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Morphology and crystallinity of $KNbO_3$-based nano powder fabricated by sol–gel process

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Abstract

Lead-free $KNbO_3$ (KN) powder was fabricated by sol–gel process from metal alkoxides. KN precursor solutions were prepared by different preparation conditions such as the order of reflux process for alkoxides and the kinds of solvent. KN powders were sintered at 900 °C with a heating rate of 10 °C/min. Single phase KN powder was obtained using precursor solution prepared by reflux at 120 °C. We considered that the crystallinity of KN powder was affected by the dimer in Nb-pentaethoxide of the starting chemicals. On the other hand, grain shape of the KN powder also depended on the existence of secondary phase $K_4Nb_6O_{17}$, and the grain size of the fine powder fabricated from precursor solution prepared by reflux at 80 °C using 2-methoxethanol and ethanol solvents was estimated to be about 500 nm and 1 μm, respectively.

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Keywords: $KNbO_3$; Sol–gel process

1. Introduction

$KNbO_3$ (KN) has orthorhombic structure at room temperature, and is an attractive material that shows the Curie temperature (T_c: 435 °C) much higher than $BaTiO_3$ systems. KN single crystal shows an excellent electromechanical coupling coefficient k_t of 69%.[1] Therefore, KN materials have attracted considerable attentions for the applications of lead-free piezoelectric materials, since the lead in $Pb(Zr, Ti)O_3$ (PZT) which is used in many electronic devices may affect the natural environment and the human body.

Recently, the studies for fabrication of KN powder by low energy processing such as colloid chemistry,[2] microemulsion mediated synthesis[3] and sol–gel process were carried out. Because it is rather difficult to control the stoichiometry of KN materials, since their alkaline elements tend to volatilize easily from a comparatively low temperature. Compared to the conventional ceramics processing, sol–gel process[4–6] enables to fabricate the complex oxide powder and thin films at lower temperature, and it is also superior to control the composition, so that it is considered to be a promising process for the fabrication of alkaline niobate materials, especially for powder and thin film applications. However, the number of the reports of KN by sol–gel process is considerably less than that of other ferroelectrics such as $BaTiO_3$ and PZT series. Though Wu et al. fabricated the KN powder from K- and Nb-ethoxide, the single phase was not obtained.[7] On the other hand, Amini and Sacks have succeeded in obtaining single phase KN powder from the same starting chemicals by controlling the hydrolysis and the sintering temperature.[8] But they were also describing that the orthorhombic phase in the single phase KN powder was not observed from split of peaks in the X-ray diffraction (XRD) patterns.

In KN series powder and thin films, the secondary phase such as $K_4Nb_6O_{17}$ which is considered to a low temperature phase and a volatilization of K_2O is often appeared and might be preventing the crystallization of the single-phase or the orthorhombic phase. In this study, we have fabricated the KN powder by sol–gel process using K- and Nb-ethoxide. From the KN precursor solutions with a different preparation conditions, we report the relationship between the crystallinity and the morphology of the KN powder.

2. Experimental

Starting chemicals and solvents for KN precursor solutions were selected as K-ethoxide, Nb-pentaethoxide, 2-methoxyethanol and absolute ethanol. Precursor solutions were prepared by different preparation conditions such as the order of

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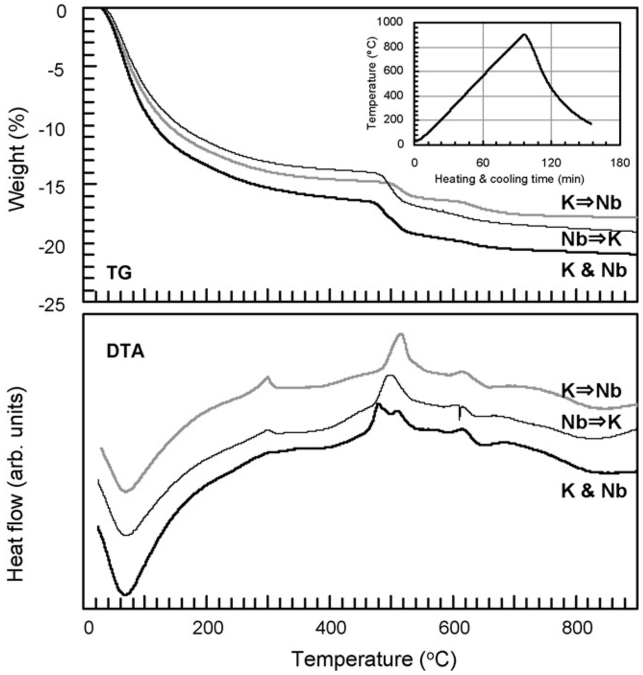


