

Preparation of Ion-Exchangeable Thin Films of Layered Niobate $K_4Nb_6O_{17}$

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An ion-exchangeable thin film which has the layered structure of $K_4Nb_6O_{17}$ was prepared from a suspension of fine particles of $K_4Nb_6O_{17}$. The superfine particles which were obtained by wet grinding were coated onto a substrate, and they were calcined between 873 and 1073 K. Crystallization of the fine particles by calcination was observed by XRD, SEM, and AFM, and very flat crystals of ~ 500 nm with the b -axis perpendicular to the substrate surface were obtained by calcination at 1027 K. The obtained thin film had a layered structure similar to that of the original $K_4Nb_6O_{17}$ powder. Furthermore, it had ion-exchange properties which enabled the exchange of interlayer cations from potassium to others without destroying the layered structure.

Introduction

Inorganic thin films have generally been prepared by processes using a gessoes phase-like chemical vapor deposition (CVD) or a vacuum system such as sputtering, molecular beam epitaxy (MBE), etc., which requires expensive equipment and particular conditions such as high temperature or ultrahigh vacuum. Recently, novel methods, which do not require such elaborate conditions, through the so-called soft chemical process have been studied. We have already reported the soft chemical method for preparation of the layered titanate thin film which takes advantage of the exfoliation of the layered compound $Cs_xTi_{(2-x/4)}□_{x/4}O_4$.¹ However, the thin film obtained from this method could not retain layered structure when calcined at high temperature. Therefore, a new method was attempted by using wet grinding of $K_4Nb_6O_{17}$.

$K_4Nb_6O_{17}$ is known as a typical photocatalyst for decomposition of water into H_2 and O_2 .^{2–7} As shown in Figure 1, $K_4Nb_6O_{17}$ consists of octahedral units of NbO_6 which form a two-dimensional layered structure via

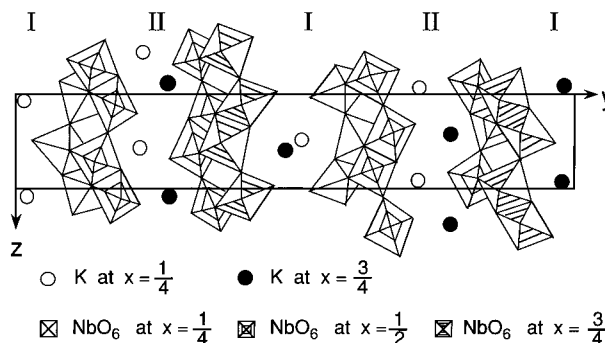


Figure 1. Crystal structure of $K_4Nb_6O_{17}$.

bridging oxygen atoms.^{8,9} The layers are negatively charged, and K^+ ions exist between the layers to compensate for the negative charges of the layers. There exist two types of interlayers (interlayers I and II) alternately, and they are different from each other in their properties of hydration and ion exchange.¹⁰ For example, Ni^{2+} ions replace the K^+ ions only in interlayer I. It has been suggested for the reaction mechanism of nickel-loaded $K_4Nb_6O_{17}$ for the decomposition of H_2O that the ultrafine particles of Ni at interlayer I work as H_2 evolution sites and interlayer II work for O_2 evolution. However, a detailed investigation using spectroscopic methods has not been carried out because such methods were not suitable for applying to a 1–10 μm size powder sample, because of photoscattering. Therefore, the preparation of thin films of $K_4Nb_6O_{17}$ has been desired from this point of view. Furthermore, if

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thin films having the same structure as $K_4Nb_6O_{17}$ could be obtained, they would be expected to have photocatalytic activity and some interesting optical properties by modifying the interlayer space.

One of the characteristics of $K_4Nb_6O_{17}$ is a spontaneous hydration of its interlayer spaces under atmospheric conditions.⁹ Because of its hydration property, the $K_4Nb_6O_{17}$ powder was easily pulverized to fine particles by wet grinding, and the suspension containing fine particles of $K_4Nb_6O_{17}$ was obtained.¹¹ The suspension could be coated onto a substrate by spin coating, and a homogeneous thin film composed of the layered small particles was obtained.

In this work, the synthesis of thin films having the ordered, layered structure of $K_4Nb_6O_{17}$, crystallized by calcination at various temperatures, and characterization of them are reported.

