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CuO-doped (K,Na)NbO_3 lead-free piezoelectric ceramics synthesized with hydrothermal powders

水熱合成法を用いた CuO ドープ(K,Na)NbO_3 非鉛圧電セラミックスの合成

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1. Introduction

Among various lead-free piezoelectric materials, (K,Na)NbO_3 is a promising candidate because of its large piezoelectricity and high Curie temperature.[1)] In this study, $KNbO_3$ and $NaNbO_3$ powders were prepared by hydrothermal method.

The hydrothermal method utilizes ionic reaction under high temperature and pressure, so that pure crystalline powders are obtained without any other process. Besides its simple process, the reaction temperature is low (around 200°C).[2)]

Until now, we confirmed that the piezoelectric constant d_{33} could be improved to 203 pC/N with Li-doping on hydrothermal (K,Na)NbO_3 ceramics.[2)] However the mechanical quality factors Q_m is also an important factor for ultrasonic transducer applications. Enzhu Li *et al* reported that the Q_m was 1202 when 0.66 mol%-CuO-doping by solid-phase method.[3)] Moreover, addition of CuO improves the sintering performance, so the density becomes large.[4)5)] Therefore, in this study, we synthesized $KNbO_3$ and $NaNbO_3$ powders with hydrothermal method and doped CuO for making hard type piezoelectric ceramics. The controlling parameters of the process conditions were syntering temperature and the amount of CuOdoping.

2. Experimental Procedure

For synthesizing $KNbO_3$ powder, 9.18 g of Nb_2O_5 was put into 140 ml of a 8.8 N KOH solution in a pressure vessel (Tainetsu Techno TAF-SR type). After sealing the pressure vessel, it was placed in an oven pre-heated at 210 °C (reaction time: 12h). For making $NaNbO_3$ powder, 37.2 g of Nb_2O_5 was put into 70 ml of a 9 N NaOH solution in a pressure vessel (Parr 4748), and it was placed in an oven pre-heated at 210 °C (reaction time: 6h). The $KNbO_3$ and $NaNbO_3$ powders were mixed to the molar ratio $KNbO_3$:$NaNbO_3$=0.48:0.52. After filtering and drying, the powders and CuO powder were mixed in 1.5 mol% ethanol for 20 hours boll milling. This powder was filtered and then pressed into disc shape using the cold isostatic pressing (CIP) under 150 MPa, and this disk (diameter: 1.3 mm, ϕ: 8.3 mm) was sintered at 1105°C in air for 2h. Gold electrodes were deposited on each side of the disk using the sputter coater (Sanyu Electron SG-701) for measuring the radial vibration mode. A poling treatment was carried out in silicone oil at 100°C. Electrical field of 3.0-4.0 kV/mm was applied for 15 min.

3. Results and Discussion

After sintering, the XRD patterns of CuO-doped KNN indicated that all ceramics had no impurity (Figure 1). The peaks shifted slightly, it was considered that the incorporation of Cu ions into the KNN ceramics changed the crystal structure. Hwi-Yeol Park *et al* showed same Cu effects.[6)]

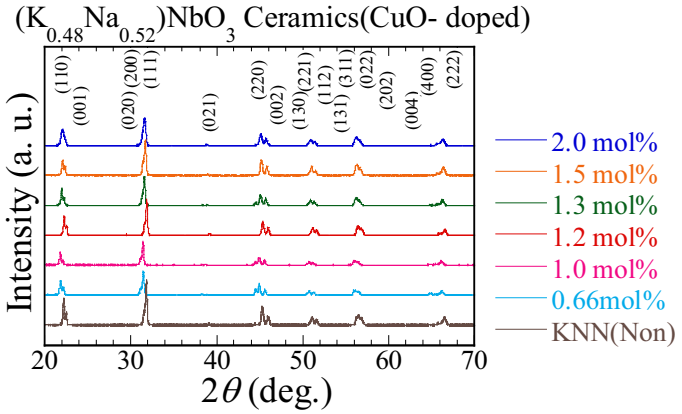

Fig.1 XRD pattern of each conditions

Enzhu Li *et al* reported that the Q_m was 1202 when 0.66 mol% CuO-doping by solid-phase method.[3)] In our study, the 1.2 mol% doping showed the highest Q_m (radial: 859). In addition to this, after 3 days it was 1023 because the domain became stable with aging effect. Further consideration about this aging effect is ongoing work.

