Domain orientation controlled KN family piezoelectric materials with hydrothermal powders

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Abstract

In this study, the domain orientation controlled $KNbO_3$ and $(K,Na)NbO_3$ ceramics were fabricated from hydrothermal powders using a single crystal $SrTiO_3$(100) substrate as a template. Putting the hydrothermal powders of $KNbO_3$ or (K, Na) NbO_3 on the template, powders were heated up to over 1000 degrees for a few hours. After cooling down with the cooling rate of 1-2 degrees/minute, the domain orientation controlled $KNbO_3$ or $(K,Na)NbO_3$ ceramic was obtained. The XRD measurement, the electrical property measurements, the surface observation using AFM (Atomic Force Microscope) and ferroelectric domain observation using PFM (Piezoresponse Force Microscope) were performed to confirm the orientation control.

Key words: Hydrothermal synthesis method, $KNbO_3$, (K, Na) NbO_3, Domain orientation control

Introduction

In recent years, concern about an environmental problem is increasing worldwide. Therefore, in the field of piezoelectric materials, the research and the development of lead-free piezoelectric materials are actively studied. Especially, the $KNbO_3$ and the $(K,Na)NbO_3$ ceramics get a lot of attention, due to their excellent piezoelectric properties [1]. Additionally, it has been reported that the $KNbO_3$ single crystal shows a high electromechanical coupling coefficient for the surface acoustic wave extinction; therefore this material is expected as a promising piezoelectric single crystal substrate for SAW devices [2]. Piezoelectric single crystal has better piezoelectric constant than the ceramics because there is no grain boundary. So, the domain orientation control of ceramics is useful for improving the piezoelectric characteristics. Based on the above mentioned background, we propose a new fabrication process realizing the domain oriented KN family piezoelectric materials.

Preparation of $KNbO_3$ and $(K,Na)NbO_3$ source materials

In this study, the domain orientation controlled $KNbO_3$ and $(K,Na)NbO_3$ ceramics were fabricated from hydrothermal powders using a single crystal $SrTiO_3$ substrate. A hydrothermal method is a technique promoting a chemical reaction under high temperature and high pressure using the water vapor pressure. This method enables high purity and quality material because the chemical reaction is carried out in a closed vessel. It was clarified that $(K,Na)NbO_3$ ceramics sintered with hydrothermal powders had the high dielectric constant, the piezoelectric constant, the large density and so on [3].Additionally, the Q value also increased by doping [4]. So we decided to use the hydrothermal powders as source materials for this study. Table 1 and 2 show the hydrothermal synthesis conditions for $(K,Na)NbO_3$ and $KNbO_3$ powders. The $(K,Na)NbO_3$ powders were prepared by mixing $KNbO_3$ and $NaNbO_3$ powders after obtaining them by hydrothermal synthesis. In $NaNbO_3$ powders, using NaOH and Nb_2O_5 as starting materials, 24 hours synthesis were performed at 210 degrees. $KNbO_3$ and $NaNbO_3$ powders were mixed using ball mill, for smaller particle size. On the other hand, $KNbO_3$ powders, using KOH and Nb_2O_5 as starting materials, 24 hours synthesis was performed at 210 degrees.

Tab.1: Hydrothermal synthesis condition of $(K.Na)NbO_3$

$KNbO_3$ powder		**$NNbO_3$ powder**	
KOH 9 mol/l	140 ml	NaOH 9 mol/l	70 ml
Nb_2O_5 (3N5)	14.88 g	Nb_2O_5 (3N5)	37.2 g
Solution volume	140 ml	Solution volume	70 ml
Temperature	210°C	Temperature	210°C
Reaction time	12 h	Reaction time	24 h

Mixed condition	
$KNbO_3$	5.50g
$NaNbO_3$	5.43 g
Mixing liquid	Ethanol 200 ml
Zirconia ball	Ø 10 mm : 100 balls, ø 2 mm : 100 g
Rotation speed	228 rpm
Rotation time	12 h

