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Growth of Silver Niobate Based Single Crystals from Their Stoichiometric Composition Melts

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Single crystals of ferroelectric silver niobate ($AgNbO_3$) and $AgNbO_3$ - antiferroelectric sodium niobate ($NaNbO_3$) solid solution ($(Ag,Na)NbO_3$) were grown using a conventional flux method with AgCl flux. Using this method, 5mm cube crystals were obtained. A dielectric measurement of $AgNbO_3$ crystals indicated the existence of two additional dielectric maximum at 460°C and 520°C as well as some dielectric peaks reported in $AgNbO_3$ ceramics. The detail investigation using an in-situ optical observation revealed that these changes originated from the melting behavior of the residual AgCl (m.p.=455°C) in the crystals. This behavior was also observed for $(Ag,Na)NbO_3$ crystals. To study an intrinsic electrical property of $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals, impurity-free single crystals must be required. Fortunately, it was found that $AgNbO_3$ crystals melted completely at 1200~1300 °C, and from these liquid phase, the $AgNbO_3$ crystals with their stoichiometric composition were formed with decreasing temperature. Finally, we developed a crystal growth technique from the stoichiometric melts for $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals. Moreover, their electric properties were investigated.

Key words: silver niobate, silver sodium niobate, piezoelectric property, single crystal, slow cooling method

1. INTRODUCTION

To date, the ferroelectrics were used in many applications for their numerous ferroelectric related properties originated from the spontaneous polarization (Ps). In the many ferroelectrics, $Pb(Zr,Ti)O_3$ (PZT) ceramics was mainly used owing to their high ferroelectric related properties.1) Recently, lead-free ferroelectrics became to highly attractive materials on the viewpoint of a solution of the environmental problem. However, as compared with PZT ceramics, these ferroelectric related properties were very low, and it is very difficult to replace the PZT ceramics. To create a new lead-free ferroelectrics with high ferroelectric related properties, we must consider the origin of the ferroelectricity.

The lattice vibration is the most important factor for the appearance of the ferroelectricity. To create a new lead-free ferroelectrics, we must consider the lattice vibration energy. Nakamura *et al.* proposed a new model on the basis of the mass effect for the lattice vibration to estimate a relationship between the Curie temperature (T_c) and the lattice vibration energy.2-5) They induced a ferroelectric evoking factor (*F*) as an index to estimate the lattice vibration energy.4) We calculated the *F* factors for the all of perovskite-type materials, and found that the *F* factors of some materials were close to that (0.345) of lead titanate ($PbTiO_3$) with a high Ps. Especially, the *F* factor of $AgNbO_3$ was 0.335 (Fig. 1), and it is expected the possibility that the $AgNbO_3$ can possess a high ferroelectricity as the same as that of $PbTiO_3$.1)

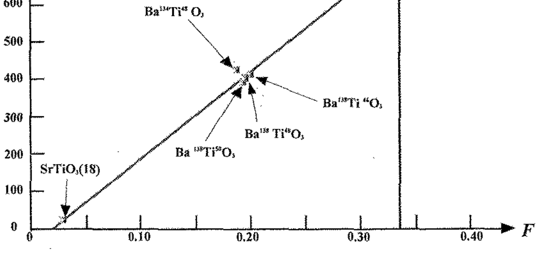

Fig. 1 The relationship between Tc and ferroelectric evoking factor (*F*) on the basis of Nakamura model.

The ferroelectricity of the $AgNbO_3$ was first investigated by Francombe and Lewis,6) and then, the crystal structure, the phase transition behavior and the dielectric property were studied by some researchers.7-18) However, at present, there are still many unknown things about the $AgNbO_3$. Most of researchers studied their structure and properties using not $AgNbO_3$ crystals, but $AgNbO_3$ ceramics15-17). To clarify an intrinsic ferroelectric property, the investigation using the $AgNbO_3$ crystals must be required. To date, a few researchers grew the pure $AgNbO_3$ crystals by the flux methods with the different solvents.8-14) However, the best way to obtain the pure $AgNbO_3$ crystals still did not established. Therefore, it is highly important to modify the conventional crystal growth method or to establish a new crystal growth method for pure $AgNbO_3$ crystals.