Fig. 1. Reflux order dependence of TG-DTA curves of the $KNbO_3$ precursor gels. Inset shows the heating and cooling pattern of TG-DTA.

reflux process for alkoxides and the kinds of solvent. K-ethoxide and Nb-pentaethoxide were dissolved in 2-methoxyethanol or absolute ethanol and refluxed at 80 °C for 90 min in dry N_2 (process A). Nb-pentaethoxide was first dissolved in 2-methoxyethanol and refluxed at 80 °C for 90 min in dry N_2, and then K-ethoxide was added to the Nb alkoxide solution and refluxed again at 80 °C for 90 min in dry N_2 (process B). Process C denotes that the reflux was carried out in the reverse order of process B. The precursor solution prepared by process A using 2-methoxyethanol solvent was refluxed again at 120 °C for 90 min (process D). The concentration of all precursor solutions was adjusted to approximately 0.35 mol/l. To analysis of the crystallization behavior, the amorphous precursor gel powder was fabricated by drying at room temperature in air from the above precursor solutions. Then, to obtain the crystalline powder, weighed the gels (11–12 mg) in Pt cell were sintered at 900 °C for 1 min in air with a heating rate of 10 °C/min. The heating and cooling pattern shows the inset of Fig. 1.

The precursor gel powder were analyzed and sintered by a thermogravimetry differential thermal analysis (TG-DTA, Rigaku Thermoflex TAS-300 TG8101D). The crystal structure of powder was confirmed by a XRD (Philips X'pert MPD) analysis using Cu Kα. The morphology of powder was confirmed by a scanning electron microscope (SEM, JEOL JSM-5200).

3. Results and discussion

3.1. KN powder fabricated by process A, B and C

Fig. 1 shows the TG-DTA curves of KN precursor gel fabricated by process A, B and C using 2-methoxyethanol solvent. The weight of gel decreased rapidly up to the temperature about 150 °C and the large endothermic peak also appeared at 70 °C. This is due to the evaporation of the water contained in the Al_2O_3 powders used for the standard referential sample. Three DTA curves showed almost similar behaviors. With increasing the temperature, the next exothermic peaks emerged at about 300 and 500 °C. The former peak seems to have caused by the decomposition of the alkoxides included in the gels, and the latter one was resulted from the combustion of the residual carbon in the polymetric network. In process A, an exothermic peak at 300 °C was very small and a peak at 500 °C was separated clearly, compared with the other processes. This is considered to correlate the total reflux time of process A, which had a half time of other processes. That is, an alkyl group of K-ethoxide and Nb-pentaethoxide was different from a ligand of 2-methoxyethanol, and the speed of the hydrolysis and polycondensation reaction in each metal alkoxide differed. Due to these facts, therefore, the substitution of alkyl group and the formation of complex alkoxides may have been difficult by reflux at 80 °C for 90 min only. On the other hand, combustion of carbon was also confirmed by the decrease in weight starting from at about 470 to 550 °C, and this temperature range corresponded to the largest exothermic peak in each process. According to the relationship between the carbon combustion confirmed by TG-DTA and the crystallization behavior detected by XRD,[9] crystallization from the amorphous gel is considered to have started with the combustion of carbon. In the temperature range from 550 to 900 °C, the decrease of the weight after the carbon combustion is likely to the volatilization of K_2O. In addition, the exothermic peak also appeared at 620 °C. The exothermic peaks at 500 and 620 °C might be corresponding to the crystallization of two phases, which will describe later, respectively.

