

## Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> Based Lead-Free Sol-Gel Composite Ultrasonic Transducers

Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> ベース非鉛ゾルゲル複合体超音波トランスデューサ

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### 1. Introduction

In recent years, on-line non-destructive testing (NDT) in industrial fields has been desired for safety and economic reasons. Conventional ultrasonic transducers are not suitable for high temperature use because they lack of high temperature durability in piezoelectric materials, backing materials, and couplant, even though there is on-line monitoring demands during industrial operation at elevated temperatures.

Sol-gel composite ultrasonic transducers has been developed for industrial monitoring purpose and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BiT)/Pb(Zr,Ti)O<sub>3</sub> (PZT) sol-gel composite ultrasonic transducer shows high temperature durability from room temperature to 500°C.<sup>1)</sup> BiT is lead-free material, and has high temperature durability. In addition, poling is easier than CaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (CBT) based sol-gel composite.<sup>2)</sup> However, for CBT/PZT, PZT sol-gel phase contains lead (Pb) and it eliminates lead-free BiT advantage. Lead causes environmental pollution and concern about adverse effects on the human body. Even though ceramics is generally very stable, lead can evaporate above 300°C, and can accelerate the steel oxidation above 600°C. Therefore, development of lead-free ultrasonic transducers is desired, especially for high temperature application.

In this research, BiT based lead-free sol-gel composite materials have been investigated. For sol-gel solution material, it should be lead-free and it is preferable to have higher enough dielectric constant than that of BiT powder phase. BaTiO<sub>3</sub> (BT), BiT, Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> (BST) were chosen as sol-gel solution in this time as lead-free material and PZT was also used for reference. BiT/PZT, BiT/BT, BiT/BiT and BiT/BST samples were fabricated and compared the ultrasonic measurement results at various temperatures.

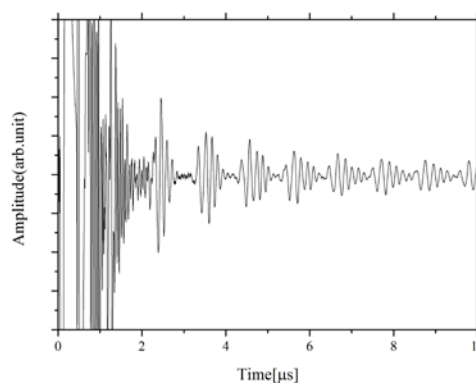
### 2. Fabrication of BiT based sol-gel composite samples

BiT based samples were prepared by sol gel spray technique.<sup>3-5)</sup> The BiT powder and each sol-gel solution were mixed by a ball mill machine. The mixed solution was sprayed onto a titanium

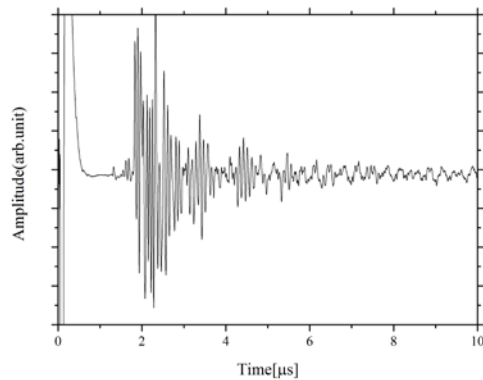
substrate having a thickness of 3 mm. The samples were dried at 150 °C, and fired at 650 °C for 5 minutes. This process was repeated until the target thickness of 50 μm. After that, an electrode with a diameter of 1 cm was made of platinum paste at the top of the sample and polarization was performed. The polarization was executed by DC corona discharge.