Experimental Section

Materials. $K_4Nb_6O_{17}$ was prepared by calcination of a stoichiometric mixture of K_2CO_3 and Nb_2O_5 in a platinum crucible at 1473 K in air for 15 min. The melt mixture was cooled rapidly to room temperature and was pulverized in a mortar to form a powder with particle sizes of 1–10 μm . The crystal structure was confirmed by X-ray diffraction.

Wet grinding was carried out as follows: The suspension of $K_4Nb_6O_{17}$ (10 g) in distilled water (20 mL) was put into a centrifugal planetary ball mill (Fritsch) with zirconia beads and vigorously stirred for 2 h at room temperature. After the milling, the slurry was filtered to remove zirconia beads and washed with distilled water. The slurry was centrifuged at 10000 rpm for 30 min, and the precipitate was removed from the slurry. The centrifuged slurry containing fine particles of $K_4Nb_6O_{17}$ was used for the preparation of thin films.

Synthesis of Thin Films. A quartz plate or a Si wafer (2 \times 2 cm) was fixed on the spin-coater and rotated at 1000–3000 rpm. Then the suspension was added dropwise to the plate one or a few times, and the plate was rotated until the suspension spreaded homogeneously on the plate. The obtained thin films were calcined at various temperatures for 12 h in air. The sample before calcination is referred to as thin film **a**. Thin film **a** was then calcined in air at 873, 973, or 1073 K, and the resulting thin films are referred to as thin films **b**, **c**, and **d**, respectively. Calcination at temperatures higher than 1073 K causes a decrease of K^+ ions due to vaporization from the surface. To prepare a thin film calcined at 1073 K with a stoichiometric molar quantity, a thin film was calcined in a powder of $K_4Nb_6O_{17}$ in air, which is referred to as thin film **e**. After calcination, thin film **e** was washed with distilled water to remove small powders from the surface. Thin film **b** was immersed in 0.5 N aqueous H_2SO_4 solution for 24 h to exchange surface K^+ for H^+ , the result of which is referred to as thin film **b'**. To induce hydration of the interlayer space, thin film **d** was immersed in distilled water at room temperature for 1 h and then dried in air, the result of which is referred to as thin film **d'**.

Characterization of Thin Films. The following methods were used for characterization of the thin films. The structural studies were carried out by means of X-ray diffraction (XRD, Geigerflex RAD-B system, Cu $K\alpha$, 15 mA; Rigaku) and scanning electron microscopy (SEM, Akashi ISI DS130S). For the XRD measurement, a thick thin film was prepared by repetition of coating more than 5 times. The surface morphology of the thin films was studied in ambient air by atomic force microscopy (AFM, TopoMetrix TMX-2100) in the constant-force mode. The chemical state of the surface of the thin films was examined by X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA 3200) with a Mg $K\alpha$ X-ray source operating at 5.0 kV.

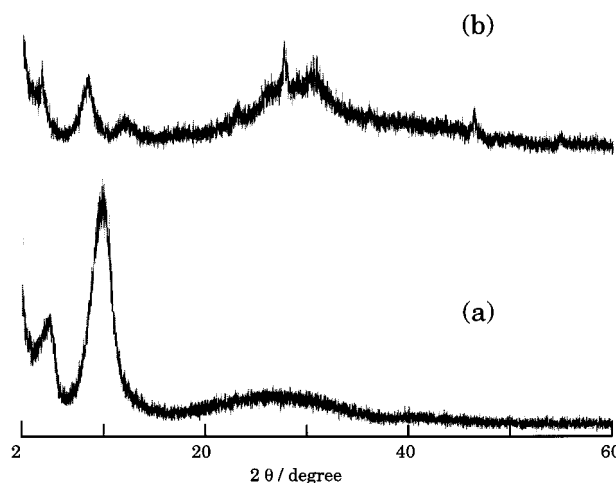


Figure 2. XRD patterns of two different types of thin film. One was obtained from spin coating of the suspension (a); the other was obtained from simple drying of the suspension without spin coating (b).

An Ar^+ ion beam was used to etch the film surface. The etching rate was about 100 $\text{\AA} \text{min}^{-1}$. The binding energy of the impurity C (1 s) peak was adjusted to 284.6 eV.

