Curie Temperature Estimation of Pb(Zr, Ti)O_3-based Sol-gel Composites

Pb(Zr, Ti)O_3 ベースのゾルゲル複合体におけるキュリー温度の推定

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1. Introduction

One of the uses of piezoelectric elements is non-destructive inspection in industrial facilities such as power plants and chemical plants. Ultrasonic transducers are used to find cracks and corrosion in such industrial facilities [1]. Sol-gel composites are prepared by mixing piezoelectric powder and sol-gel solution and have fine pores. Therefore, there is no need for a mechanism with low heat resistance such as backing material or coplant, which is found in conventional ultrasonic transducers. Therefore, ultrasonic transducers using sol-gel composites have the potential to be used for non-destructive inspection in high temperature environments [2].

Pb(Zr, Ti)O_3 (PZT) material is commonly used as ultrasonic transducers due to their high piezoelectricity and relatively high Curie temperature. In the past, research has been conducted on PZT/PZT ultrasonic transducers manufactured by the manual spray method. The Curie temperature of the PZT piezoelectric powder obtained from the bulk material is about 300°C, but there is an ultrasonic response even if it exceeds about 450°C, suggesting that the Curie temperature may have risen [3]. In addition, when the temperature at the limit where the ultrasonic response can be confirmed was measured in PZT/PZT manufactured by the automatic spray method, the ultrasonic response was confirmed up to 530°C in the negative poling sample, and even if it was measured at room temperature thereafter, piezoelectricity remained [4].

Based on those results, in this study, PZT sol-gel solution were used. First, PZT/PZT ultrasonic transducers were manufactured by the automatic spray method. Next, each capacitance was measured, and a Curie temperature estimate was performed.

2. Fabrication method

The PZT sol-gel solution and PZT piezoelectric powder are crush and mixed in a ball milling machine for about a day. Spray this coating on a 30 mm square, 3 mm thick titanium substrate. Next, dry at room temperature for 5 minutes and in a drying oven at 150°C for 5 minutes. Finally, perform firing for 5 minutes in a firing oven at 650°C. The procedure of spraying, drying and firing is repeated until the film thickness reaches 50 μm. Next, poling processing is performed. The poling process used corona discharge poling and pulse poling with pulser receiver. For corona discharge poling, the distance between the needle and the substrate was 40 mm, and 40 kV was applied for 5 minutes. After the poling process, the upper electrode is made. In this study, the upper electrode uses high performance silver paste. In this study PZT/PZT were produced. Four PZT/PZT are used in this study, each measuring capacitance before and after poling to estimate Curie temperature. The piezoelectric constants d_{33} of the PZT/PZT samples after poling were 51.0 [pC/N] and 2.0 [pC /N], respectively. **Figure 1** shows the optical image of PZT/PZT after fabrication completion.

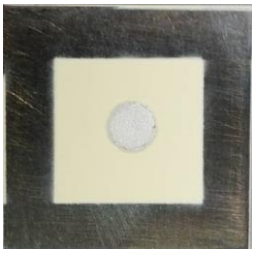

Fig.1 Optical image of PZT/PZT film on 3mm thick titanium substrate.

3. Experimental Results of PZT-based Sol-gel Composites

Capacitance measurements were operated to estimate the Curie temperature. Set two PZT/PZT samples before poling in a furnace, raise the substrate temperature from room temperature to 600°C, and measure the capacitance at each temperature. **Figure 2** shows the capacitance measurement environment. **Figure 3** shows the transition of the capacitance of the PZT/PZT ultrasonic transducer manufactured by the automatic spray method before poling. The two samples had peaks at 500 °C and 530 °C, respectively. Next, two PZT/PZT samples after poling were set in the furnace, and the capacitance was measured. **Figure 4** shows the transition of the capacitance of the PZT/PZT ultrasonic transducer after poling.

