycle test and long-term monitoring test in furnace were performed for Mn-doped CBT/PZT and BiT/PZT, respectively.

II. Sample Fabrication

The samples of Mn-doped CBT/PZT and BiT/PZT were fabricated by a sol-gel spray technique. Detailed fabrication process can be found elsewhere [2-4]. First, ferroelectric powders, Mn-doped CBT powders and BiT powders were prepared and then the mixture was ball-milled for more than one day until an appropriate viscosity for spray coating was achieved. After ball-mill process, Mn-doped CBT/PZT and BiT/PZT films were fabricated by sol-gel spray technique onto titanium substrates with 3.3 mm thickness, ~30 mm length, and ~30 mm width for comparison purpose. As a substrate material, titanium was chosen because of high temperature durability above 600°C. After spray coating, thermal treatments were performed. The spray coating and thermal treatment process were repeated several times until the film thickness reach to ~50 µm.

After fabricated both samples ~50µm thickness film on titanium substrate, the electrically poled was performed using corona discharge on the hot plate at 400°C. Corona discharge was chosen because high electrical field could apply on the film without destroying. Finally, high temperature silver paste top electrodes were fabricated for long-term high temperature test by stencil printing. Optical images of the samples were shown in Figs.1 and2, respectively. There was no significant difference except color. Mn-doped CBT/PZT presented dark yellow whereas BiT/PZT sampled had white yellow color. The piezoelectric constant d_{33} was measured using a d_{33} meter at room temperature and it was 10 pC/N for Mn-doped CBT/PZT sample and 12 pC/N for the BiT/PZT sample. Since dielectric constant of CBT is slightly higher than that of BiT [3] so that it was expected that ultrasonic performance of BiT/PZT is better than that of CBT/PZT at room temperature.

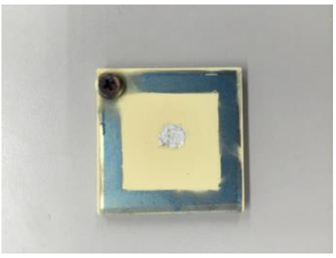


Fig. 1. Optical images of Mn-doped CBT/PZT films fabricated onto 3.3 mm thickness, ~30 mm length, and ~30 mm width titanium substrate.

Fig. 2. Optical images of BiT/PZT films fabricated onto 3.3 mm thickness, ~30 mm length, and ~30 mm width titanium substrate.

III. Ultrasonic Measurement at High temperatures

Measurement schematic was shown in Fig. 3. In order to evaluate high-temperature durability and on-line monitoring capability, the sample was put into a furnace and high temperature electrical cables were contact with a top electrode and titanium substrate (ground) through holes of the furnace. The cables were connected with coaxial cable which was outside of the furnace and connected with Pulser/Receiver machine. Pulser/Receiver machine was connected with a digital oscilloscope. Every 50°C temperature rise, the ultrasonic response was recorded in pulse echo mode.

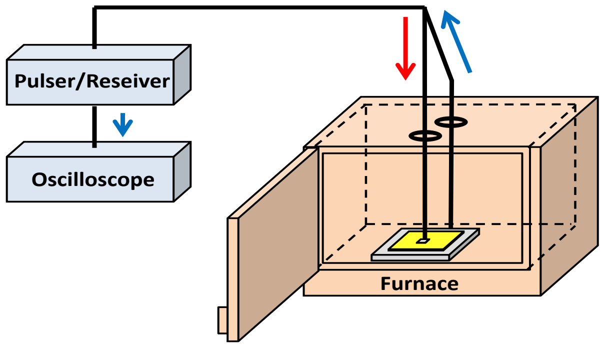
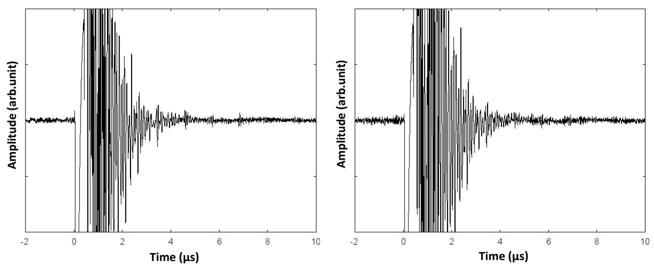


Fig. 3. Schematic diagram for ultrasonic measurement at high temperatures.