Moreover, PZT ceramics was solid solution between $PbTiO_3$ (ferroelectrics) and $PbZrO_3$ (antiferroelectrics), and the highest piezoelectric property was always obtained near the morphotropic phase boundary.1) Therefore, for the $AgNbO_3$ system, the combination between ferroelectrics and antiferroelectrics should be considered. For the niobate system, $NaNbO_3$ is famous antiferroelectrics.1) Thus, it is very important to investigate the ferroelectric related properties for the $AgNbO_3$ - $NaNbO_3$ system.

In this study, the objective is to grow the pure $AgNbO_3$ and $(Ag,Na)NbO_3$ single crystals and to clarify their dielectric property. For this objective, we used two kinds

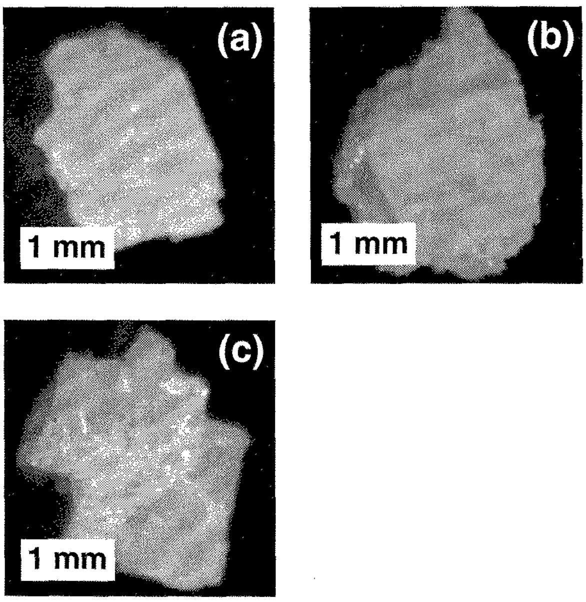

Fig. 2 Photographs of (a) the $AgNbO_3$ crystal, (b) the $Ag_{0.8}Na_{0.2}NbO_3$ crystal and (c) $Ag_{0.6}Na_{0.4}NbO_3$ crystal grown by the flux method using AgCl solvent.

of the crystal growth methods, *i.e.*, (1) the conventional flux method using an AgCl solvent and (2) a new developed method without flux. Moreover, in situ domain observation was also performed with the dielectric measurement.

2. EXPERIMENTAL

The $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals were grown by two methods. One is a flux method using an AgCl solvent while another is a new method without flux developed in this study. The flux method using an AgCl solvent was performed on the basis of that reported by Lukaszewski and Ratuszna.[8-10] The Ag_2O (Wako chem., reagent grade), Na_2CO_3 (Wako chem., >99.98%) and Nb_2O_5 (Rare Metallic, 99.9%) were used as raw materials while AgCl (Kishida chem., >99.5%) was used as a solvent. Ag_2O, Na_2CO_3, Nb_2O_5 and AgCl as a solvent were weighed in various molar ratio ($AgNbO_3$, $Ag_{0.8}Na_{0.2}NbO_3$, $Ag_{0.6}Na_{0.4}NbO_3$ and $Ag_{0.4}Na_{0.6}NbO_3$), and mixed using a ball milling for 24 h. The powders were filled in an alumina crucible with a cap, then this crucible was moved into a larger alumina crucible with a cap, and completely closed using an alumina cement. This closed double crucible was dried at 100°C, and then moved in the conventional furnace. The powders were heated up to 1200°C, and kept at this temperature for 3 h. After that, temperature was decreased down to 200°C at a cooling rate of 15°C/h. The residual AgCl solvent in the crucible was washed by an aqueous ammonia, and then the crystals were obtained by the crash of the crucible. On the other hand, a new method without flux will be described later. The domain structure of the obtained crystals was observed under crossed nicols by using a polarizing microscope (Nikon, LABOPHOTO2-POL). The crystal structure was investigated by using an X-ray diffractometer (XRD) (Rigaku, RINT2000, 30kV, 20mA). The chemical composition was investigated by using an EDX microanalyzer (EDAX Co., Eagle μ-probe).

