Characterization of KNbO₃ Particles Prepared by Heating of Complex between Nb-peroxo Compound and K ion

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The complex between the Nb-peroxo compound and KNO₃ was prepared by heating the Nb-peroxo compound aqueous solution with KNO₃ at 573 K for 1 h. The single phase of KNbO₃ was obtained by firing the complex between the Nb-peroxo compound and KNO₃ at 873 K for 2 h. The obtained KNbO₃ had tetragonal crystal system. On the other hand, when the stoichiometric mixed powder of Nb₂O₅ and K₂CO₃ with the molar ratio of Nb : K = 1 : 1 was fired at 873 K for 2 h, orthorhombic KNbO₃ was obtained. In general, tetragonal phase can be obtained under high pressure condition at more than 6.6 GPa. When the complex between the Nb-peroxo compound and KNO₃ was used for the KNbO₃ preparation, the tetragonal KNbO₃ was obtained at normal pressure condition. The lattice parameter of a axis of the KNbO₃ obtained from the Nb-peroxo compound solution was less than that of the stoichiometric one. According to this fact and the result of UV–VIS spectra, the KNbO₃ prepared by firing the complex between the Nb-peroxo compound and KNO₃ had oxygen vacancies, which affected the lattice parameter and the crystal system.

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1. Introduction
Potassium niobate (KNbO₃) is a ferroelectric material with high nonlinear optical coefficient. Thus, KNbO₃ has very important applications for electrooptical materials. Furthermore, ferroelectric materials containing no lead atom are required for improvement of environmental problems. KNbO₃ is one of the lead-free ferroelectrics and it is expected to develop the preparation method of KNbO₃ particles and sintered compacts with low temperature and a little environmental load.

KNbO₃ can be obtained by firing the mixed powder of potassium carbonate (K₂CO₃) and niobium oxide (Nb₂O₅). However, evaporation of potassium occurred during the firing process to form deficient in potassium. It is important to examine stoichiometry and presence of defects in the obtained product. In last decade, some solution processes to prepare KNbO₃ materials were reported by some researchers. Furthermore, sol–gel processing for KNbO₃ preparation was also reported by Mostafa et al. In this case, potassium and niobium ethoxide precursors were used for the preparation. Here, niobium alkoxides are easily hydrated to form a precipitate. Then, it is difficult to use niobium alkoxides as the precursor for preparing KNbO₃. Therefore, simple aqueous solution process is required. The KNbO₃ preparation process by using aqueous solution expected to become low environmental load process. However, few aqueous solution processes to obtain KNbO₃ were reported. Because a niobium ion (Nb⁵⁺) is easily hydrated and the precipitation of niobic acid (Nb₂O₅·xH₂O) is formed.

Here, the authors showed the preparation method of the stable aqueous solution of niobium (Nb) peroxo compounds by peptization of niobic acid with the aid of hydrogen peroxide (H₂O₂). Some researchers indicated the preparation method of an aqueous solution of the peroxo niobic acid. An aqueous solution can easily dissolve potassium compounds. Then, the aqueous solution of Nb-peroxo compound with potassium ion can be used for the precursor of KNbO₃. In this study, the preparation method of a single phase KNbO₃ by using an aqueous solution of the Nb-peroxo compound was investigated.

2. Experiments
2.1 Preparation of Nb-peroxo compound aqueous solution
The Nb-peroxo compound aqueous solution was prepared as follows: Niobium chloride (NbCl₅) powder was dissolved into 10 ml of ethanol, and a clear yellow solution was obtained. This NbCl₅ solution was then added into 200 ml of NH₄Cl aqueous solution, which had a concentration of 1.0 mol/l. At this point, a white precipitate of niobic acid (Nb₂O₅·nH₂O) was obtained. The precipitate was separated from the solution by a centrifuge at 3000 r.p.m. for 5 min. The niobic acid precipitate obtained was dispersed into distilled water, and was again separated by a centrifuge. This procedure was repeated three times, and the impurities in the precipitate were removed. The niobic acid precipitate was then dispersed in 20 ml of a 30 wt% H₂O₂ aqueous solution. The molar ratio of Nb⁺⁵ : H₂O₂ was 1 : 10. After the solution was stirred for 5 min under cooling with ice, a transparent yellow aqueous solution was obtained.

2.2 Preparation of KNbO₃
Potassium nitrate (KNO₃) was dissolved into the Nb-peroxo compound aqueous solution. The molar ratio was adjusted to be K/Nb = 1. The Nb-peroxo compound solution with KNO₃ was dried at 573 K for 2 h and the complex between Nb-peroxo compound and KNO₃ was obtained. The powder was fired for 2 h at one of the following temperature: 773 K, 873 K, 973 K, 1073 K, 1173 K, and 1273 K. KNbO₃ powder was prepared by the conventional powder process as follows: The mixture of the powders of Nb₂O₅ and K₂CO₃ with the stoichiometric molar ratio (Nb : K = 1 : 1) was prepared. The mixed powders were fired at 873 K, 973 K, 1073 K, and 1173 K for 2 h.

