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Mn-doped $CaBi_4Ti_4O_{15}$/PZT Ultrasonic Transducers at High Temperature

Mn 添加 $CaBi_4Ti_4O_{15}$/PZT 超音波トランスデューサの高温特性

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1. Introduction

The safety assessment of infrastructure becomes the critical issues, though it is preferable to monitor minor defects on-line which are found during periodical off-line monitoring for economical operation.[1)] Ultrasonic testing is commonly used for structural health monitoring due to following advantages such as non-destructivity, non-invasivity, internal inspction capalility, high sensitivity of defects/flaws and material properties, fastness and robustness.[2)] However, the operation temperature of traditional ultrasonic transducer is limited and not suitable for high temperature on-line industrial inspection, not only Curie temperature of piezoelectric materials but also couplant and backing material.

High temperature ultrasonic transducers made by sol-gel composite has been developed. Sol-gel composite was composed of piezoelectric powder phase, high dielectric constant sol-gel phase, and air phase and it could work without couplant and backing material. The temperature limitation caused by Curie temperature still remained so that several sol-gel composites were investigated in the past.[3)] Recently new sol-gel composite material, $CaBi_4Ti_4O_{15}$(CBT)/PZT, was investigated for high temperature ultrasonic transducer applications.[4)] CBT was chosen because of high Curie temperature such as ~790°C.[5)] CBT/PZT films onto steel substrates showed CBT/PZT showed reasonable temperature stability up to 550°C, even though, the signal strength of CBT/PZT was low and signal to noise ratio (SNR) was deteriorated at high temperature. The resistance decrease of CBT at high temperature was suspected as SNR deterioration reason and it could be improved by Mn additive. In this research, slight amount of Mn was added to CBT powders in order to improve signal strength and SNR.

2. Mn-doped CBT powder

First, CBT powders with various amount of $MnCO_3$ additive were manufactured in order to optimize the amount of Mn doping. CBT powders were prepared by the conventional solid state reaction method with starting metal oxide Bi_2O_3, $CaCO_3$, TiO_2 and $MnCO_3$. The purity of all row materials was more than 99.9%. The mixed powders were calcinated at 850°C for 2 hours after drying and sintered at 1210°C for 2 hours. The resistivity of each sample made by different amount of $MnCO_3$ (0-0.5wt%) was measured by HP4339B high resistance meter and the results were shown in **Fig. 1**. It seems that addition of 0.2wt% $MnCO_3$ was best to improve resistivity. Therefore CBT powder with 0.2wt% $MnCO_3$ additive was used for following experiments.

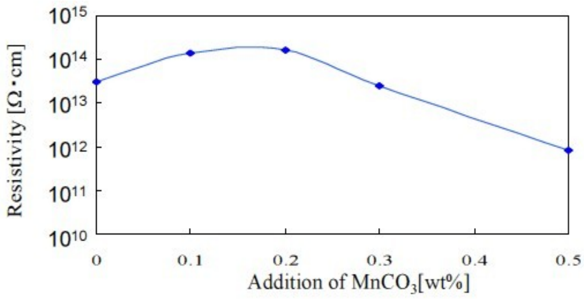

Fig.1 Resistivity dependency on $MnCO_3$ addition.

3. Mn-doped CBT/PZT

The fabrication process is based on a sol-gel spray technique developed previously.[3,4)] First, piezoelectric powders, Mn-doped CBT, were prepared by above mentioned procedures. Then Mn-doped CBT powders were mixed with PZT so-gel solution. The mixture was ball milled until appropriate viscosity for spray coating was obtained. After certain period, the mixture was sprayed onto titanium plates with dimensions of 3.3mm thickness, ~30mm length, and ~30mm width since titanium has high temperature durability above 500°C. After spray coating, thermal treatments such as drying and firing were carried out based on sol-gel method. Spray coating process and thermal treatment process were repeated several times until ~50µm thickness was achieved. The films were electrically poled using corona discharge at room temperature.