The dielectric property of the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals was measured from 20°C to 600°C using an impedance analyzer (Agilent, HP4192A). The crystals were cut, polished, and sized into $3x3x0.5\ mm^3$. The silver electrodes were annealed at 800°C on the top and bottom surfaces with a size of $3x3\ mm^2$. The crystals were placed in a cryostat with an optical-isotropic glass window (Linkam, LK-600PM). The temperature was changed from 20°C to 600°C at the heating and cooling rates of 10°C/min, and after keeping for 15 sec at a measurement temperature, the dielectric property was measured at 100kHz. To investigate the origin of some dielectric changes, in situ domain observation was also performed at the same time. The crystals were cut, polished, and sized into $2x2x0.08\ mm^3$. The both surfaces were mirror-finished. The crystal was placed in the cryostat, and temperature was changed from 20°C to 600°C. The domain structure of the crystal was always observed under crossed nicols.

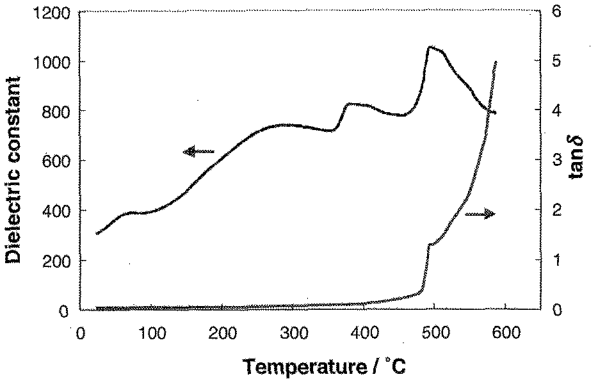

Fig. 3 Temperature dependence of the dielectric constant and dielectric loss measured at 100 kHz for the $AgNbO_3$ single crystals grown by the flux method.

3. RESULT AND DISCUSSION

3.1. Growth of the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals by the flux method

The $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals were grown by the flux method with an AgCl solvent. First, on the basis of the growth conditions reported by Lukaszewski and Ratuszna,[8-10] the mixed powders of Ag_2O, Na_2CO_3, Nb_2O_5 and AgCl were filled in the alumina double crucible. After the thermal treatment of the crucible at 1200°C for 3 h, the formation of the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals was confirmed. However, as the by-products, a formation of $AlNbO_4$ crystals and a lot of deposition of the metallic silver were also observed. To solve this problem, the use of the $AgNbO_3$ and $(Ag,Na)NbO_3$ ceramics powders was proposed in this study. Thus, the mixed powders of Ag_2O, Na_2CO_3 and Nb_2O_5 were calcined at 900°C for 3 h in oxygen atmosphere of 1 atm to inhibit the thermal decomposition of Ag_2O. As a result, the light-yellow colored powders were obtained without silver deposition. Then, the $AgNbO_3$ or $(Ag,Na)NbO_3$ ceramics powders with AgCl as a solvent were weighed in a 1:1 molar ratio, and mixed. After thermal treatment at 1200°C for 3 h, the yellowish green colored crystals were obtained as shown in Fig. 2-(a). The biggest size of the $AgNbO_3$ crystals was 5mm cube, and the average sizes were around 3mm cube. From XRD measurement, it was confirmed that the obtained crystal was the $AgNbO_3$ single crystal without any by-products. The chemical composition of the $AgNbO_3$ crystals was also measured, and then, a molar ratio of Ag and Nb was almost 1.00. Therefore, the $AgNbO_3$ single crystals were grown using the modified flux method with an AgCl solvent. About the $(Ag,Na)NbO_3$ crystals, the similar results were obtained (Figs. 2-(b) and (c)).