Fig. 2 shows the XRD patterns of KN powder fabricated by the three processes. Each powder was crystallized to a perovskite phase with random orientation and secondary phase $K_4Nb_6O_{17}$. The perovskite peaks near $2\theta = 45.0°$ did not split 2 2 0 and 0 0 2 clearly. From the intensity of the lines in the XRD patterns, $K_4Nb_6O_{17}$ phase was particularly increased in process C, which reflux time of K-ethoxide is twice as long as that of

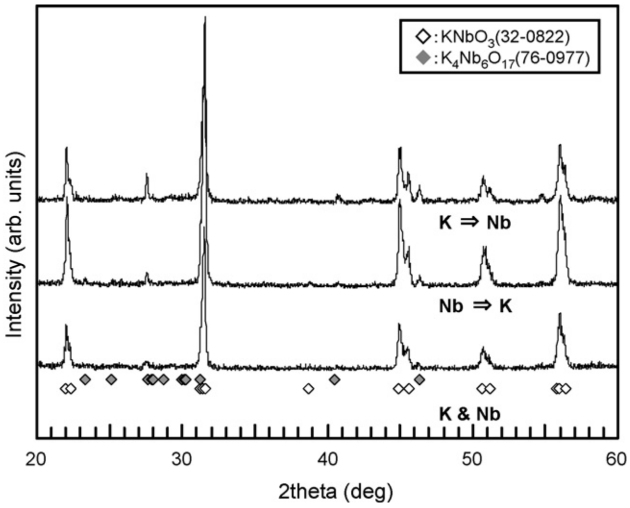
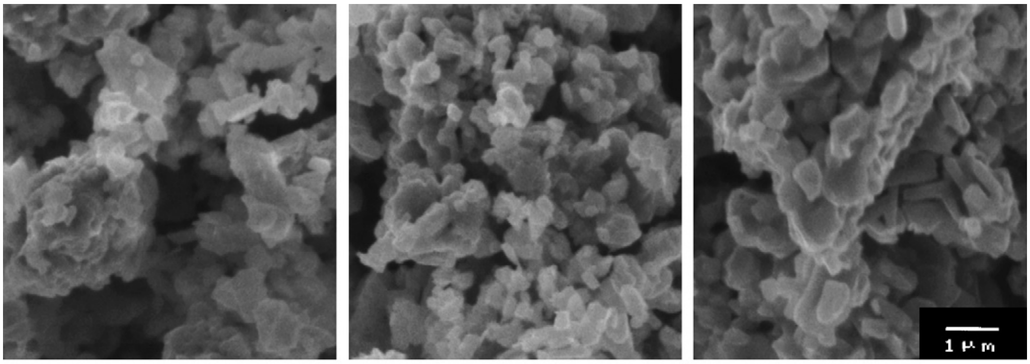


Fig. 2. Reflux order dependence of XRD patterns of the $KNbO_3$ powder.



K & Nb Nb ⇒ K K ⇒ Nb

Fig. 3. Reflux order dependence of SEM images of the $KNbO_3$ powder.

Nb-pentaethoxide. Hence, there is some possibility in precursor solution prepared by process C that K-ethoxide as starting chemicals was decomposed or a substitution reaction between Nb-pentaethoxide and 2-methoxyethanol is incomplete.

Fig. 3 shows the SEM images of KN powder fabricated by the three processes. Average grain size of KN powder fabricated by process A and B was estimated to be about 300–500 nm. In case of the process C, the grain size was increased to about 500 nm to 1 μm, and the shape became a plate-like. It seems that the existence of secondary phase $K_4Nb_6O_{17}$ was affected the powder morphology.

