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Characteristic change of sol-gel composites by PZT sol-gel phase in the high temperature environment

PZT ゾルゲル相によるゾルゲル複合体の高温環境における特性変化

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1. Introduction

The authors have studied the piezoelectric thick film by sol-gel composites, which is composed by ferroelectric powder phase, dielectric sol-gel phase, and air phase, and it was found that the operation temperature of sol-gel composites increased even above Curie temperatures of raw materials, when lead zirconate titanate (PZT) was used as ferroelectric powder phase and dielectric sol-gel phase material, i.e. PZT/PZT.[1)] G.A Rossetti *et. al.* reported that the Curie temperature of PZT thin film was different and higher by ~200°C than that of bulk PZT.[2,3)] Similar phenomena could happen to PZT/PZT thick film, however, Curie temperature shift of PZT/PZT sol-gel composite has not been confirmed yet.

In this study, in order to measure Curie temperature shift of PZT/PZT, piezoelectric constant d_{33} was measured after heating. In concrete, one PZT/PZT sample was heated up at specified temperature for 1h by a furnace and then cooled down to room temperature. After cooling, piezoelectric constant d_{33} was measured before and after ultrasonic monitoring at room temperature in order to confirm the temperature of piezoelectricity extinguishment, i.e. Curie temperature.

2. Experimental method

2-1. PZT/PZT sample fabrication

Fabrication process of PZT/PZT films was the same as the past studies; [1,4)] First, PZT powders and PZT sol-gel solution were prepared and mixed by ball milling. The material properties of PZT powder and PZT sol-gel are shown in **Table I**. Next, the mixture was sprayed directly onto titanium substrates. The dimension of the titanium substrate was 30mm×30mm ×3mm. This dimension was chosen because of heating facility and reflected echo visibility. Titanium was chosen as substrate material because of high temperature resistance.

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Drying process at 150°C by a hot plate and firing process at 650°C by a furnace were operated for 5min each. Those spray coating process and thermal process were repeated several times in order to obtain ~100μm thickness. Corona discharge was used for polarization at room temperature.

Table I: Material properties used in this experiment

Material Property	PZT powder	PZT sol-gel
Curie Temperature(°C)	300	350
d_{33}(pC/N)	410	200
ε_r	2100	1100

2-2. Measurement method

First, piezoelectric constant d_{33} was measured before and after ultrasonic measurement before poling for no piezoelectricity reference. Piezoelectric constant d_{33} was measured by ZJ-3EN Piezo d_{33} meter supplied by Institute of Acoustic, Chinese Academy of Science. For ultrasonic measurement, JSR DPR300 Pulser/Receiver (P/R) was used. The optional setting except gain was kept as the same conditions during whole measurement. In this setting, the initial pulse voltage was approximately -100V, pulse energy was 1.55 μJ, and the pulse duration was 10-70 ns. Then the sample was heated at 400°C for 1h by a furnace. Initial heating temperature was 400°C because it was clearly higher temperature than both Curie temperatures shown in Table I. After 400°C heating, the sample was immediately removed from the furnace and was cooled to room temperature. Ultrasonic measurement in pulse-echo mode was carried out in order to confirm/evaluate piezoelectricity in addition to d_{33} measurement. Piezoelectric constant d_{33} was measured before and after ultrasonic measurement to evaluate piezoelectricity. The same experimental process such as 1h heating, cooling down, d_{33} measurement, ultrasonic measurement and d_{33} measurement was repeated for every 100°C until the piezoelectricity of PZT/PZT was determined as vanished.

3. Experimental results

Table II showed d_{33} measurement result. P/R contact means ultrasonic measurement with using P/R, i.e. negative pulse voltage excitation. First, unpoled sample before P/R contact showed very small value of d_{33}. Then after P/R contact, d_{33} value turned to negative, due to negative -100V pulse voltage. After poling, d_{33} showed relatively high positive value, though it was still much smaller than those of raw materials in Table I, because of porosity. After heating at 500°C and 600°C, the values became smaller but they were still positive values. Finally after heating at 600°C, it was determined as no piezoelectricity because before the P/R contact, the value of d_{33} was less than 1, and after P/R contact, d_{33} showed a negative value, and it was similar tendency as unpoled sample, reference sample of no piezoelectricity. Measurement error of d_{33} was ±5% ±1 for 1 to 20 pC/N when the resolution of d_{33} meter was 0.1 pC/N. Therefore the absolute value of d_{33} of 1 pC /N or less might be no piezoelectricity as well.

Table II: Piezoelectric constant d_{33} of PZT/PZT after high temperature experience.

Temperature(°C)	**d_{33}[pC/N]**
30(before poling, before P/R contact)	0.2
30(before poling, after P/R contact)	-0.8
30(after poling, after P/R contact)	65.7
400(before P/R contact)	11.3
400(after P/R contact)	8.6
500(before P/R contact)	2.3
500(after P/R contact)	1.6
600(before P/R contact)	0.5
600(after P/R contact)	-2.1

In order to summarize the ultrasonic performance, the sensitivity for each measurement was calculated and the result was shown in **Table III**. In this paper, the sensitivity was calculated by -1 multiplied P/R gain to achieve 4Vp-p of 1st reflected echo. -1 was multiplied in order to assist intuitive understanding. It should be mentioned that the sensitivity of the sample before poling could not be calculated because 1st reflected echo was hidden in noise, though there were multiple reflected echoes which showed that the sample was poled by P/R pulse voltage. It seemed that the sensitivity was not so much deteriorated after 400°C for 1h. It was interesting that after the exposure of 600°C for 1 h, the sensitivity was higher than that of 500°C exposure, probably higher than sample before heating, and it agreed with d_{33} results in Table II. 600°C was closed to crystallization temperature of PZT sol-gel so that crystallization of PZT sol-gel maybe further progressed.

From, those results, it was assumed that Curie temperature of PZT/PZT existed between 500°C and 600°C and it was agreed with the past study result, i.e. Curie temperature shifted about 200°C to high temperature. [4)]

Table III: Sensitivity of PZT/PZT after high temperature experience.

Temperature(°C)	**Sensitibity(dB)**
30 before poling	N/A
30 after poling	-43.6
400	-48.4
500	-60.8
600	-56.1

4. Conclusions

Piezoelectric constant d_{33} and ultrasonic performance of PZT/PZT film fabricated onto 3mm thick titanium substrate was measured after high temperature exposure in order to study about the Curie temperature shift of PZT/PZT. The results indicated that the piezoelectricity of PZT/PZT remained after 500°C exposure for 1h, and it was vanished after 600°C for 1h exposure experience, therefore it could be assumed that Curie temperature existed between 500°C from 600°C and shifted to about 200°C higher temperature. In future, in order to support those results, capacitance should be measured by LCZ meter while heating the sample within a furnace.

References

1. S. Fujimoto, T. Namihira and M. Kobayashi: Proc. Symp. Ultrason. Electron. **34** (2014) 27.
2. G.A. Rossetti, Jr, L.E. Cross, and K. Kushida: Appl. Phys. **59** (1991) 2524.
3. K. Wasa, T.Matsushima, T. Yamamoto, H.Addachi and T. Matsunaga: Piezoelectric. Mater. Devices. Symp. (2012) 35 [in Japanese].

4 T. Inoue and M. Kobayashi: Jpn. J. Appl. Phys. **53** (2014) 07KC11.