Ion Exchange of the Thin Film. Ion exchange of thin film **d** was carried out in several aqueous solutions. Proton exchange of thin film **d** was carried out in 0.5 N aqueous H_2SO_4 solution at room temperature for 4 days. Li^+ , Na^+ , Ca^{2+} , and Ni^{2+} exchange were carried out in 1.0 N aqueous solutions of the respective chloride at 363 K for 4 days. The ion exchange of the thin film was confirmed by energy-dispersive X-ray spectrometry (EDX, Philips EDAX 9100), except for Li^+ . The Li^+ exchange was confirmed by depth profile measurement using XPS. The extent of ion exchange was estimated from the decrease of potassium.

Results and Discussion

Appearance of the Thin Films. The as-coated thin film (thin film **a**) had a good transparency. Equally very good transparency was confirmed for the thin films calcined below 1027 K (thin films **b–e**), while the one calcined above 1127 K was white.

XRD. Figure 2 shows XRD patterns of two different types of thin film, one spin-coated (a) and the other non-spin-coated (b). For the spin-coated thin film (Figure a), only two obvious peaks ($2\theta = 4^\circ$ and 10°), which are probably due to (020) and (040) diffraction originating from a layered structure, were observed (a broad peak around $2\theta = 30^\circ$ is derived from the quartz plate). On the other hand, for the thin film which was obtained from simple drying of the suspension (without spin coating), several peaks except for (0k0) diffraction were observed in the region of $2\theta = 10\text{--}60^\circ$ (Figure 2b). The difference in the XRD patterns indicates the preferable effect of spin coating on the efficient orientation of the superfine particles with the b -axis perpendicular to the substrate surface.

XRD patterns of the as-coated thin films after calcination at various temperatures are shown in Figure 3. The XRD patterns of powder $K_4Nb_6O_{17}$ anhydride and $K_4Nb_6O_{17}\cdot 3H_2O$ are also shown as references. A very strong peak attributed to (040) diffraction was observed for the powder of $K_4Nb_6O_{17}$ anhydride. The d value of (040) diffraction increased from 8.2 to 9.4 \AA with hydration of the interlayer space ($K_4Nb_6O_{17}\cdot 3H_2O$). Furthermore, other diffraction peaks attributed to (020)

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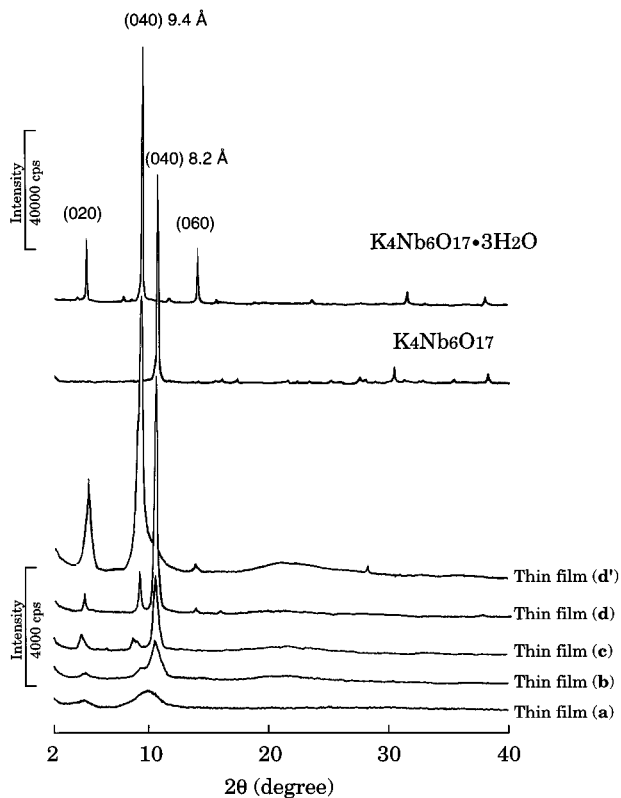


Figure 3. XRD patterns of $K_4Nb_6O_{17} \cdot 3H_2O$, $K_4Nb_6O_{17}$ anhydride, and spin-coated thin films after calcination at various temperatures.

and (060) diffraction were observed for $K_4Nb_6O_{17} \cdot 3H_2O$, while they were not obvious for the anhydride. In thin film **a**, some weak and broad peaks were observed around $2\theta = 4^\circ$ and 10° . With a rise of calcination temperature, these peaks became stronger and sharper. This result indicates the crystallization of the dispersed fine particles on the substrate by calcination. However, the crystallization was not observed for the thin film obtained from simple drying of the suspension (Figure 2b). Therefore, it is considered that crystallization could not proceed unless the superfine particles oriented on the substrate by spin coating.