2.3 Characterization
The structure of the powders obtained was characterized by means of X-ray diffraction (XRD). The XRD patterns of the samples were measured by using Mac Science M18X–HF–SRA. Cu was used as the target (Cu Kα, 40 kV, 200 mA). An
optical system of SS = 1", DS = 1", RS = 0.30 mm, and a graphite monochromator was used. Kα1 and Kα2 peaks were separated using the Rachingen method. In order to obtain the exact peak positions, the diffraction peaks at close positions were separated by using the curve fitting technique. The Raman spectra of the prepared powders were measured by using JASCO NRS1000. The particle shape was observed by field emission–SEM (FE–SEM Hitachi S4700). The UV–VIS absorption spectra of the obtained KNbO3 powder were measured using JASCO V–560 spectrometer.

3. Results and Discussion
3.1 Formation Behavior of KNbO3 Phase.

Figures 1(a), (b), and (c) show the X-ray diffraction patterns of the powders prepared by firing the complex between the Nb–peroxo compound and KNO3. In the case that the firing temperature was 773 K, the dominant phase was K4Nb6O17. When the firing temperature was 823 K, the dominant phase was still K4Nb6O17 and the formation of a little amount of K2NiO3 phase was observed. The single phase of K2NiO3 was obtained by firing at 873 K for 2 h. When the mixed powder of Nb2O5 and K2CO3 with stoichiometric composition was fired at 873 K for 2 h, the almost single phase of K2NiO3 was also obtained as shown in Fig. 1(d). Thus, the almost single phase of K2NiO3 was obtained by firing at 873 K for 2 h in both cases that the complex between the Nb–peroxo compound and KNO3 was used and that the conventional powder process was employed.

Figure 2 shows the FE–SEM images of the obtained K2NiO3 particles prepared by firing at 873 K for 2 h. The FE–SEM image of the particles obtained by firing the mixed powder of Nb2O5 and K2CO3 (the conventional powder process) was shown in Fig. 2(a). The strongly aggregated structure of the particles whose average diameter was 120 nm was observed. The particle shape was irregular. The image of the particles prepared by firing the complex between the Nb–peroxo compound and KNO3 was shown in Fig. 2(b). In this case, the obtained K2NiO3 particles are highly crystallized and had a rectangular parallelepiped shape whose size was in the range from 0.2 μm to 0.8 μm. Thus, the heat treatment of the complex between the Nb–peroxo compound and KNO3 enabled to prepare highly crystallized K2NiO3 particles.

3.2 Characterization of Crystal System of the K2NiO3

Electronic and optical properties of K2NiO3 particles depend on crystal structure and defects in the crystal lattice. In order to investigate details of a crystal system of the obtained K2NiO3, Raman spectra were measured. Figure 3 shows the Raman spectra of the K2NiO3 particles prepared by firing the mixed powder of Nb2O5 and K2CO3 (the conventional powder process). The Raman scattering peaks at 590 nm and 525 nm were observed in the spectra of Figs. 3(a), (b), (c), and (d). These scattering peaks can be assigned to the orthorhombic K2NiO3.11 Accordingly, when the mixed powder of Nb2O5 and K2CO3 was fired at more than 873 K for 2 h, orthorhombic K2NiO3 can be obtained. In general, this orthorhombic phase was stable under normal pressure. On the other hand, when the complex between the Nb–peroxo compound and KNO3 was fired at 873 K and 973 K, the Raman spectra of the obtained K2NiO3 showed the only one peak around 577 nm as shown in Fig. 4(a). This fact indicates that the crystal system of the obtained K2NiO3 phase was tetragonal. It was reported that the tetragonal phase of K2NiO3 forms under high pressure condition at more than 6.6 GPa.11 However, in this research, we can obtain the tetragonal K2NiO3 under normal pressure condition. Thus, in the case that the complex between the

![Fig. 1. XRD patterns of the powder prepared by firing the complex between the Nb–peroxo compound and KNO3 for 2 h. The firing temperatures are: (a) 773 K, (b) 823 K, (c) 873 K, and (d) the mixed powder of Nb2O5 and K2CO3 was fired at 873 K. (●) K2NiO3 and ○: K4Nb6O17.](image1)

![Fig. 2. FE–SEM images of the obtained K2NiO3 particles prepared by firing at 873 K for 2 h. (a) the particles obtained by firing the complex between the Nb–peroxo compound and KNO3 and (b) the particles obtained by firing the mixed powder of Nb2O5 and K2CO3.](image2)
Nb–peroxo compound and KNO₃ was used, the anomalous phase was obtained. Here, the difference of the lattice constant between the orthorhombic KNbO₃ and the tetragonal KNbO₃ is very small so that the difference in the XRD pattern was not observed.