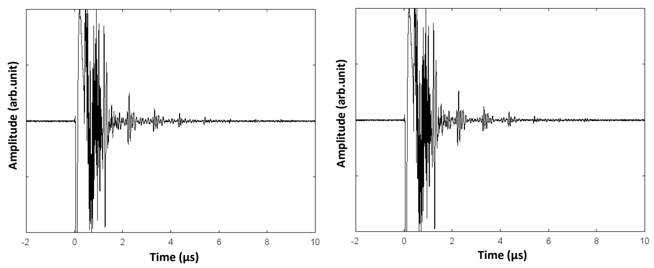
First, maximum operation temperatures of Mn-doped CBT/PZT and BiT/PZT were investigated. For Mn-doped CBT/PZT sample, thes clear reflected echoes with high SNR was observed till ~600°C, and the SNR was gradually deteriorated above 650°C. For BiT/PZT, stable signal was observed up to 500°C, however, no clear signal was observed at 550°C, due to depoling of BiT phase since Curie temperature of BiT is lower by 140°C than that of CBT [3]. From these results, the maximum temperatures of thermal cycle tests for Mn-doped CBT/PZT and BiT/PZT were decided as 700°C and 500°C, respectively.

Next, thermal cycle tests were executed between room temperature and the maximum temperatures determined by previous section. Measurement setup was the same as before and every 50°C temperature rise with 5 min holding time, the ultrasonic response was recorded in pulse echo mode. Thermal cycles were repeated three times since depoling of PZT sol-gel phase should occur during the first thermal cycle. The 2nd and 3rd thermal cycle results for Mn-doped CBT/PZT and BiT/PZT were shown in Figs 4 and 5, respectively. No significant deterioration was observed for BiT/PZT at 500°C, whereas deterioration progressed for CBT/PZT at 700°C. It indicated that CBT/PZT can operate at 700°C temporally, and it is not suitable for continuous use.



(a) (b)

Fig. 4. Ultrasonic responses of Mn-doped CBT/PZT at 700°C in (a) 2nd thermal cycle and (b) 3rd thermal cycle.



(a) (b)

Fig. 5. Ultrasonic responses of BiT/PZT at 500°C in (a) 2nd thermal cycle and (b) 3rd thermal cycle.

In order to evaluate ultrasonic performance at elevated temperatures quantitatively, sensitivity and SNR during 3rd thermal cycle were calculated. The sensitivity of the ultrasonic probe was calculated by following equation;

$$\text{Sensitivity} = -\left[20\log_{10}(V_1/V_2) + \text{gain of Pulser/Receiver}\right] \quad \text{(dB)} \qquad (1)$$

where V_1 is the reference amplitude, 0.4 Vp-p (V) in this experiment, and V_2 is the signal amplitude (V) of the 3rd reflected echo from the bottom surface of the titanium substrate. In this manuscript, the sensitivity was determined as the negative calculated value of Pulser/Receiver gain needed to achieve 0.4Vp-p of the 3rd reflected echo. The 3rd reflected echo was used because the 1st reflected echo was hidden and the 2nd reflected echo had a bias voltage for Mn-doped CBT/PZT at high temperatures as shown in Fig. 6. The negative value was used for intuitive understanding. The temperature dependency results of the sensitivity is shown in Fig. 6. The sensitivity showed no exponential decrease but rather a linear decrease up to 450°C, then the sensitivity reduced more rapidly above 500°C even for Mn doped CBT/PZT. It might be caused by not only depoling of piezoelectric material but also higher attenuation by titanium substrate at high temperatures.