For thin film **d**, which was calcined at 1027 K, a strong peak at $2\theta = 10.8^\circ$ was observed like that of the powder $K_4Nb_6O_{17}$, which indicates the well-ordered layered structure of thin film **d**. The d value of the thin film was 8.3 Å, which approximately agreed with that of the powder $K_4Nb_6O_{17}$ anhydride, 8.2 Å. An XRD pattern very similar to that of the thin film **d** was obtained for thin film **e**. In thin film **d** additional peaks were observed at $2\theta = 7.3^\circ$ and 9.0° . They were attributable to the partly hydrated species kept in atmospheric conditions. These peaks dominated after thin film **d** had been immersed in distilled water for 1 h (thin film **d'**). The two peaks ($2\theta = 7.3^\circ$ and 9.0°) of thin film **d'** agreed with the (020) and (040) diffractions of $K_4Nb_6O_{17} \cdot 3H_2O$, respectively. The same XRD pattern as that for thin film **d'** was observed for thin film **d** when it was left in air for more than 2 weeks. Accordingly, these thin films have approximately the same property of hydration as the powder one.

It is mentioned here that no transparent or homogeneous thin film was obtained by a simple calcination of K_2CO_3 and Nb_2O_5 powder on a substrate.

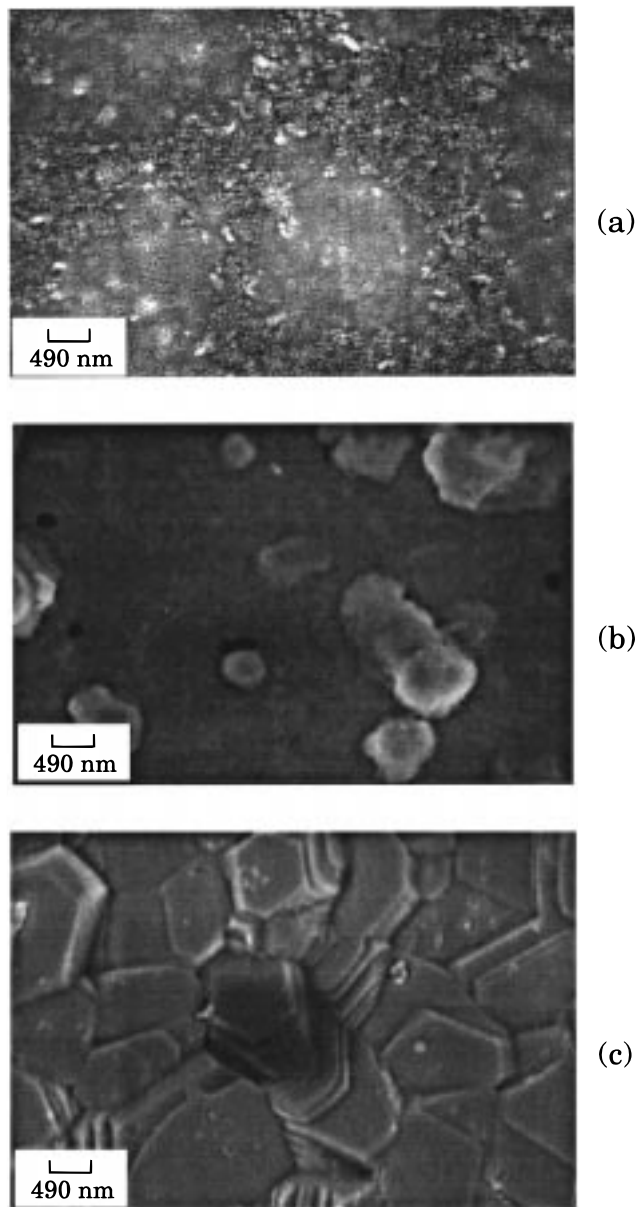


Figure 4. SEM photographs of the thin film before calcination (a), after calcination at 973 K (b), and after calcination at 1073 K (c).

