# High Temperature properties of $\mathbf{C a B i}_{2} \mathrm{Ta}_{2} \mathrm{O}_{9} / \mathbf{B i}_{4} \mathrm{Ti}_{3} \mathbf{O}_{12}$ 

$\mathrm{CaBi}_{2} \mathrm{Ta}_{2} \mathrm{O}_{9} / \mathrm{Bi}_{4} \mathrm{Ti}_{3} \mathrm{O}_{12}$ の高温特性

Tomoya Yamamoto ${ }^{1 \ddagger}$ ，Syohei Nozawa ${ }^{1}$ ，Minori Furukawa ${ }^{1}$ ，Hajime Nagata ${ }^{2}$ ， and Makiko Kobayashi ${ }^{1}$（ ${ }^{1}$ Kumamoto Univ．，${ }^{2}$ Tokyo Univ．of science）山本智也 ${ }^{1 \text { }}$ ，野澤勝平 ${ }^{1}$ ，古川美徳 ${ }^{1}$ ，永田肇 ${ }^{2}$ ，小林牧子 ${ }^{1}$（ ${ }^{1}$ 熊本大学，東京理科大学）

## 1．Introduction

Non－destructive testing（NDT）is widely used in thermal power plants and is important because small defect lead to serious accidents．Therefore， various NDT methods have been developed．Sol－gel composite ultrasonic transducers have been developed to improve high temperature durability， because so－gel composite transducers do not require couplant，nor backing material，and can apply for curved surfaces ${ }^{1-5}$ ．For carbon dioxide emissions reduction，new－generation thermal power plants has been developed，though NDT method is the issue． In thermal power plants，ultrasound NDT is often used for cooling pipe inspection，though operation temperature of new－generation thermal power plant will be $\sim 700^{\circ} \mathrm{C}$ in order to increase efficiency．In previous research，the $\mathrm{CaBi}_{2} \mathrm{Ta}_{2} \mathrm{O}_{9}(\mathrm{CBTa}) /$ $\mathrm{Pb}(\mathrm{Zr}, \mathrm{Ti}) \mathrm{O}_{3}$（PZT）ultrasonic transducers were developed and confirmed that there was high temperature durability up to $840^{\circ} \mathrm{C}$ in a short time ${ }^{5)}$ ． However，at high temperatures，lead contained in PZT vaporizes and adversely affects environment， so it is necessary to develop lead－free substances． Therefore，it is necessary to develop new lead－free sol－gel composite．

In this research，new sol－gel composite， $\mathrm{CBTa} / \mathrm{Bi}_{4} \mathrm{Ti}_{3} \mathrm{O}_{12}(\mathrm{BiT})$ was developed．CBTa was chosen as ferroelectric powder phase material because Curie temperature is sufficiently high such as $923^{\circ} \mathrm{C}$ ．BiT was adopted because it is lead－free and the Curie temperature is relatively high such as $675^{\circ} \mathrm{C}$ ．The bulk property was used because it is difficult to measure BiT sol－gel solution property． In this research，high temperature durability of $\mathrm{CBTa} / \mathrm{BiT}$ transducers were examined．Ultrasonic performance of $\mathrm{CBTa} / \mathrm{BiT}$ samples were investigated at various temperatures．

## 2．Sample fabrication

Samples were manufactured by sol－gel spray technique ${ }^{1,3-5}$ ．First，BiT sol－gel solution was manufactured． $\mathrm{CBTa} / \mathrm{BiT}$ sol－gel composite was prepared by mixing CBTa piezoelectric powders and BiT sol－gel solution by a ball mill machine for about 1 day．Next，the dimensions of titanium substrates were $30 \times 30 \times 3 \mathrm{~mm}$ was covered with an
$80-\mu$ m－thick paper mask with a $20 \times 20 \mathrm{~mm}$ ，then $\mathrm{CBTa} / \mathrm{BiT}$ sol－gel composite was sprayed onto the titanium substrate．Titanium was chosen as substrate material because of high temperature durability and low thermal capacitance．Thermal process，drying at $150^{\circ} \mathrm{C}$ and firing at $650^{\circ} \mathrm{C}$ were carried out for 5 min each other，was processed after spray coating．These processes repeat until the target films thickness became about $50 \mu \mathrm{~m}$ ．When $\mathrm{CBTa} / \mathrm{BiT}$ thin film reached the target film thickness，a platinum upper electrode was formed by drying at $150^{\circ} \mathrm{C}$ and firing at $700^{\circ} \mathrm{C}$ for 2 h each other．The upper platinum electrode was formed in the center of the film with 10 mm diameter．Next， poling process was performed．For poling，corona discharge was used．Poling was carried out by heating at $950^{\circ} \mathrm{C}$ for 10 min ．There were two reasons for the temperature set for polling．First， since the titanium substrate was thin，it is rapidly cooled down and it reached the target temperature which was slightly higher than Curie temperature of BiT sol－gel phase．Second，it was high enough to promote molecular movement to assist poling．The output voltage was about 31 kV and the output current was about 0.13 mA ．The electrical filed was supplied until the sample was cooled down to room temperature． $\mathrm{CBTa} / \mathrm{BiT}$ fabricated on a titanium substrate is shown in Fig． 1.