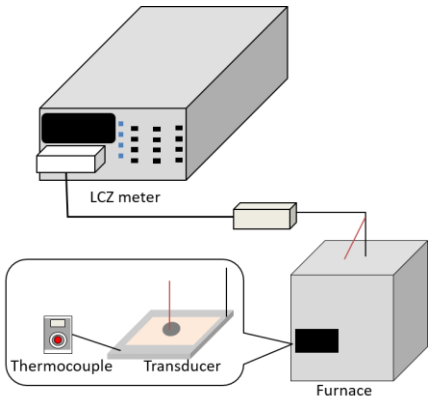

Fig.2 Capacitance measurement setup

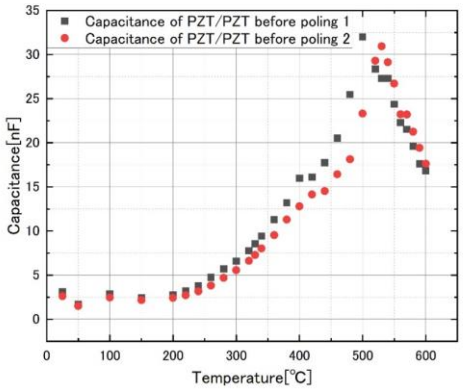

Fig.3 Capacitance of PZT / PZT before poling fabricated on a titanium substrate about 3 mm thick

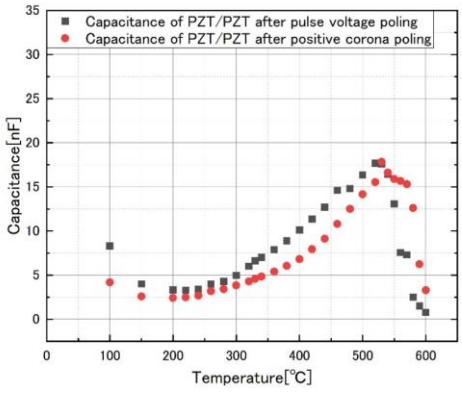

Fig.4 Capacitance of PZT / PZT after poling fabricated on a titanium substrate about 3 mm thick

Since the furnace used in this experiment was overshoot, it was not possible to measure at a temperature lower than 100°C, indicating a capacitance of 100°C or higher. However, assuming that the Curie temperature of the PZT piezoelectric powder is about 300 °C and rises above that, data for temperatures below 100°C are considered insignificant. From Fig. 4, the sample poled by the pulse voltage showed a peak of capacitance at 520°C, and the sample with positive corona discharge poling showed a peak at 530°C. In addition, although the capacitance is smaller after poling, it is possible that there are individual differences in the top electrodes. In both cases, the tendency that the capacitance drops once and reaches the peak of the capacitance at 500°C or higher is consistent, and it can be said that it is consistent with the tendency of the previous studies. Considering that the conditions such as substrate, film thickness, and electrode size have changed from the PZT/PZT ultrasonic transducers in the past research, the PZT/PZT ultrasonic transducers may reach the peak capacitance at 500 °C or higher. It can be said that it was confirmed with reproducibility. From those results, it is highly possible that the Curie temperature of PZT has changed to 500°C or higher.

4. Conclusion

PZT/PZT ultrasonic transducers were manufactured by the automatic spray method, the capacitance was measured, and the Curie temperature was estimated. First, the PZT/PZT ultrasonic transducer was set in the furnace and the capacitance was measured. Before poling, the peak capacitance was confirmed at substrate temperatures of 500°C and 530°C. In the sample after poling, peak capacitance was confirmed at 520°C and 530°C. As a result, it was considered that the Curie temperature in PZT/PZT had risen from 300°C to 500°C or higher even before the poling treatment was performed.

In this study, silver paste electrode was used. It is very likely that individual differences will occur in the performance of the electrodes by applying them manually to create the electrodes, and they can also deteriorate at high temperatures. Therefore, in the future, top electrodes by sputtering method will eliminate human error, more accurate measurement will be performed, and reproducibility will be further confirmed in addition to increase the number of samples.

References

1. V. Tanasoiu, C. Miclea, C. Tanasoiu: Journal of Optoelectronics and Advanced Materials Vol. 4, No. 4, December 2002, p. 949 – 957.
2. M. Kobayashi and C.-K. Jen: Smart Mater. Struct. 13, 951 (2004).
3. S. Fujimoto, T. Namihira, K. Iwata, and M. Kobayashi: Japanese Journal of Applied Physics 54 (2015), 07HB04.
4. M. Hidaka, T. Hara, K. Nakatsuma, and M. Kobayashi: Proceedings of Symposium on Ultrasonic Electronics, Vol. 41 (2020).