SEM. SEM photographs (20400 \times) of thin films **a**, **c**, and **d** are shown in Figure 4. For thin film **a**, only very small particles of 100–200 nm diameter were observed to be spread (Figure 4a). With an increase of the calcination temperature, the morphology of the thin film remarkably changed. For thin film **c**, which was calcined at 973 K, some crystals of 500–600 nm were observed, and boundaries of the small particles disappeared (Figure 4b). For thin film **d** (Figure 4c) crystals of 500–1000 nm were observed to be spread horizontally to the substrate. They had a very flat surface, while the boundaries tended to corrugate. The results of the SEM photographs coincide well with the XRD results, which clearly show the crystallization of the fine particles and the formation of flat crystals.

AFM. The surface morphologies of thin films **a** (800 \times 800 nm) and **d** (800 \times 800 nm) are shown in Figure 5. As shown in Figure 5a, very small particles of 50–200 nm were observed for thin film **a**, similar to the

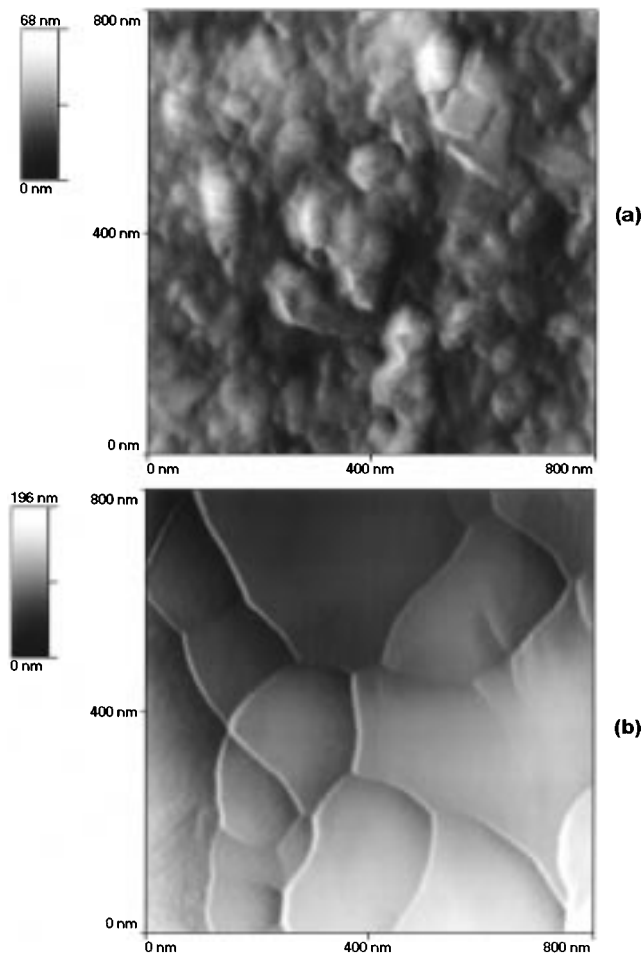


Figure 5. AFM height images of the thin film before (a) and after calcination at 1073 K (b).

SEM photograph. On the other hand, crystals of 400–600 nm with a very flat surface were observed for thin film **d**, which was calcined at 1027 K. Similar to those in the SEM photograph, some corrugations were observed at the boundaries of the crystals. The important information obtained from AFM was the height image indicating the homogeneity of the surface. The height images of thin films **a** and **d** indicated that both of them had moderately homogeneous surfaces within several hundred nanometers. This AFM result again confirms the crystallization of the fine particles by calcination and indicates the homogeneity of the thin films as a whole in submicron order.