3.2. KN powder fabricated by process A and D

Fig. 4 shows the XRD patterns of KN powder sintered at 900 °C. When reflux temperature is 80 °C regardless of solvents, the resultant powder was also crystallized to the perovskite phase and the secondary phase. There was little change in the crystallinity by the solvents. However, the KN powder with perovskite single phase was obtained from precursor solution refluxed at 120 °C using 2-methoxyethanol solvent, and the perovskite peaks near $2\theta = 45.0°$ split 2 2 0 and 0 0 2 comparatively. Suzuki et al. reported about the fabrication of K(Ta, Nb)O_3 thin films by chemical solution deposition using metal alkoxides and indicated the existence of a monomer and a dimer in the Nb-pentaethoxide.[10] We considered that crystallinity of the KN powder was affected by the dimer in Nb-pentaethoxide. In case of the reflux at 80 °C for 90 min, the dimer did not separate completely, and the remained dimer in the precursor solution prevented from forming of homogeneous double alkoxides. Fig. 5 shows the XRD patterns of the sintering and reflux temperature dependence of KN powder using 2-methoxyethanol solvent. Regardless of the reflux temperature, the $K_4Nb_6O_{17}$ phase appeared from 500 °C and the KN phase appeared from 600 °C. Each crystallization temperature corresponded to the exothermic peaks of about 500 and 620 °C in the DTA curves of Fig. 1. The crystallization temperature of the KN phase was a little lower than that of the exothermic peak because the cooling process had promoted the sintering. By increasing of sintering temperature, the $K_4Nb_6O_{17}$ phase disappeared at 700 °C by using the precursor solution refluxed at 120 °C though it remained in the solution refluxed at 80 °C. Therefore, the formation of $K_4Nb_6O_{17}$ phase is considered that the remained dimer in the precursor solution became the nuclei of this phase rather than the volatilization of K_2O during heat treatment. To prepare the homogeneous KN precursor solutions, it was necessary to increase the reflux temperature. 2-Methoxyethanol is suitable as the solvent for homogeneous KN precursor solutions because the boiling point is higher than ethanol.

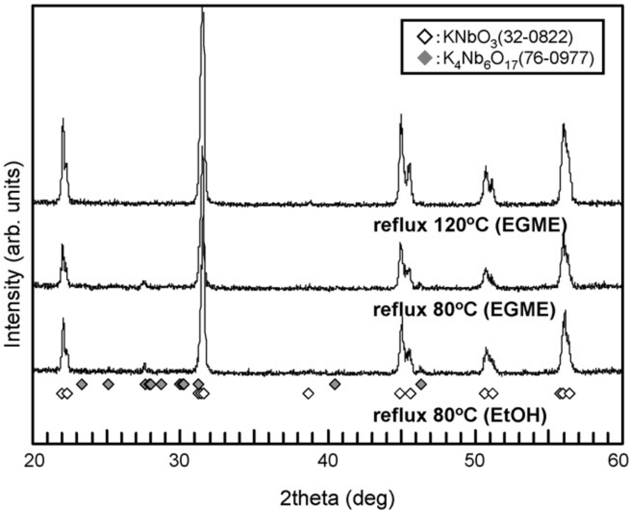


Fig. 4. Solvent and reflux temperature dependence of XRD patterns of the $KNbO_3$ powder.

Fig. 6 shows the SEM images of KN powder sintered at 900 °C. Average grain size of the powder fabricated using ethanol solvent was estimated to be about 1 μm and was larger than that of using 2-methoxyethanol solvent. In our previous study, we carried out the thermal analysis of the KN precursor gels. As the results, the weight loss due to combustion of carbon in the gel prepared using ethanol solvent was lower than that of using 2-methoxyethanol solvent.[11] Hence, ethanol solvent is suitable for the fabrication of KN powder at lower temperature. From Fig. 6, the relatively large grains were obtained from ethanol solvent due to promotion of the grain growth though the secondary phase existed in the powder. On the other hand, single phase KN powder obtained by process D using reflux at 120 °C

