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Effect of TiO_2 Sol-Gel Phase on Ultrasonic Properties

酸化チタンゾルゲル相による超音波センサ特性への影響

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1. Introduction

Ultrasonic transducers are widely used for non-destructive testing (NDT). The ultrasonic transducer fabricated by the sol-gel composite material produces an oxide film with high adhesion strength to the measurement object by thermal process at the time of manufacture. In addition, no couplant and backing material are required due to porosity existence inside sol-gel composite films.[1)] $Bi_4Ti_3O_{12}$(BiT)-based sol-gel composite is expected to operate at high temperatures up to about 400℃. In previous study, BiT/Pb(Zr,Ti)O_3 (PZT) had been developed and it showed high temperature stability up to about 400°C.[2)] However, PZT is lead-contained material, so there is a concern about lead pollution. Various BiT based lead-free sol-gel composite materials had been developed in past study. [3)] However, except BiT/BiT, most of lead-free sol-gel composite could not demonstrate comparable ultrasonic performance at high temperatures. BiT/BiT could demonstrate reasonable ultrasonic performance at 600°C, though room temperature poling of BiT/BiT was difficult due to relatively low dielectric constant of BiT sol-gel phase. Development of new BiT based sol-gel composite which can demonstrate comparable ultrasonic performance with poling facility has been desired.

In this study, BiT/TiO_2 sol-gel composite was investigated. TiO_2 was chosen as sol-gel phase material because TiO_2 had relatively high dielectric constant and relatively high resistivity. Moreover, in order to confirm the performance difference by resistivity, two types of TiO_2 sol-gels were fabricated. BiT/TiO_2(Sr) using Sr doped TiO_2 sol-gel solution to reduce crystallinity of TiO_2 were also fabricated and compared with BiT/TiO_2.

2. Sample Fabrication

BiT/TiO_2 sol-gel composite films were fabricated by sol-gel splay technique. First, X-ray diffraction (XRD) was performed for TiO_2 sol-gel solution. XRD patterns of TiO_2(Sr) showed a broad pattern so that no clear identification was made, whereas by pure TiO_2 sol-gel solution, crystallization of rutile type and anatase type was confirmed. Therefore, TiO_2 sol-gels with different crystallinity were prepared in this study. Then, BiT powders and TiO_2 sol-gel solutions were mixed appropriately and the mixture was milled for more than 24 hours. After that, the mixture was sprayed on titanium substrates. The titanium substrate had a length of 30mm, a width of 30mm, and a thickness of 3mm. After spray coating process, the samples were dried at 150°C and fired at 650°C for 5 minutes each. The spray coating process and the thermal processes were repeated until the film thickness reaches 50µm. After reaching the target film thickness, 1cm diameter top electrodes were fabricated on the films by using platinum paste. Poling process was carried out at room temperature by DC corona discharge for 5 minutes. The max output voltage of power supply was 36kV. **Table I** shows the results of measuring capacitance C (F), the resistance value R (Ω), the loss coefficient D and d_{33} (pC/N) values. Both BiT/TiO_2 samples were inferior in capacitance as compared to BiT/PZT. However, piezoelectric constant g_{33} could be comparable so that sensor performance could be comparable as well. Although the BiT/TiO_2(Sr) sample appears to have a seemingly higher capacitance and higher dielectric constant than those of BiT/TiO_2 sample, it is apparent because the loss factor is very high. In addition, it is generally said that the resistivity of amorphous materials is higher than that of crystallized materials, but in this experiment pure TiO_2 had higher resistivity. The cause is presumed to be that the quantity of strontium is too high.

Table I The results of measuring values

	C[pF]	R[kΩ]	D	d_{33}[pC/N]
BiT/TiO_2(Sr)	793	195	0.69	8.7
BiT/TiO_2	600	323	0.19	7.4
BiT/PZT	1300	127	0.01	13.8

3. Experiments

In order to check high temperature durability of BiT/TiO_2 samples, thermal cycle test was carried out. The sample set onto a hot plate. After that, the temperature of the hot plate increased by 50°C and after holding for 5 minutes. After that, ultrasonic responses recorded by a digital oscilloscope. This test is repeated until the hot plate temperature reaches 450°C. After reaching 450°C, the hot plate was turned off and the temperature of hot plate decreased to room temperature. Then, measurement of the second and the third cycle was carried out. The measurement results at 450℃ in the third cycle are shown in **Figs. 2-3**. Through Figs. 2-3, multiple reflected echoes were clearly observed from both samples.

