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Synthesis process of the hydrothermal $(K,Na)NbO_3$ ceramics
水熱合成$(K,Na)NbO_3$セラミックスの製造プロセス

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1. Introduction

As a candidate for replacing the PZT, alkaline-niobate system received attention because of their high piezoelectric constants [4]. Among them, $(K,Na)NbO_3$ is considered as a promising candidate for the lead-free piezoelectric ceramics due to its high Curie temperature. In this study, we propose the hydrothermal method to obtain the source powders for these alkaline-niobate ceramics. Usually, their row ceramic powders have been obtained through the solid-solution method. However, the potassium carbonate, K_2CO_3, which is a potassium source for potassium niobate, has the deliquescence property, so that it is difficult to weigh adequately. During calcinations process, the potassium atoms are easily evaporated; therefore the stoichiometric chemical component between potassium and niobium is a problem in $KNbO_3$ synthesis[1-3].

On the contrary, the hydrothermal method overcomes these problems because of its unique performances. First of all, the low reaction temperature, around 200^{o}C, results in the high quality powders, due to its small residual stress inside the powder. Secondary, the potassium source can be alkaline hydroxide in spite of unstable K_2CO_3. During the hydrothermal process, the chemical component ratio becomes stoichiometric automatically. Moreover, the hydrothermal powder is so fine that the ball milling time could be eliminated, or can become a little time.

In this study, sodium niobate materials were synthesized using the hydrothermal method, and after mixing with potassium niobate, powders were sintered into potassium–sodium niobate ceramics. We characterized their piezoelectric properties of its sintered ceramics.

2. Experimental Procedure

To synthesis $NaNbO_3$ powder, 70ml of the 9N NaOH solution and 37.20g of the Nb_2O_5 powder were mixed in 125ml of Teflon vessel of high pressure container and the hydrothermal reaction was carried out at 210^{o}C for 6H. For $KNbO_3$ powder, 140ml of the 8.8N KOH solution, 9.18g of Nb_2O_5 powder were put into 300ml Teflon vessel of the high pressure container and the reaction temperature was 210^{o}C for 12H.

After these reactions, the white alkaline-niobate sediments were obtained after filtering process. Each alkaline-niobate powder was washed with 300ml of pure water and neutralized with 0.01mol/l HCl solution. The obtained powders were filtered and washed with 1L of pure water again. After filtering, powder was dried.

To synthesize $(Na_{0.52}K_{0.48})NbO_3$ ceramics, $KNbO_3$ and $NaNbO_3$ powders were mixed using ball mill for 12H. The mixture powder was dried and pressed into disks. The disk was pressed with cold isostatic pressing under 200MPa. The obtained disks were sintered at 1100^{o}C for 2 hours. The appropriate shape is required to measure the piezoelectric coefficient [5]. Therefore, the sintered ceramics were cut by the diamond cutter. Poling treatments were carried out using a high voltage supply in silicone oil at 150^{o}C. The electrical field 2kV/mm was applied in the thickness direction for 1 hour for both kinds of specimens.

3. Results and Discussion

Figure 1 shows the XRD result of the sintered ceramics, whose peaks correspond to those of the potassium-sodium niobate. SEM photographs of the ceramics verified that the grain size was 1~5μm as shown in **Figure 2**. Using the hydrothermal powders, we could get high density non-doped $(K_{0.48}Na_{0.52})NbO_3$ ceramics of 98.8% (theoretical density 4.51g/cm^3).

The electromechanical coupling factors k_{31} and k_{33} were calculated from the resonant-antiresonant method on the basis of IEEE standards [5]. The relative free permittivity $\varepsilon_{33}^T/\varepsilon_0$ was determined from the capacitance value at 1 kHz of the poled specimen. The stiffness c_{ij}^E was calculated from the resonant frequency. With these parameters, the piezoelectric factors d_{31} and d_{33} were calculated from the coupling factor, permittivity and the stiffness. Mason's equivalent circuit was fitted to