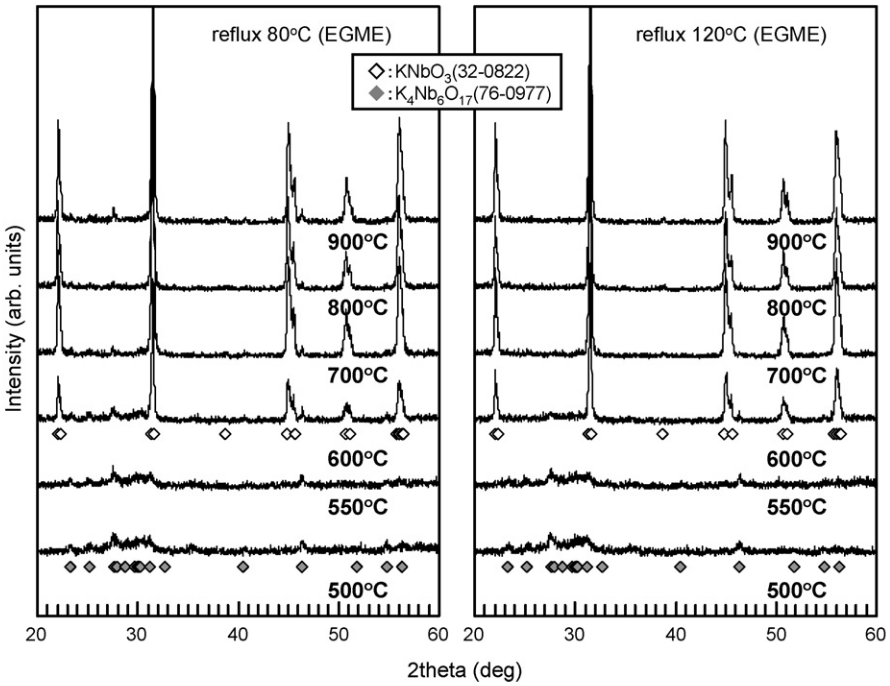
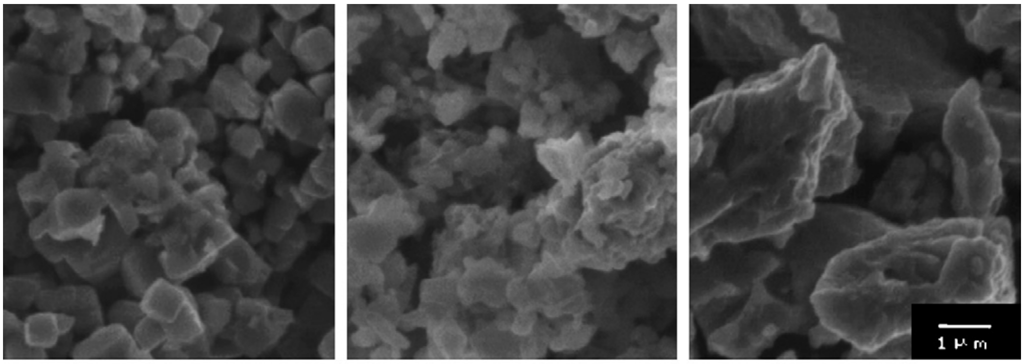


Fig. 5. Sintering and reflux temperature dependence of XRD patterns of the $KNbO_3$ powder.



reflux 80°C (EtOH) reflux 80°C (EGME) reflux 120°C (EGME)

Fig. 6. Solvent and reflux temperature dependence of SEM images of the $KNbO_3$ powder.

was consisted of relatively coarse grains. Though we succeeded in the disappearance of the secondary phase, it is necessary to control the shape and size of grain to apply this KN powder to the raw materials of ceramics.

4. Conclusion

We have prepared the lead-free $KNbO_3$ (KN) precursor solutions by sol–gel process. Their crystallization behaviors converted from the KN precursor gels were confirmed by TG-DTA, and crystallinity and morphology of the KN powder were also confirmed by XRD patterns and SEM images, respectively. The precursor solutions were prepared by different preparation conditions such as the order of reflux process for alkoxides and the kinds of solvent. From the TG-DTA, the three exothermic peaks emerged at about 300, 500 and 620 °C. Each crystalline powder fabricated from the precursor solution refluxed at 80 °C was crystallized to the perovskite phase KN and the secondary phase $K_4Nb_6O_{17}$. Single phase KN powder was obtained using the precursor solution prepared by reflux at 120 °C. We considered that crystallinity of the KN powder was affected by the dimer in Nb-pentaethoxide of the starting chemicals. Therefore, the formation of $K_4Nb_6O_{17}$ phase occurs not due to the volatilization of K_2O during heat treatment, but the existence of the remained dimer in the precursor solutions. To obtain the single phase KN powder, it was necessary to prepare the homogeneous double alkoxide solution with increasing of the reflux temperature. Grain shape of the powder was also depended on the existence of $K_4Nb_6O_{17}$ phase, and the grain size of fine powder fabricated from 2-methoxethanol and ethanol solvents was estimated to be about 500 nm and 1 μm, respectively.

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