3.3 Defects in the KNbO₃ Crystal Lattice

The presence of defects in the KNbO₃ crystal lattice affects the electrical and optical characteristics. In order to examine more details of the effect of using the Nb–peroxo compound on the crystal lattice of the obtained KNbO₃, the lattice parameter of the obtained KNbO₃ was investigated. Figure 5 shows the relation between the lattice parameter of the a axis and the firing temperature. In the case that the mixed powder of Nb₂O₅ and K₂CO₃ was fired, the average lattice parameter (a axis) of the obtained KNbO₃ was 0.5695 nm and the value did not depend on the firing temperature in the range from 873 K to 1173 K. Furthermore, this value was close to that of 0.5695 nm in the literature. Therefore, we can conclude that the KNbO₃ prepared by the conventional powder process had stoichiometric composition. On the other hand, when the complex between the Nb–peroxo compound and KNO₃ was fired at 873 K, the lattice parameter (a axis) was 0.5686 nm. This value was quite less than that of the conventional powder process. Furthermore, the value of the lattice parameter increased with an increase of the firing temperature. In general, the presence of oxygen vacancy and lattice defects affects the lattice parameter. The lattice parameter of the KNbO₃ prepared from the complex between the Nb–peroxo compound and KNO₃ was less than that of the stoichiometric KNbO₃. Accordingly, this fact indicates that the KNbO₃ obtained by using the Nb–peroxo compound contains more defects than that obtained by the conventional powder process. Furthermore, the continuous change of the lattice parameter around 1000 K at which the phase transition from tetragonal phase to orthorhombic phase was observed. This was the conventional phenomena for perovskite ferroelectric compounds such as BaTiO₃.

Figure 6 shows the UV–VIS spectra of the obtained KNbO₃ particles. As shown in Fig. 6(e), the stoichiometric KNbO₃ particles prepared by firing the mixed powder of Nb₂O₅ and K₂CO₃ showed a strong absorption band whose edge was around 400 nm. This strong absorption corresponds to the band gap transition of electrons. The absorption spectrum of the KNbO₃ particle prepared by firing the complex between the Nb–peroxo compound and KNO₃ at 873 K had the broad absorption band at longer wave length than 400 nm as shown in Fig. 6(a). This broad adsorption band corresponds to the charge transfer between the Nb⁴⁺ and Nb⁵⁺. In general, the valence state of niobium ion in KNbO₃ is 5. However, it is considered that the KNbO₃ particle obtained from the complex between the Nb–peroxo compound and KNO₃ had not only Nb⁵⁺ but also Nb⁴⁺. In previous paper, we reported that the decomposition of peroxo ion O₂²⁻ forms oxygen vacancies in the oxide lattice by the following reduction reaction: \( \text{O}_2^{2-} \rightarrow \text{O}_2 + 2e^- \). Therefore, it is considered that the oxygen vacancy formed by the decomposition of the peroxo ions affected the lattice parameter and the crystal system of the obtained
K\textsubscript{2}O particles. When the firing temperature increased from 873 K to 1173 K, the absorption intensity at longer wave length than 400 nm decreased to close to the stoichiometric K\textsubscript{2}O\textsubscript{3} as shown in Figs. 6(b), (c), and (d). This result indicated that the oxygen vacancy decreased to close to the stoichiometric K\textsubscript{2}O\textsubscript{3} when the firing temperature increased.

4. Conclusion

The single phase of K\textsubscript{2}O\textsubscript{3} was obtained by firing the complex between the Nb–peroxygen compound and K\textsubscript{2}O\textsubscript{3} at 873 K for 2 h. The obtained K\textsubscript{2}O\textsubscript{3} had tetragonal crystal system. In general, tetragonal phase can be obtained under high pressure condition at more than 6.6 GPa. When the complex between the Nb–peroxygen compound and K\textsubscript{2}O\textsubscript{3} was used for the K\textsubscript{2}O\textsubscript{3} preparation, the tetragonal K\textsubscript{2}O\textsubscript{3} was obtained at normal pressure condition. The lattice parameter of a axis of the K\textsubscript{2}O\textsubscript{3} obtained from the Nb–peroxygen compound was less than that of the stoichiometric one. According to this fact and the result of UV–VIS spectra, the K\textsubscript{2}O\textsubscript{3} prepared by firing the complex between the Nb–peroxygen compound and K\textsubscript{2}O\textsubscript{3} had oxygen vacancies, which affected the lattice parameter and the crystal system.

References

12) JCPDS Card No. 32–822