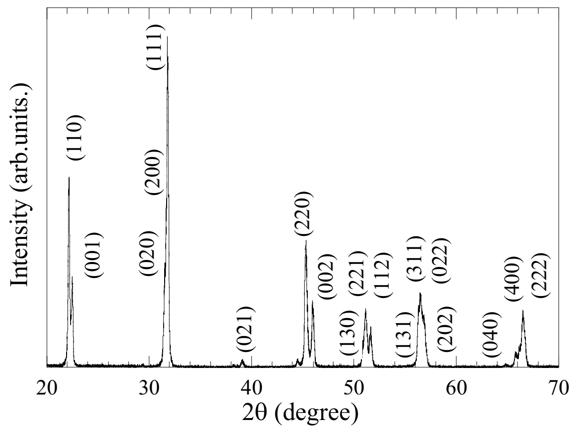

Fig.1 XRD pattern of $(K_{0.48}Na_{0.52})NbO_3$ ceramics

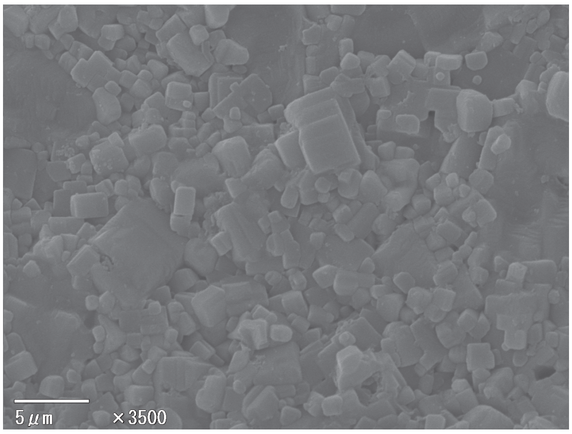

Fig.2 SEM micrograph of surface of $(K_{0.48}Na_{0.52})NbO_3$ ceramics

the admittance curve and the mechanical quality factor Q_m were calculated.

Figure 3a and 3b show the admittance curves near the resonant vibration frequency of the radial and the thickness vibration mode of the $(K_{0.48}Na_{0.52})NbO_3$ specimens. The obtained piezoelectric properties were as follows: the electromechanical coupling factors k_{31}, k_{33}, the relative free permittivity $\varepsilon_{33}^T/\varepsilon_0$, the piezoelectric factor d_{31}, d_{33} and the mechanical quality factor Q_m(radial /thickness), were 0.40, 0.55, 446, -75pC/N, 130pC/N, 73(radial mode) and 53(Thickness mode), respectively .

4. Conclusion

In high density (98.8%) of $(K_{0.48}Na_{0.52})NbO_3$ ceramics was synthesized from the hydrothermal powders. And the excellent piezoelectric properties were measured.

Acknowledgment

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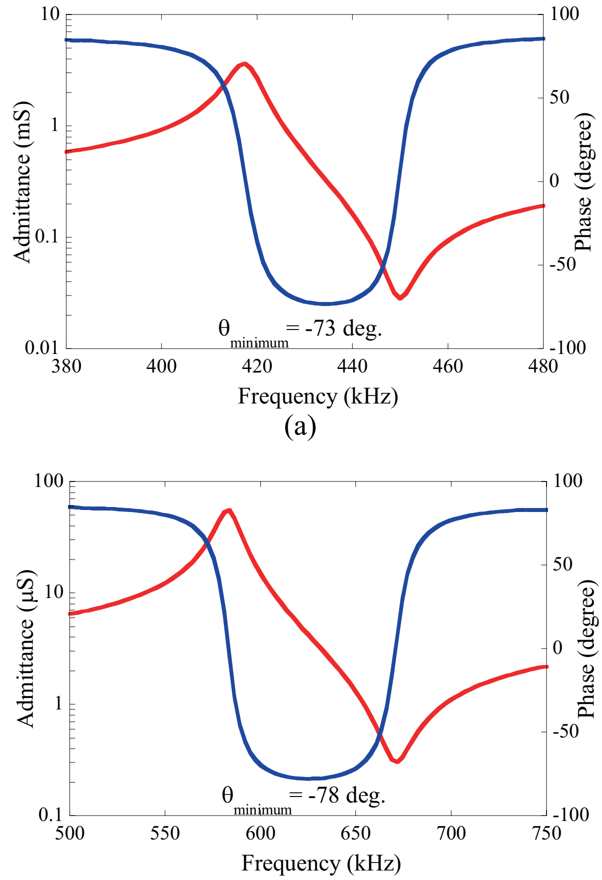

(b)

Fig.3 Admittance characteristics for (a) the radial and (b) the thickness vibration mode of $(K_{0.48}Na_{0.52})NbO_3$ ceramics

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