Finally silver paste top electrodes were fabricated onto sol-gel composite films.

The sample was placed onto a hotplate then heated up to 550°C, which is the maximum operation temperature of the hot plate. The capacitance of each film was measured by Agilent U1701B handheld capacitance meter. The relative dielectric constants were calculated by capacitance, top electrode area, and film thickness. The result was shown in **Fig. 2**. At room temperature, relative dielectric constant of Mn-doped CBT/PZT was ~130 and it was similar to those of pure CBT/PZT and CBT bulk material. The measured temperature was not that of substrate but that of hotplate. From Fig. 2, there was no clear peak around 350°C by PZT sol-gel phase. This tendency was similar with pure CBT/PZT and it could be the reason for that peak was hidden by CBT peak, though above 500°C, capacitance measurement was no longer available, probably due to resistance deterioration at high temperature.

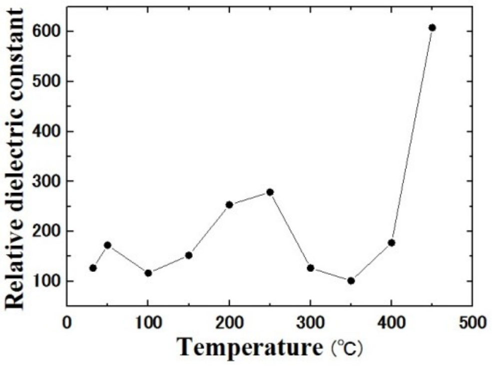

Fig.2 Relative dielectric constant dependency on temperature.

Ultrasonic response was also measured during the heating simultaneously. The ultrasonic response of Mn-doped CBT/PZT was clearly observed up to 550°C, maximum operation temperature of hot plate. It is noticed that SNR at 550°C was significantly deteriorated. Low signal strength at high temperature could be one of the reasons in addition to resistance decrease at high temperature. The sensitivity, which was calculated by gain to achieve 4Vp-p of 3rd reflected echo multiply -1 is shown in **Fig. 3**. Sensitivity was decreased up to 350°C, around PZT sol-gel phase Curie temperature, and then it became stable. However, after cooling, signal strength was deteriorated. Silver paste top electrode could be considerable factor so that alternative top electrode is required. The signal strength itself was improved by 30dB compared with pure CBT/PZT. In order to determine further, poling conditions, especially temperature, should be optimized.

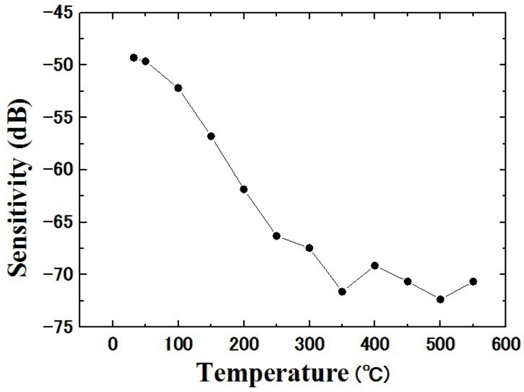

Fig.3 Sensitivity dependency on temperature

4. Conclusions

Mn-doped CBT/PZT ultrasonic transducers were investigated for high temperature applications. Resistivity of Mn-doped CBT was varied by amount of $MnCO_3$ addition and it seems that 0.2wt% addition was the best to improve the resistivity. Using 0.2wt% $MnCO_3$ addition CBT powder and PZT sol-gel solution, ~50μm thick Mn-doped CBT/PZT film was fabricated onto 3.3mm thick titanium substrate and dielectric constant and ultrasonic response were measured from room temperature to 550°C. Reflected echoes from bottom surface of the substrates were observed up to 550°C and the signal strength of Mn-doped CBT/PZT was improved compared with that of pure CBT/PZT. Further research regarding poling condition optimization is required to improve CBT/PZT signal strength further.

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