3P1-4

High Temperature Properties of $LiNbO_3/Bi_4Ti_3O_{12}$

$LiNbO_3/Bi_4Ti_3O_{12}$ の高温特性

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

1. Introduction

In recent years, development of on-line non-destructive inspection technology in the industrial field has been advanced for safety and economic reasons. In particular, non-destructive inspection during high-temperature operation is a technology that needs development even in the environmental aspect such as CO_2 reduction.

A sol-gel composite ultrasonic transducer was developed for industrial non-destructive inspection and $Bi_4Ti_3O_{12}$ (BiT)/Pb(Zr,Ti)O_3(PZT) sol-gel composite ultrasonic transducer has high temperature durability from room temperature to 500°C. [1)] However, lead (Pb) is contained in the PZT sol-gel phase of BiT/PZT, and lead has a danger of adversely affecting the environment and human health. There is a possibility that lead leads to sublimation above 300 °C and promoting oxidation of steel above 600 °C. Therefore, development of a lead-free ultrasonic transducer is desired especially for high temperature applications.

In the previous study, high temperature properties of sol-gel composites, BiT piezoelectric powder and several types of lead-free sol-gel solution, were studied and BiT sol-gel solution demonstrated high potential for lead-free high temperature ultrasonic transducer application, though BiT/BiT showed severe deterioration at 600°C. $CaBi_4Ti_4O_{15}$ (CBT)/BiT, in which powder phase has a higher Curie temperature than that of BiT/BiT, was developed and it realized long-term high temperature durability up to 600°C. [5.6)] However, since new type of thermal power plants requires further high operation temperature, development of an ultrasonic transducer having high temperature durability over 600 °C is required.

In this research, $LiNbO_3$ (LN)/BiT was developed to improve high temperature durability over 700°C because LN has very high Curie temperature such as 1200°C. In past study of LN/BiT, [7)] it seems that poling was insufficient and safficient signal strength was not obtained. Furthermore, steel substrate which cannot withstand 1000°C was used so that there was no thermal cycle test. In this study, titanium substrate was used to imrove thermal durability of substrate, and sufficiently high electrical field was supplied by corona discharge to evaluate LN/BiT thermal durability more precisely.

2. Fabrication of $LiNbO_3$/BiT sol-gel composite samples

LN/BiT samples were manufactured by sol-gel spray technique.[1-4)] LN piezoelectric powders and BiT sol gel solution were mixed in a ball mill machine. The thoroughly mixed solution was coated onto a 3 mm thick titanium substrate by spray method. The spray-coated sample was dried at 150 °C and calcined at 650 °C for 5 minutes each. These processes were repeated to produce a LN/BiT sample having a film thickness of 50 µm. Thereafter, an electrode having a diameter of 1 cm was formed on the sample by using platinum paste, and the electrode was subjected to poling treatment. Poling was performed by applying a corona discharge to a sample from 900°C to room temperature conditions. The optical image of LN/BiT sample is shown in **Fig. 1**.

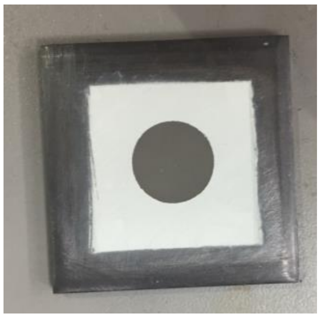

Fig.1 A LN/BiT sample.

3. Experimental results

First, the ultrasonic response of LN/BiT at RT was measured in pulse echo mode and the data was recorded by a digital oscilloscope as shown in **Fig. 2**. Clear multiple echoes from the back surface of the titanium substrate were confirmed. Next, a high temperature test of LN/BiT from RT up to 1000 °C was carried out. Between RT and 900°C, the data was recorded every 100°C change. After 900 °C, the data was recorded every 10 °C change. For all the measurements, after 5 min holding time at each temperature, ultrasonic response was recorded. The ultrasonic response of LN/BiT at 940 °C is shown in **Fig. 3**. There are still clear multiple echoes though time delay between echoes becomes longer because of velocity change. Ultrasonic response of LN/BiT was confirmed up to 1000 °C. However, the signal strength and signal to noise ratio (SNR) suddenly deteriorated above 950 °C. It is considered that SNR deteriorated due to high thermal disturbance and electrical impedance mismatch at high temperature, since resistance of LN became lower. Ultrasonic response of LN/BiT at RT after high temperature test is shown in **Fig. 4**. The SNR recovered and even better than before the experiment, it could be due to platinum paste curing.