Fig．1．Optical image of $\mathrm{CBTa} / \mathrm{BiT}$ on $30 \times 30 \times 3 \mathrm{~mm}$ titanium substrate．

## 3．Experimental results

The maximum temperature test was carried out to confirm the operable limit temperature of $\mathrm{CBTa} / \mathrm{BiT}$ ultrasonic transducer．The
sample was put into the furnace and platinum electrical cables were connected to a platinum top electrode and titanium substrate through holes of the furnace. Platinum electrical cables were connected to the digital oscilloscope and pulser/receiver ( $\mathrm{P} / \mathrm{R}$ ). A digital oscilloscope was used for data recording. The furnace temperature was changed from room temperature by $100^{\circ} \mathrm{C}$ increments, and from the $800^{\circ} \mathrm{C}$, which is around the Curie temperature of CBTa , the data was recorded every $10^{\circ} \mathrm{C}$. Every temperature, holding time was 5 min . Ultrasonic measurement results in pulse-echo mode at room temperature and $800^{\circ} \mathrm{C}$ are shown in Figs. 2 and 3, respectively. Multiple reflected echoes are clearly observed with reasonable signal-to-noise ratio (SNR).


Fig. 2. Ultrasonic response of $\mathrm{CBTa} / \mathrm{BiT}$ sample fabricated on 3 -mm-thick titanium substrate at room temperature.


Fig. 3. Ultrasonic response of $\mathrm{CBTa} / \mathrm{BiT}$ sample fabricated on 3-mm-thick titanium substrate at $800^{\circ} \mathrm{C}$.

Fig. 4 shows the sensitivity calculation results of the acceleration deterioration test. The sensitivity was calculated by following equation:

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\begin{equation*}
\text { Sensitivity }=-\left(20 \log _{10} \mathrm{~V}_{1} / \mathrm{V}_{2}+\text { gain of } \mathrm{P} / \mathrm{R}\right)(\mathrm{dB}) \tag{1}
\end{equation*}
$$

Where $\mathrm{V}_{1}$ is the ideal amplitude, $0.1\left(\mathrm{~V}_{\mathrm{p}-\mathrm{p}}\right)$ in this experiment, $\mathrm{V}_{2}$ is the amplitude ( $\mathrm{V}_{\mathrm{p}-\mathrm{p}}$ ) of the second reflected echo from the bottom surface of the substrate. From Fig. 4, the sensitivity was suddenly decreased above $700^{\circ} \mathrm{C}$. It is caused by depoling of CBTa piezoelectric powder phase.


Fig. 4. Temperature dependence of $\mathrm{CBTa} / \mathrm{BiT}$ sensitivity of $\mathrm{CBTa} / \mathrm{BiT}$

## 5. Conclusions

$\mathrm{CBTa} / \mathrm{BiT}$ sol-gel composite was developed for high temperature ultrasonic applications at $700^{\circ} \mathrm{C}$. $\mathrm{CBTa} / \mathrm{BiT}$ films were fabricated at on titanium substrates by sol-gel spray technique. The maximum operation temperature test was carried out and the ultrasonic performance of the $\mathrm{CBTa} / \mathrm{BiT}$ was confirmed with reasonable SNR at $800^{\circ} \mathrm{C}$. The result of the maximum temperature test was comparable with that of $\mathrm{CBTa} / \mathrm{PZT}$. Therefore, $\mathrm{CBTa} / \mathrm{BiT}$ demonstrated the potential for NDT of the new-generation thermal power plants. Long term operation test is required and will be operated soon.

## References

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