Using the obtained $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals, the dielectric constant and loss were measured from 20°C to 600°C. Figure 3 shows the temperature dependence of the dielectric property for the $AgNbO_3$ crystals measured at 100 kHz. Kania reported that the six phase transition temperatures of the pure $AgNbO_3$ ceramics were 67°C (M_1-M_2), 267°C (M_2-M_3), 353°C (M_3- O_1), 361°C (O_1-O_2), 387°C (O_2-T) and 579°C (T-C), respectively.[15-17] Here, M_1, M_2 and M_3 phases are orthorhombic symmetry in rhombic direction, O_1 and O_2 phases are orthorhombic symmetry in parallel orientation, T phase is tetragonal symmetry and C phase is cubic symmetry.[16] However, a dielectric measurement of the $AgNbO_3$ crystals revealed the existence of two additional dielectric maximums of around 460°C and 520°C. Especially, the dielectric maximum around 460°C was accompanied with the sudden increase of dielectric loss, and it is sure that there was a dielectric anomaly at around 460°C. Moreover, Kania reported that around 579°C, there was a phase transition between T and C phases.[15-17] However, in this study, this phase transition was not observed at 579°C. On the contrary, Lukaszewski and Ratuszna measured the crystal structure of the $AgNbO_3$ single crystal grown by the flux method using an AgCl solvent, and observed two phase transitions at 460°C and 520°C by the XRD measurement.[8] Moreover, they also observed the phase transition between T and C at 620°C.[8]

To clarify these dielectric anomalies, in situ domain observation was performed from 20°C to 600°C. Before the as-polished $AgNbO_3$ crystal plate was heated above 460°C, the surface of the plate was very clear, but after temperature decreased below 460°C, some fine structure appeared on the surface. Moreover, when the temperature increased above 460°C, the surface became again to flat without the fine structure. This slight visible change at around 460°C was reversible. Around 520°C, the different visible change was also observed. These changes at 460°C and 520°C were partially occurred, and quite different from the other phase transition behaviors observed at the other temperatures. Thus, we considered the possibility that the change was caused by the melt of the residual AgCl solvent because of the melting point (455°C) of AgCl.

To confirm the melt behavior of AgCl, the $AgNbO_3$ crystal including residual AgCl was heated above 460°C. This in situ domain observation revealed that the AgCl region melted at around 460°C. At around 520°C, the visible change was also observed. Therefore, it was confirmed that the dielectric anomalies at 460°C and 520°C were related to the melt of the residual AgCl. After the washing of the $AgNbO_3$ crystal plate by using the aqueous ammonia, there was no visible change at 460°C and 520°C. It should be noted that the residual AgCl was not detected by a XRD measurement, which suggested that a slight residual AgCl can cause the dielectric anomalies. Therefore, to study the intrinsic dielectric property of the $AgNbO_3$ single crystal, an impurity-free $AgNbO_3$ single crystal must be required. The similar results were obtained for the $(Ag,Na)NbO_3$ crystals.

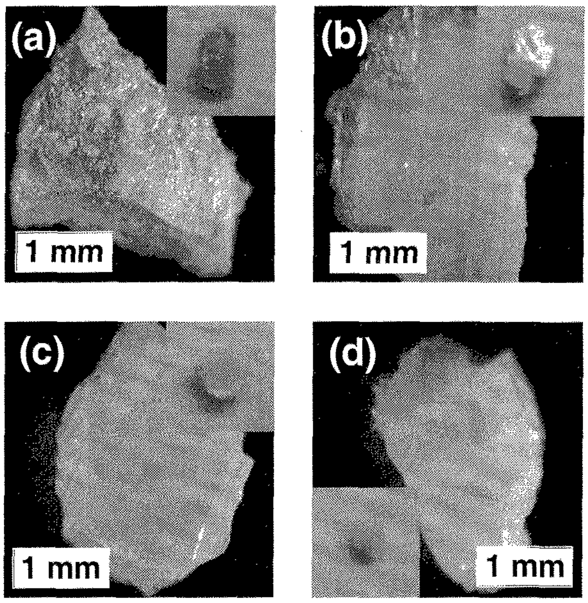

Fig. 4 Photographs of (a) the $AgNbO_3$ crystal, (b) the $Ag_{0.8}Na_{0.2}NbO_3$ crystal, (c) $Ag_{0.6}Na_{0.4}NbO_3$ crystal and (d) the $Ag_{0.4}Na_{0.2}NbO_3$ crystal grown by the slow cooling method.