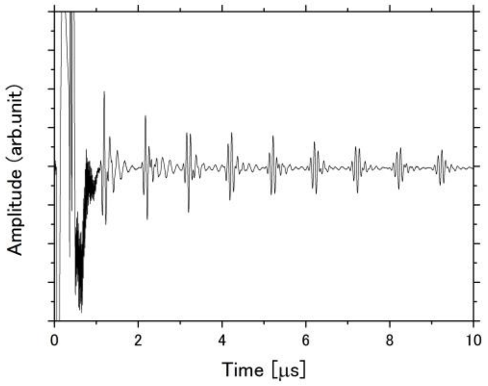

Fig.2 Ultrasonic response of LN/BiT on 3mm thick titanium substrate at RT.

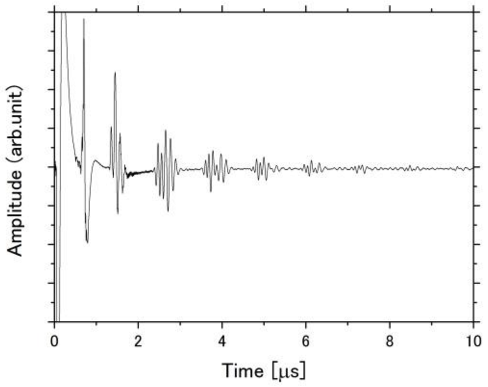

Fig.3 Ultrasonic response of LN/BiT on 3mm thick titanium substrate at 940 °C.

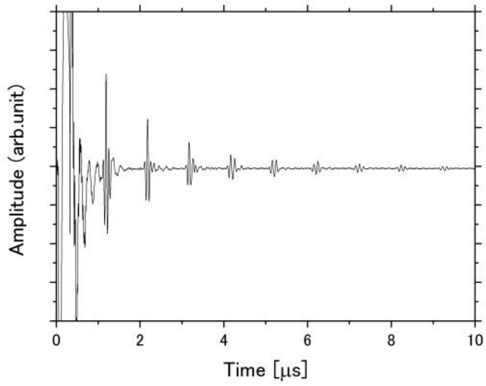

Fig.4 Ultrasonic response of LN/BiT at RT after high temperature test.

4. Conclusions

In this research, high temperature performance of LN/BiT lead free sol-gel composite was investigated for ultrasonic transducer applications with high operation temperature over 700°C. High temperature test of LN/BiT up to 1000 °C was conducted and ultrasonic response was confirmed even at 1000°C. Clear signal could be confirmed at 940°C. However, the SNR was significantly deteriorated above 950°C. LN/BiT ultrasonic transducers showed the potential for non-destructive inspection of new thermal power stations above 700 °C even if polarization is relatively difficult. It is necessary to carry out thermal cycle tests and long-term measurement at high temperatures for further evaluation.

References

1. M. Kobayashi and C.-K. Jen: Smart Mater. Struct. **13** (2004) 951.
2. M. Kobayashi, T.R. Olding, M. Sayer and C.-K. Jen: Ultrasonics **39** (2002) 675.
3. K. Kimoto, M. Matsumoto, T. Kaneko, and M. Kobayashi: Jpn. J. Appl. Phys. 55 (2016) 07KB04.
4. K. Kiyofuji, K. Keisuke and M. Kobayashi: Proc. USE. (2016) 2P1-1.
5. M. Yugawa, T. Yamamoto, and M. Kobayashi: Proc. USE. (2017) 3P1-7.
6. K. Okada, T. Yamamoto, M. Yugawa, and M. Kobayashi: Proc. USE. (2017) 1P1-2.
7. C.T. Searfass, A. Baba, B.R. Tittmann, and D. K. Agrawal: Rev. Quant. Nondest. Eval. **29** (2010) 1035.