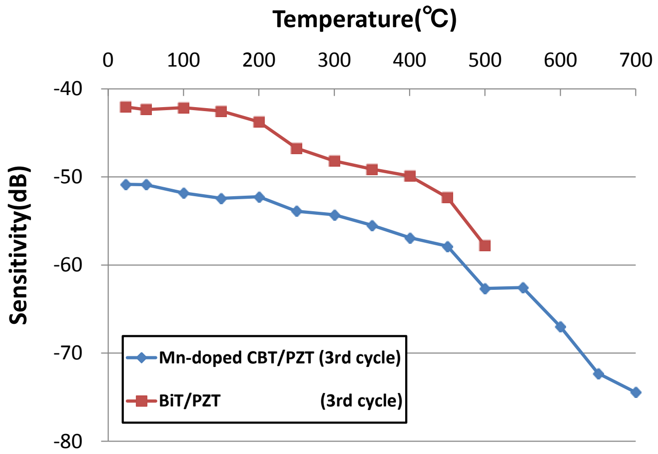


Fig. 6. Temperature dependency of sensitivity for Mn-doped CBT/PZT and BiT/PZT in 3rd cycle.

The SNRs of Mn-doped CBT/PZT and BiT/PZT were also compared at various temperatures. In this manuscript, the SNR was determined using the 3rd reflected echo amplitude and noise amplitude between the 3rd reflected echo and the 4th reflected echo. The SNR of the ultrasonic transducer was calculated by

$$\text{SNR} = 20\log_{10}(V_S/V_N) \quad \text{(dB)} \qquad (2)$$

where V_S is the signal amplitude (V) of the 3rd reflected echo and V_N is the noise amplitude between the 3rd reflected echo and the 4th reflected echo. The temperature dependency results of the sensitivity is shown in Fig. 7. There was not so significant deterioration up to 500°C, then the deterioration happened above 500°C, as similar as sensitivity results.

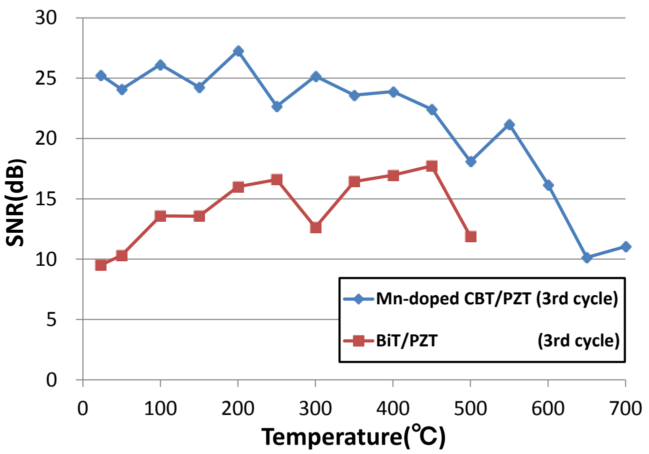
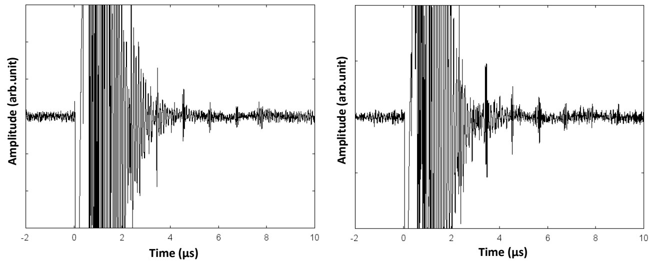


Fig. 7. Temperature dependency of SNR for Mn-doped CBT/PZT and BiT/PZT in 3rd cycle.

