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Evaluation of the Piezoelectric Materials Synthesized by the Ultrasonic Assist-Hydrothermal Method

超音波アシスト水熱合成法による圧電材料の合成とその評価

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1. Introduction

The hydrothermal method utilizes a chemical reaction in solution to obtain piezoelectric thin films or powders [1, 2]. The obtained materials have interesting features owing to the low reaction temperature because the small residual stress results in high-quality crystals. In addition, the three-dimensional structure is acceptable as a substrate for the thin film deposition since the chemical reaction is caused in solution [1-3]. However, the hydrothermal method has some problems: for example, the slow reaction rate and the rough surface of the thin film in the case of polycrystalline lead-zirconate-titanate (PZT) deposition [1-3].

To solve these problems, we have proposed a strong ultrasonic irradiation system during the hydrothermal reaction [3]. The sonochemical effect is expected in the hydrothermal method but such trials are difficult and have never been done before because the hydrothermal method is carried out in a sealed container under high pressure and high temperature. Therefore, in this study, a ultrasonic transducer was developed to irradiate a strong ultrasound into the reaction vessel for hydrothermal method and its effect was examined for PZT thin film deposition and (K, Na)NbO_3 powder fabrication.

2. Ultrasonic transducer design

The hydrothermal method is conducted in a sealed container at high temperature and high pressure. In addition, the high alkaline condition is severe for the ultrasonic transducer [1-3]. To overcome these problems, a high-power ultrasonic transducer for the hydrothermal method was designed. The scheme of the transducer is shown in **Fig. 1**. The piezoelectric parts are outside the reaction vessel, and the irradiation surface is inside. And the transducer was held tightly to the lid of the container at the nodal position. Such a design enables the solution to be directly exposed to the high-power ultrasonic irradiation. To prevent the performance degradation of the transducer under a high temperature condition, we clamped the piezoelectric device between duralumin washers with a high thermal expansion coefficient. Such a structure can prevent a degradation of the pre-stress to the piezoelectric device due to the temperature rise. In addition, to magnify the vibration speed at the tip, we designed a horn structure.

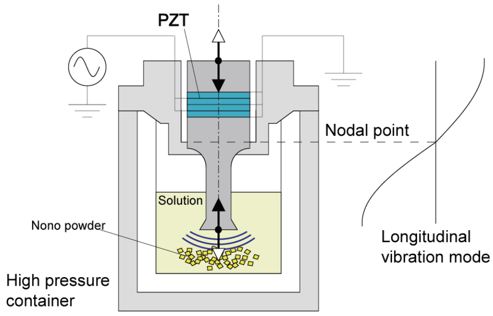


Fig. 1 The scheme of the ultrasonic transducer

3. Ultrasonic transducer characteristics

The transducer was driven with the fundamental mode. The resonant frequency of the transducer was 31.4 kHz. The frequency range around 30 kHz is more adequate for the ultrasonic cavitations. The magnification factor of the horn structure was 5.2. In addition, the temperature dependency on the vibration speed was measured using the LDV. The ultrasonic transducer was put into the oven, and the laser was irradiated from the outside through the window of the oven. From **Fig. 2**, no vibration performance degradation occurred, not even at temperature higher than 250 ^{o}C. This maximum temperature of 250 ^{o}C is sufficient because the optimum reaction temperature for a lead-free piezoelectric powder is 210 ^{o}C and that for PZT is 140 ^{o}C.

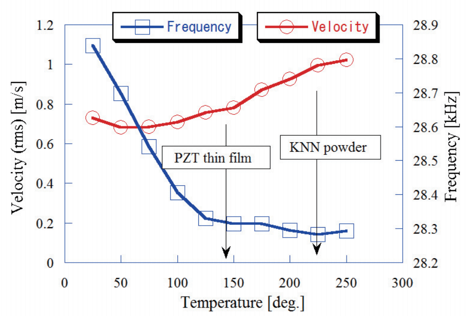


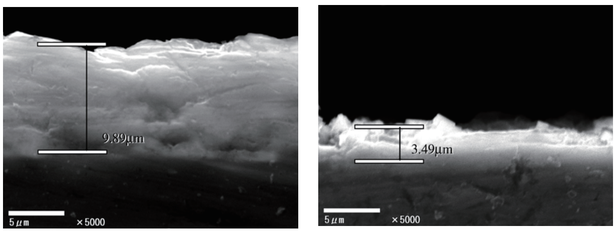
Fig. 2 The vibration speed of the transducer