3.2 Growth of the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals by a new slow cooling method

The above discussion clarified that the flux method was not suitable to grow the pure $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals. To obtain the pure crystals, we must develop a new crystal growth method without a solvent. When the $AgNbO_3$ crystals were heated above 1200°C to investigate thermal decomposition of the $AgNbO_3$ crystals, a melt of the $AgNbO_3$ crystals and a deposition of a new $AgNbO_3$ crystal were accidentally observed. This phenomenon suggested that the $AgNbO_3$ crystals can be grown from a melt with a stoichiometric chemical composition of $AgNbO_3$. Thus, we tried to grow the $AgNbO_3$ crystals from the $AgNbO_3$ melt. The $AgNbO_3$ ceramics powders were filled in alumina crucible with a cap, and moved into the larger alumina crucible. The opened double crucible was heated up to 1210°C, and kept at this temperature for 5 h. After that, temperature slowly decreased down to 200°C at a cooling rate of 15°C/h. The color of the $AgNbO_3$ crystals grown using the alumina crucible was translucent light-green as shown in Fig. 4-(a). The XRD measurements indicated that in the $AgNbO_3$ crystals, the main product was a perovskite-type $AgNbO_3$ phase, but as a by-product, a slight formation of the pyrochlore $Ag_2Nb_8O_{21}$ phase was observed. This time, the crystal growth was performed in air. As a result, a part of $AgNbO_3$ ceramics powders was decomposed into metallic silver and Nb_2O_5. In fact, a slight deposition of the metallic silver was observed. This residual Nb_2O_5 may cause to the formation of the $Ag_2Nb_8O_{21}$ phase. The chemical composition of the as-grown $AgNbO_3$ single crystals showed that a molar ratio of Ag and Nb was almost 0.68:1.00, and was very Ag-poor. This suggested that on the surface of the as-grown $AgNbO_3$ single crystals, there was the fine $Ag_2Nb_8O_{21}$ phase. Thus, the as-grown $AgNbO_3$ single crystals were polished, and then the chemical composition was measured again. As a result, a molar ratio of Ag and Nb was almost 0.96:1.00, which suggested that the most of the crystal was $AgNbO_3$ phase. The $Ag_{0.8}Na_{0.2}NbO_3$ (Fig. 4-(b)), $Ag_{0.6}Na_{0.4}NbO_3$ (Fig. 4-(c)) and $Ag_{0.4}Na_{0.6}NbO_3$ (Fig. 4-(d)) crystals were also successfully grown using the above slow cooling method.

Using the $AgNbO_3$ and $Ag_{0.6}Na_{0.4}NbO_3$ crystals, the dielectric constant and loss were measured from 20°C to 600°C. Figure 5 shows the temperature dependence of the dielectric property for the $AgNbO_3$ and $Ag_{0.6}Na_{0.4}NbO_3$ crystals measured at 100 kHz. For the $AgNbO_3$ crystal, the six dielectric maximums were clearly observed at 67°C, 180°C, 267°C, 353°C, 361°C and 387°C. In the $AgNbO_3$ crystals grown by the flux method with an AgCl, two additional maximums were observed at 460°C and 520°C, but in the $AgNbO_3$ crystals grown by the slow cooling method, there was no peaks at 460°C and 520°C. This temperature dependence in Fig. 5 was almost consistent to that of the pure $AgNbO_3$ ceramics reported by Kania and Kwapulinski[17]. Moreover, it should be noted that no phase transition between C and T was observed below 600°C from the dielectric measurement. In situ domain observation also revealed that the tetragonal phase was observed up to 600°C. Therefore, we concluded that there must be the phase transition between C and T above 600°C. On the other hand, the dielectric loss of this $AgNbO_3$ crystal was almost 1% below 400°C, and above 400°C, the loss drastically increased. On the contrary, the dielectric loss of the $AgNbO_3$ ceramics increased with increasing temperature, and approached to 10% at around 400°C.[17] Therefore, the dielectric loss of the $AgNbO_3$ crystal was almost 1/10 of that of the $AgNbO_3$ ceramics, which revealed that the $AgNbO_3$ crystal grown by the slow cooling method had an excellent dielectric property.

