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High Temperature Properties of $CaBi_4Ti_4O_{15}/Ba_{0.7}Sr_{0.3}TiO_3$

$CaBi_4Ti_4O_{15}/Ba_{0.7}Sr_{0.3}TiO_3$ の高温特性

Tomoya Yamamoto[1 ‡], Kazuho Kiyofuji[1], Masaki Yugawa[1], and Makiko Kobayashi[1] ([1]Kumamoto Univ.)
山本智也 [1 ‡]，清藤和穂 [1]，湯川雅己 [1]，小林牧子 [1] ([1]熊本大学)

1. Introduction

High temperature ultrasonic transducers using have been investigated in the field of non-destructive testing (NDT) for safety assuarance. It is difficult to apply commercial ultrasonic transducer in this application, mainly due to lack of high temperature durability caused by backing material and couplant. Sol-gel composite ultrasonic transducers have beed developed to elminate backing material and couplant problems.[1-4] It was found that $CaBi_4Ti_4O_{15}$(CBT)/Pb(Zr,Ti)O_3(PZT) sol-gel composite, made by CBT piezoelectric powders and PZT sol-gel solution, has been developed and it could operate at 600 ℃ contineously.[2),3)] However, poling of CBT/PZT was relatively difficult due to high Curie temperature and high coercive field thus poling must be operated at high temperatures in order to obtain sufficient piezoelectricity.[2),5)] In addition, PZT contains Pb and it could be vioporated at high temperature. Therefore, development of lead-free sol-gel composite material with poling facility has been desired.

It was suspected that high dielectric constant of sol-gel phase could assist poling facility.[6)] Since $Ba_{0.7}Sr_{0.3}TiO_3$(BST) is lead-free and higher dielectric constant than PZT,[7),8)] CBT powders and BST sol-gel solution could be nice combination. In previous study, $PbTiO_3$(PT)/ BST sol-gel composite were fabricated and room temperature poling was succesfully demonstrated even though PT had high coercive field and PT/PZT could not be poled sufficiently at room temperature as well.[4)] In this study, CBT/BST, which is a composite material made by CBT powder and BST sol-gel solution, will be fabricated and investigated its high temperature durability.

2. Sample fabrication

CBT/BST sol-gel composite was made by sol-gel spray technique.[1-4),6)] First, CBT powders and BST sol-gel solution were prepared. BST sol-gel solution was self-manufactured according to the reference 8) and CBT powders were purchased. The mixtures of CBT powders and BST sol-gel solution were ball milled. Then, the mixtures were sprayed onto titanium substrates by an airbrush. The dimensions of titanium substrates were 30mm×30mm×3mm. This substrate was chosen due to low thermal capacitance and high temperature durability. After spray coating, drying process at 150℃, and firing process at 650℃ for 5min each were operated. Those spray coating process and thermal process were repeated until film thickness reached 50μm. After film fabrication, poling was operated by corona discharge at 400℃. The output voltage of power supply was 25kV.

Optical image of CBT/BST film onto titanium substrate is shown in **Fig. 1**. Film thickness of CBT/BST was measured by a micrometer and the values were ~50μm. Piezoelectric constant d_{33} was measured by ZJ-3B piezo d33 meter and the value was 4.3pC/N.

Fig.1 Optical image of CBT/BST film.

3. Experimental results

After fabrication of ~1cm diameter top electrode by a conductive silver pen, ultrasonic responses of the CBT/BST film in pulse-echo mode were recorded from room temperature to 600℃. Platinum wires were used as electrical cables and electrical connection between electrodes and wires were established by a ceramic weight. The sample was set inside an electrical furnace and measurement data was recorded by a digital oscilloscope. First, the ultrasonic response was measured at room temperature in order to confirm the piezoelectricity. The result is shown in **Fig. 2**. Clear multiple echoes from the bottom surface of the titanium substrate were obtained and it was confirmed that poling was succesfull.