It was reported that tan δ was lower than 1.0% around the peak of Q_m by CuO doing using solid-phase method.[3] Figure 2 shows almost same results except for 1.5 mol% doping.

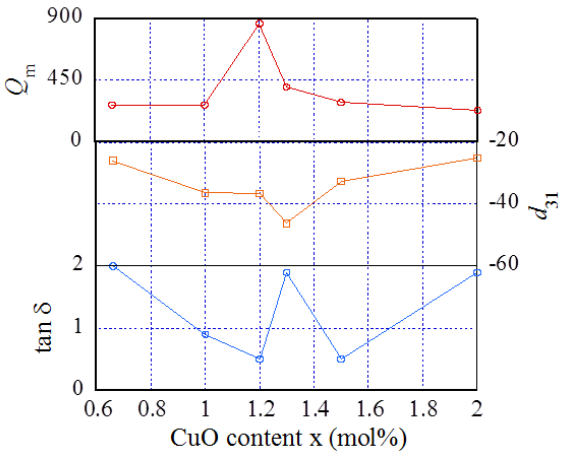

Fig. 2 Q_m, d_{33} and density of each doping

Figure 3 shows the SEM images of CuO-doped KNN ceramics (from 0.66 mol% to 2.0 mol%). The grains were rectangular in shape, and the size was deeply related to Q_m. The Q_m was high when the grain size was small. It was same tendency with the results of Enzhu Li *et al*.[3]

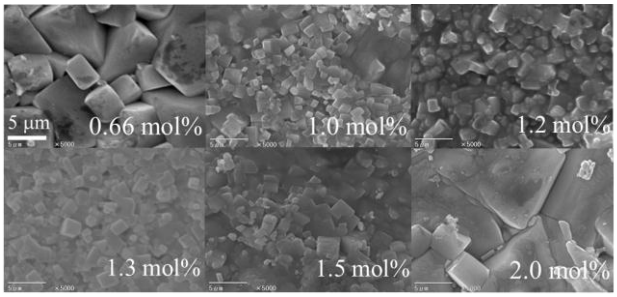

Fig. 3 SEM images of CuO-doped KNN

With the 1.2 mol%-doped KNN ceramics, we measured the admittance curve at the radial vibration mode as shown in Figure 4. At the resonant frequency, the admittance showed sharp peak and the phase changed from 90 to -90 degree, indicating the poling treatment was sufficiently carried out.

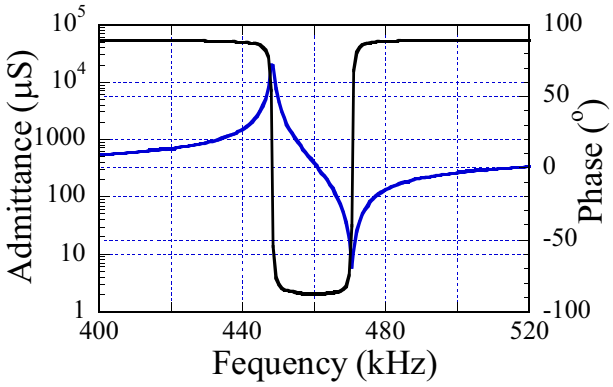

Fig. 4 Admittance curve of CuO(1.3 mol%)-doped KNN

4. Conclusions

In this study, $KNbO_3$ and $NaNbO_3$ powers were synthesized using the hydrothermal method instead of the conventional solid-phase method for obtaining highly-pure powders. The CuO addition improved the piezoelectric properties; the value was 859 (1023). Furthermore, it was effective for smaller tan δ that was 0.5% with 1.5 mol% CuO doping. In this study, CuO doping affected the grain size in the sintered ceramics. It is supposed the small grain size would be related to the higher Q_m.

Acknowledgment

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