On the other hand, for the $Ag_{0.6}Na_{0.4}NbO_3$ crystal, no peak around 67 and 180°C was observed while the peaks at 267°C, 353°C, 361°C and 387°C for the $AgNbO_3$ crystal shifted to higher temperature and became very broader. Moreover, the dielectric loss of this $Ag_{0.6}Na_{0.4}NbO_3$ crystal was almost 1% below 500°C, and above 500°C, the loss slowly increased. However, the dielectric loss of the $Ag_{0.6}Na_{0.4}NbO_3$ crystal was around 30% at 600°C, and this value was almost 1/7 of that for the $AgNbO_3$ crystal. This suggested that with increasing Na contents, the dielectric loss became smaller, *i.e.*, this loss above 400°C can be originated from Ag. Therefore, the $(Ag,Na)NbO_3$ crystals may be one of the candidate materials for high temperature piezoelectric applications.

In this study, we established the new crystal growth method for the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals, and revealed that the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals had the excellent dielectric properties. Using the $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals, other ferroelectric related properties such as piezoelectricity and pyroelectricity will be investigated.

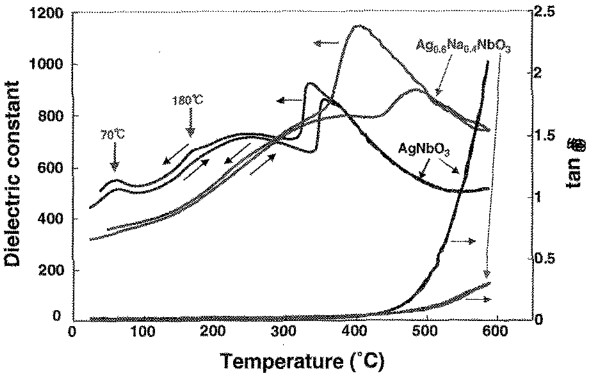

Fig. 5 Temperature dependence of the dielectric constant and dielectric loss measured at 100 kHz for the $AgNbO_3$ and $Ag_{0.6}Na_{0.4}NbO_3$ crystals

4. CONCLUSION

The $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals were grown using a conventional flux method with AgCl flux. Using this method, 5mm cube crystals were obtained. A dielectric measurement of $AgNbO_3$ crystals indicated the existence of two additional dielectric maximum at 460°C and 520°C as well as some dielectric peaks reported in $AgNbO_3$ ceramics. The detail investigation using an in-situ optical observation revealed that these changes originated from the melting behavior of the residual AgCl (m.p.=455°C) in the crystals. This behavior was also observed for $(Ag,Na)NbO_3$ crystals. To study an intrinsic electrical property of $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals, impurity-free single crystals must be required. We developed the new slow cooling method to grow pure $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals from the stoichiometric melts of $AgNbO_3$ and $(Ag,Na)NbO_3$. The dielectric property measurement using the crystals revealed that these $AgNbO_3$ and $(Ag,Na)NbO_3$ crystals had much better dielectric behaviors (lower loss tangent) than the $AgNbO_3$ ceramics, and the $(Ag,Na)NbO_3$ crystals may be one of the candidate materials for high temperature piezoelectric applications.. At the next step, we will clarify other ferroelectric properties.

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