Continuous monitoring tests were demonstrated. Operation temperatures for Mn-doped CBT/PZT and BiT/PZT were 500°C and 600°C, respectively. These temperatures were chosen because of high enough sensitivity and SNR. Ultrasonic response at setting temperatures in the beginning and the end of this experiment (after 36 h) for Mn-doped CBT/PZT and BiT/PZT were shown in Figs. 8 and 9, respectively. The signal of Mn-doped CBT/PZT was stable though SNR was not so high, probably because the same sample after heating up to 700°C during thermal cycle test was reused for Mn-doped CBT/PZT, whereas BiT/PZT sample was replaced with new sample. The sensitivity and SNR were calculated in the same manner as thermal cycle test, and the results were shown in Figs. 10 and 11, respectively. No significant deterioration was observed though there were fluctuations. From those results, it seems that Mn-doped CBT/PZT and BiT/PZT ultrasonic transducers can be useful for 600°C and 500°C continuous monitoring, though further research is required for longer time period verification.



(a) (b)

Fig. 8. Ultrasonic responses of Mn-doped CBT/PZT at 600°C after (a) 0h and (b) 36 h.

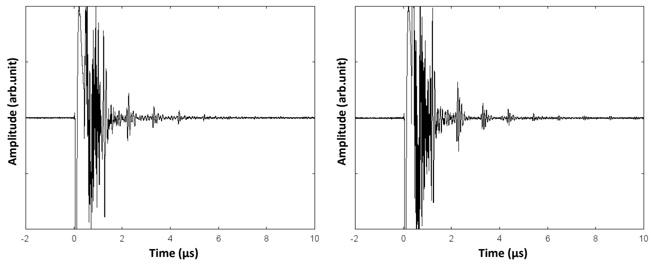


Fig. 9. Ultrasonic responses of BiT/PZT at 500°C after (a) 0h and (b) 36 h.

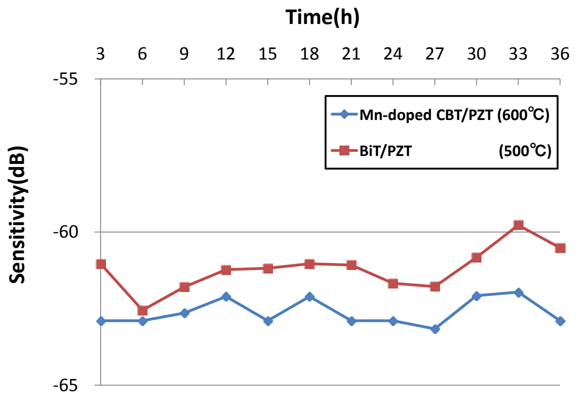


Fig. 10. Comparison of SNR of Mn-doped CBT/PZT and BiT/PZT in 3rd cycle.

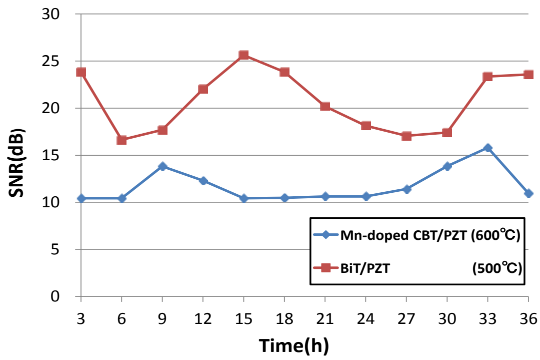


Fig. 11. Time dependence of SNR of Mn-doped CBT/PZT and BiT/PZT during 36h.

IV. Conclusion

High temperature performance of Mn-doped CBT/PZT sol-gel composite was investigated and compared with BiT/PZT. Both samples were fabricated onto a 3-mm-thick titanium substrate by spray technique, Mn-doped CBT/PZT and BiT/PZT showed comparable performance, though the sensitivity of BiT/PZT was higher than that of CBT/PZT. When the temperature increased up to 500°C, signal amplitude of Mn-doped CBT/PZT was dropped by ~12 dB, though the signal amplitude was stable for 36 h and SNR was sufficient to detect multiple reflected echoes from 3-mm thick titanium substrate. On contrast, for BiT/PZT, the SNR became too low to detect any reflected echo at 550°C. As a result, Mn-doped CBT/PZT was more suitable than BiT/PZT for long-term monitoring at 600°C.

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