Tab.2: Hydrothermal synthesis condition of $KNbO_3$

$KNbO_3$	
KOH 9 mol/l	70 ml
Nb_2O_5 (3N5)	3.72 g
Solution volume	70 ml
Agitate time	5 min
Temperature	210°C
Reaction time	24 h

Domain orientation controlled method

Figure 1 shows a proposed method for making the orientation controlled ceramics. The hydrothermal powders were put on $SrTiO_3$ (100) single crystal substrate and the heat-treatment was carried out. After heat-treatment, it was cooled down to room temperature [5]. During cooling process, the domains of melted materials on substrate were affected by the single crystal substrate. After cooling, the domain orientation controlled ceramics were obtained. In the case of $(K,Na)NbO_3$, the powders were heated up to 1130 degrees for 5 minutes and this temperature was kept for 2 hours using RTA (Rapid Thermal Annealing). After this process, it was cooled down at a rate of 2 degrees / minute. In the case of $KNbO_3$, the powders were heated for 5 hours at 1080 degrees using muffle furnace. After this, it was cooled down at a rate 0.9 degrees / minute.

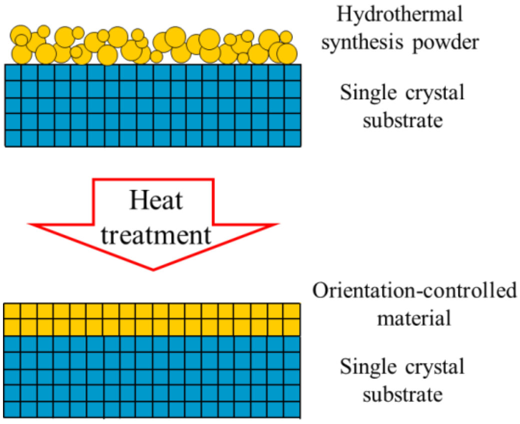

Fig.1: A concept of proposed method for orientation controlled materials

Domain orientation controlled $(K,Na)NbO_3$

Figure 2 shows photographs of orientation controlled $(K,Na)NbO_3$ ceramic. This ceramic was released from $SrTiO_3$ substrate after cooling down because of the different thermal expansion coefficient between $(K,Na)NbO_3$ and the substrate. The surface of the backside that had contacted with the $SrTiO_3$ substrate was slightly translucent. It is presumed that this surface was affected directly by single crystal substrate. Figure 3 shows a comparison between XRD results before and after orientation control. Intensity of KNN peaks around 22 and 45 degree increased after orientation control. Additionally, intensity of other KNN peaks decreased after orientation control. It was confirmed that the domain of $(K,Na)NbO_3$ was affected by $SrTiO_3$ single crystal substrate. In order to measure the piezoelectric properties, this ceramic was cut into 1mm×1mm×5mm cuboid. The polarization treatment was carried out with 3 kV/mm at 100 degrees for 20 minutes in the longitudinal direction. An admittance curve is shown in Fig.4 and the calculated piezoelectric parameters are summarized in Table 3. It was confirmed that Q value was increased to 145 from 53 by the orientation control because material became hard-type piezoelectric material. On the other hand, the piezoelectric constant d was decreased after the domain orientation control, as there is a trade-off relation between the Q value and piezoelectric constant. Dielectric constant also decreased after the domain orientation control.

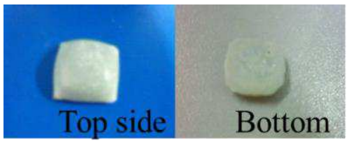

Fig.2: Obtained orientation controlled $(K,Na)NbO_3$

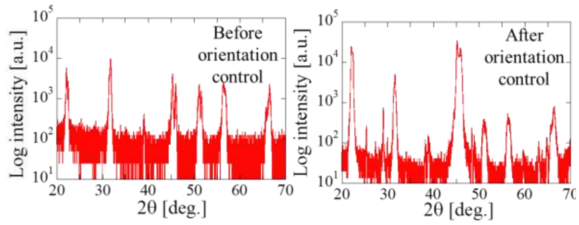

Fig.3: XRD measurements of before (left) and after (right) domain orientation controlled $(K,Na)NbO_3$