The driving frequency was automatically controlled to follow the resonant frequency since it changed slightly because of temperature rise, as shown in Fig. 2. Therefore, the outsourced PLL circuit controlled the driving frequency. This system utilizes the same principle that the phase difference between the current and the driving voltage is kept constant to maintain the resonance frequency.

4. The effect of ultrasonic assist

The effect of ultrasonic assist was examined for PZT thin film deposition. The starting materials were thrown into a reaction vessel with a titanium substrate. After the reaction vessel had been closed, it was put into the pre-heated oven. The reaction temperature was 140 °C, and the reaction time was 12 hours. The applied voltage to the ultrasonic transducer was 350 V_{pp}.

After a 12-hour synthesis, the cross sections of the obtained PZT thin films were observed by using a scanning electron microscope (JEOL JSM-5310LV), as shown in **Fig. 3**. By comparing Fig. 3(a) with Fig. 3(b), the deposition rate was increased by the ultrasonic assist. This is the first observation that such a thick film with a thickness around 10 μm could be obtained with one process by using the ultrasonic radiation.



(a) (b)

Fig. 3 Cross sectional images of PZT films: (a) ultrasonically-assisted, (b) not assisted

The ultrasonic-assist effect for the synthesis of $(K,Na)NbO_3$ powders was investigated. The starting materials, 59.5 ml of NaOH solution, 10.5 ml of KOH solution and 3.72 g of Nb_2O_5 powder, were thrown into the reaction vessel. The mixing ratio of NaOH and KOH was determined from the experiment to produce a $(K_{0.5},Na_{0.5})NbO_3$ chemical component as the obtained material. Then, the whole vessel with the ultrasonic transducer attached was put into the pre-heated oven. The reaction temperature was 210 °C. The condition for the ultrasonic irradiation was the same to that for the PZT deposition.

After hydrothermal synthesis, the obtained powder was filtered and dried at 100 °C, and its weight was measured. From the weight, the yield constant was calculated. **Figure 4** shows the relationship between the reaction time and the yield constant with and without the ultrasonic assist. This result indicates that the ultrasonic assist realized a higher reaction speed and the required time to complete the reaction becomes less than half that without ultrasonic assist.

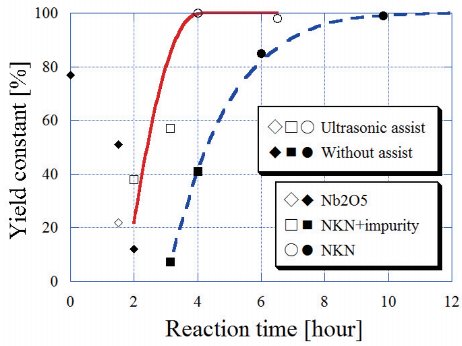


Fig. 4 Yield constant of $(K,Na)NbO_3$ powder

5. Conclusions and future works

We have developed an ultrasonic transducer, and high-power ultrasound irradiation became possible during the hydrothermal reaction. In addition, the effect of the ultrasonic assist was verified using this transducer. We found that the surface of the obtained PZT thin film became smoother with the transducer. Furthermore, the ultrasonic assist with the transducer could accelerate the reaction rate in the hydrothermal synthesis of the PZT thin films and produced thicker films with thickness of about 10 μm. The proposed method could also shorten the reaction time for synthesizing $(K,Na)NbO_3$ crystal powders as source materials for lead-free piezoelectric ceramics.

Now, we are trying to clarify the effect of ultrasonic assist from the view of fundamental physics. By improving the ultrasonic power, its effect should be increased. In addition, the piezoelectric characteristics are being measured to compare them with those obtained without the ultrasonic assist.

Acknowledgment

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