### 3. Experimental results

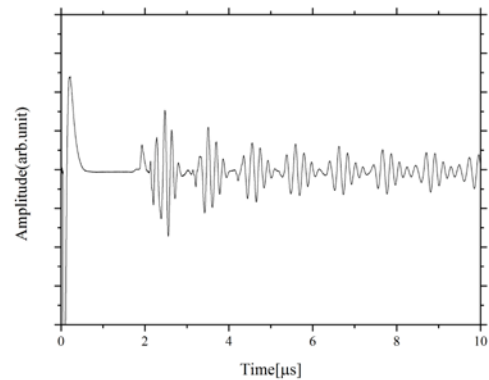
First, the ultrasonic response in pulse-echo mode of each sample at room temperature was measured. Clear multiple echo was confirmed in all samples. Next, the temperature was changed to 600°C. Data was recorded by a digital oscilloscope every 100°C after 5min holding. The ultrasonic response at 500°C of each is shown in **Fig. 1-4**. Waveforms were confirmed at 500°C for all the samples. However, for BiT/BT and BiT/BST, signal to noise ratio (SNR) was poor due to low signal strength. BiT/BiT showed the clearest signal at 500°C, and the waveform was observed even at 600°C. The ultrasonic response of BiT/BiT at 600 °C is shown in **Fig. 5**. Among those materials, BiT/BiT demonstrated best high temperature durability because the BiT sol-gel solution has highest Curie temperature, though it sacrifices poling facility.



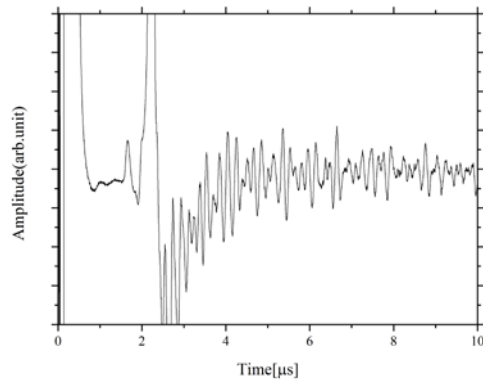
**Fig.1** Ultrasonic response of BiT/PZT at 500 °C



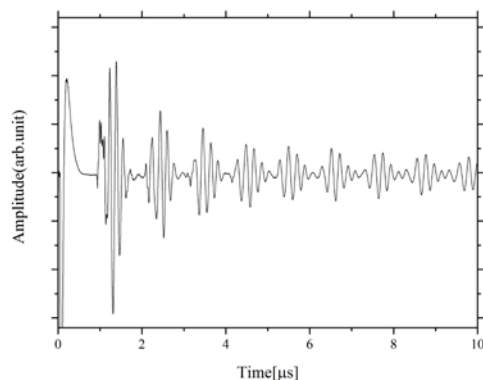
**Fig.2** Ultrasonic response of BiT/BT at 500 °C



**Fig.5** Ultrasonic response of BiT / BiT at 600 °C



**Fig.3** Ultrasonic response of BiT/BST at 500 °C



**Fig.4** Ultrasonic response of BiT/BiT at 500 °C

#### 4. Conclusions

In this experiment,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  based lead-free sol-gel composite ultrasonic transducers were investigated. Among BiT/BT, BiT/BST and BiT/BiT, BiT/BiT showed high temperature durability and clear multiple echoes were confirmed at 600°C. BiT/BiT demonstrated better performance than traditional BiT/PZT even though poling was more difficult. Further research will be required for BiT/BiT to determine high temperature durability at 600°C.

#### References

1. M. Kobayashi and C.-K. Jen: Smart Mater. Struct. **13** (2004) 951.
2. Y. Inada, T. Inoue, M. Kobayashi, H. Nagata, and T. Takenaka: Jpn. J. Appl. Phys. **53** (2014) 07KB10.
3. M. Kobayashi, T.R. Olding, M. Sayer and C.-K. Jen: Ultrasonics **39** (2002) 675.
4. K. Kimoto, M. Matsumoto, T. Kaneko, and M. Kobayashi: Jpn. J. Appl. Phys. **55** (2016) 07KB04.
5. K. Kiyofuji, K. Keisuke and M. Kobayashi: Proc. Symposium on Ultrasonic Electronics, 2016.