Thereafter, CBT/BST sample was heated to 600℃. The ultrasonic response was measured every 100 ℃ after 5min holding time. Ultrasonic measurement result at 600℃ is shown in **Fig. 3**. Clear multiple echoes were still observed at 600℃.

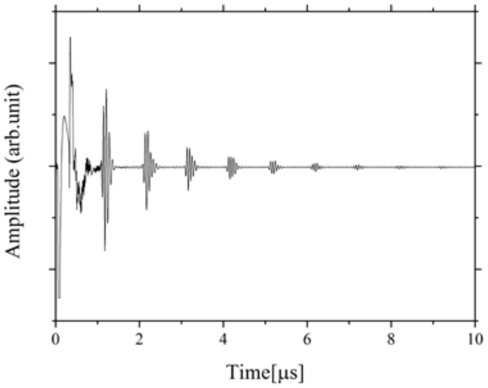

Fig. 2 Ultrasonic response of CBT/BST film fabricated on 3mm thick titanium substrate at room temperature.

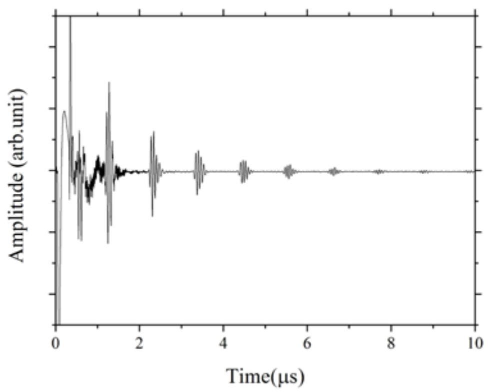

Fig. 3 Ultrasonic response of CBT/BST film fabricated on 3mm thick titanium substrate at 600℃.

As the temperature rises, the piezoelectricity weakens and the signal amplitude becomes smaller, even though signal to noise ratio (SNR) seems almost equivalent. In order to determine the temperature effect quantitatively, sensitivity was calculated as following equation;

$$\text{Sensitivity} = -\left(20\log\frac{V_1}{V_2} + \text{Gain of P/R}\right) \quad (1)$$

where V_1 is the reference amplitude, which is 0.8 $V_{p\text{-}p}$ in this experiment, V_2 is the $V_{p\text{-}p}$ of the first reflected echo from the bottom surface of the titanium substrate. P/R means pulser/receiver so that this equation calculate true required gain of pulser/receover in order to achieve 0.8V. -1 is multiplied to assist intrinsic understanding. The temperature dependence of CBT/BST sensitivity is shown in **Fig. 4**. The sensitivity was dropped exponentially above 400°C. This turning point happened much lower than that of CBT/PZT. The lower Curie temperature of BST would affect the result.

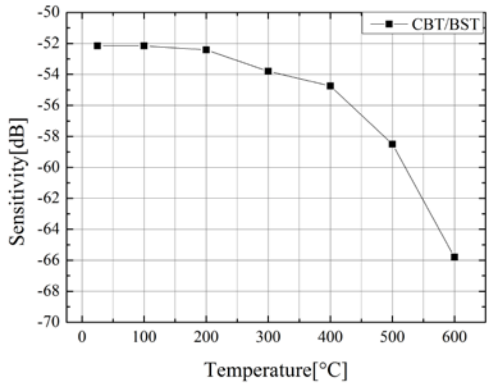

Fig. 4 Sensitivity of CBT/BST film fabricated on 3mm thick titanium substrate at various temperatures.

5. Conclusions

50μm thick CBT/BST sol-gel composite was fabricated on a 3mm titanium substrate to determine lead-free high temperature ultrasonic transducer possibility. The piezoelectric constant d_{33} was 4.3pC/N. Pulse-echo mode ultrasonic measurement was carried out from room temperature to 600°C. Even though at 600°C, clear multiple echoes were still observed and SNR was almost equivalent with that of room temperature, sensitivity dropped exponentially above 400°C. Further research is required to determine maximum long-term operation temperature.

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