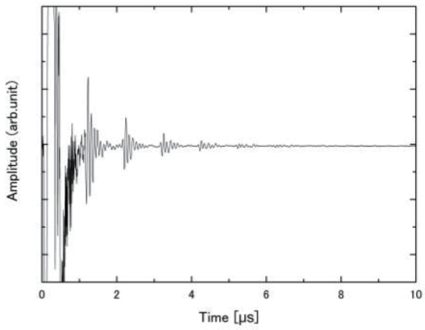

Fig. 2 Ultrasonic response at 450℃ in the third cycle of BiT/TiO_2(Sr) sample.

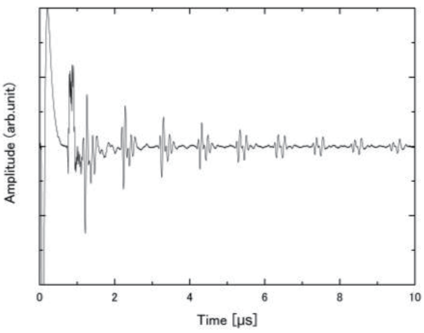

Fig. 3 Ultrasonic response at 450℃ in the third cycle of BiT/TiO_2 sample.

To evaluate the test results quantitatively, sensitivity was calculated by following equation;

$$\text{Sensitivity} = -20\log_{10}(V_1/V_2+\text{P/R Gain})\ [\text{dB}]$$

where V_1 is the value of reference amplitude, which was 0.1$V_{p\text{-}p}$ in this study, V_2 is the signal amplitude of the third echo that did not disappear even in the extension of the dead zone at higher temperatures. **Fig. 4** shows the temperature dependency of BiT/TiO_2(Sr) sensitivity, and **Fig. 5** shows the temperature dependency of BiT/TiO_2 sensitivity, respectively. From Figs. 4-5, the sensitivity at room temperature between the first and the second cycle has about 5dB drop. This phenomenon caused by depoling of BiT phase, since there is no piezoelectricity for TiO_2. It is noted that the sensitivity transitions from room temperature to 450°C were almost identical between the second and the third cycle. Furthermore, the sensitivities change between room temperature and 450°C was about 3dB during the second and the third cycle. From these results, it was found that the difference in the crystallinity of the sol-gel phase is not significant influence in the high temperature characteristics of BiT-based ultrasonic transducers. Although it cannot be denied that there is individual difference by manual splay technique, the BiT/TiO_2 sample shows sensitivities of about 5dB higher than the BiT/TiO_2(Sr) sample. Therefore, it is necessary to fabricate a sample by automatic splay technique.

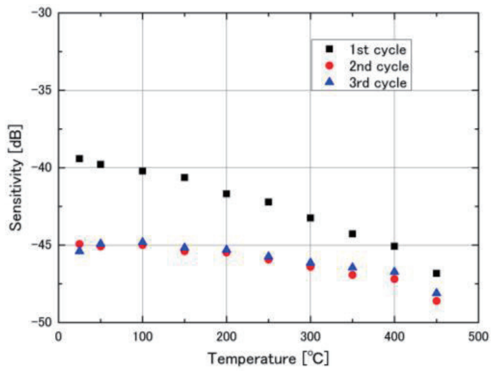

Fig. 4 Sensitivities of BiT/TiO_2(Sr) at various temperatures during thermal cycle test.

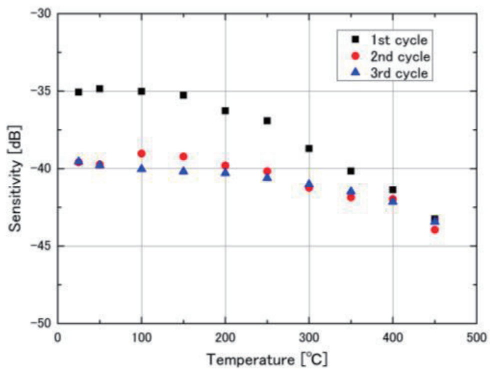

Fig. 5 Sensitivities of BiT/TiO_2 at various temperatures during thermal cycle test.

4. Conclusions

BiT/TiO_2 sol-gel composite was fabricated by using two types of TiO_2 sol-gel solutions. Both samples showed high temperature durability up to 450℃, the combination of high resistivity sol-gel solution and a relatively low dielectric phase powder phase has been identified as beneficial. In addition, the sol-gel phase crystallinity did not significantly affect the high temperature performance of the BiT-based ultrasonic transducers.

References

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