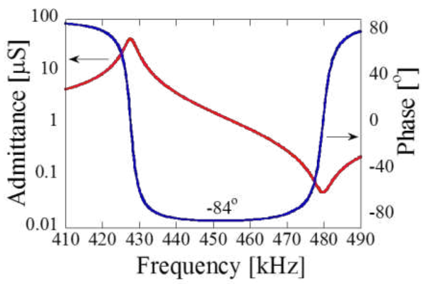

Fig.4: Obtained admittance curve in $(K, Na)NbO_3$ ceramic

Tab.3: Piezoelectric properties of $(K, Na)NbO_3$ ceramic

	k_{33}	d_{33} (pC/N)	Q_m	$\varepsilon_{33}^T/\varepsilon_0$	c_{33}^E(GPa)	tan δ(%)	ρ(g/cm³)
Non dope	0.55	130	53	446	73	2.7	4.43
Non dope Two Step Sint.	0.49	98	145	249	62	4.8	4.23

Domain orientation controlled $KNbO_3$

Figure 5 shows the optical micrograph after controlling the domain orientation of $KNbO_3$. Seeing this picture, the orientation controlled $KNbO_3$ had a single like surface. The size was about 2 mm×3 mm×0.4 mm. Figure 6 shows the XRD measurement results for before and after orientation control. In this time, there were only two peaks around 22 and 45 degrees corresponding to $KNbO_3$ (100) and $KNbO_3$ (200). It is clear that $KNbO_3$ domain orientation was controlled completely by $SrTiO_3$ single crystal substrate. By using another orientation controlled $KNbO_3$ that cooled for 30 hours, the surface and the ferroelectric domain were observed with AFM (Atomic Force Microscope) and PFM (Piezoresponse Force Microscope) as shown in Fig.7. In AFM observation, Fig.7 indicated that there are no grains that generally seen in ceramics. In addition, ferroelectric domains and the domain walls were observed by PFM measurement. From these results, it was verified that the $KNbO_3$ domain orientation controlled ceramic had a single crystal structure.

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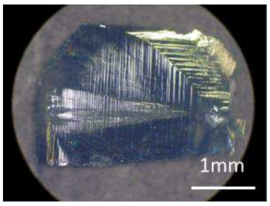

Fig.5: Obtained orientation controlled $KNbO_3$

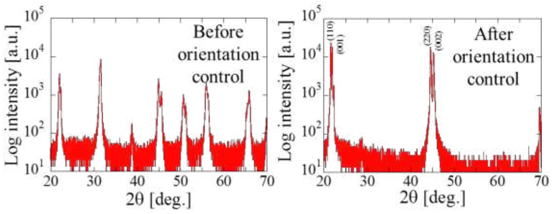

Fig.6: XRD measurements of before (left) and after (right) domain orientation controlled $KNbO_3$

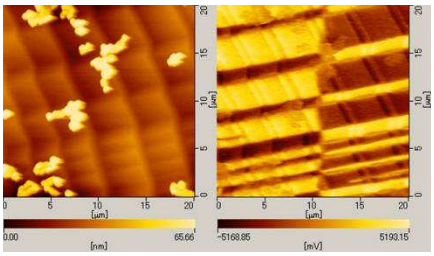

Fig.7: Result of AFM and PFM observations of $KNbO_3$

Conclusion

The results of this study are summarized as follows.

(1) Using a $SrTiO_3$(100) single crystal substrate, $(K,Na)NbO_3$ orientation controlled ceramic from hydrothermal powders was successfully obtained. The measurement of piezoelectric property of this ceramic clarified that the Q value was increased to 145 from 53 as a result of the domain control.

(2) Similarly, using single crystal substrate, $KNbO_3$ orientation controlled crystal was obtained. This crystal was affected by substrate completely. By XRD, AFM and PFM observation, it was confirmed that the $KNbO_3$ hydrothermal powders were modified the single crystal.

References

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