XPS. XPS was employed to examine the chemical states of K, Nb, and O of the thin films' surfaces. Although there was no change in the K(2s) and Nb(3d) peak positions for thin films **a–e** compared with the original powder, the O(1s) peak remarkably changed with calcination temperature. The O(1s) photoelectron peak of the thin films and the $K_4Nb_6O_{17}$ powder are shown in Figure 6. The K/Nb surface atomic ratios determined from the K(2p) and Nb(3d) peak areas are compared in Table 1. Although only one O(1s) peak at 529.5 eV was observed for the original powder of $K_4Nb_6O_{17}$, another peak at around 531 eV was observed for thin films **a**, **b**, **c**, **d**, and **e**. For thin film **a** an additional O(1s) peak was found to be centered at 531.2 eV by computer peak deconvolution, and the surface K/Nb ratio decreased from 1.62 for the $K_4Nb_6O_{17}$ powder

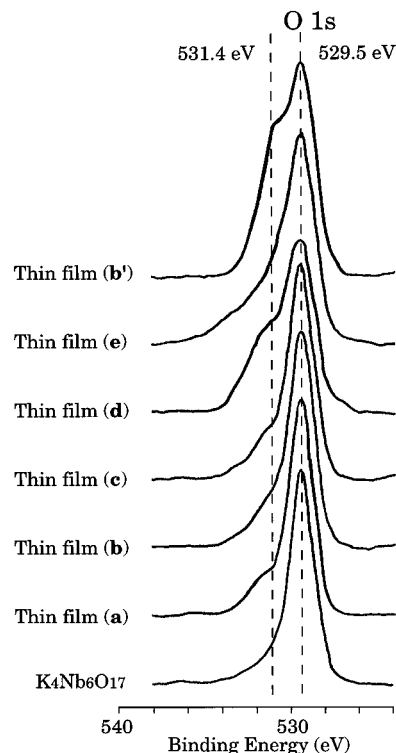


Figure 6. The O(1s) photoelectron peak of $K_4Nb_6O_{17}$ powder and thin films **a–b'**.

Table 1. K/Nb Surface Atomic Ratios of the Thin Films^a

sample	K/Nb ratio	calcination temp
$K_4Nb_6O_{17}$	1.62	
a	1.55	dried at room temperature
b	1.38	873 K
c	1.30	973 K
d	0.59	1073 K
e	1.25	1073 K

^a The surface atomic ratio of K/Nb was determined from the peak areas of K(2p) and Nb(3d).

to 1.55. The O(1s) peak at 531.2 eV is attributable to the surface hydroxyl groups formed during the wet grinding by cation exchange from K^+ to H^+ , because this peak became larger for thin film **b'** whose surface K^+ was exchanged to H^+ . Although the peak at 531.2 eV decreased with the increase of the calcination temperature as shown in thin film **b**, it again became larger for thin film **d**, and its K/Nb ratio remarkably decreased to 0.59. The decrease of K/Nb ratio of the thin film **d** is presumably due to the vaporization of potassium from the surface at 1073 K, and the O(1s) peak at 531.2 eV is assigned to oxygen remaining after the vaporization of potassium. In other words, the surface structure of the thin film changed during calcination at high temperatures, and the surface structure of thin film **d** came to be different from that of the original $K_4Nb_6O_{17}$.

When the thin film was calcined in $K_4Nb_6O_{17}$ powder to prevent the vaporization of surface potassium, approximately the same surface composition as the powder one was obtained (thin film **e**). For thin film **e** the surface K/Nb ratio was 1.25. Furthermore, the peak at 531.2 eV was much smaller than that of thin film **d**.

Ion Etching of the Thin Films. XPS depth profile analysis of thin film **d** was carried out. Figure 7 shows the O(1s) peaks of thin film **d** before etching (a), after etching for 40 s (b), and after etching for 80 s (c).

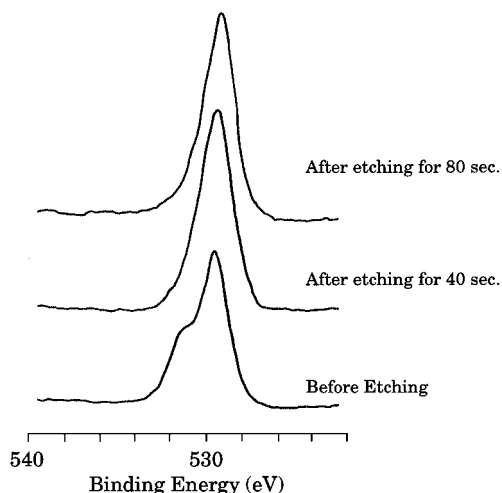


Figure 7. The O(1s) photoelectron peak of thin film d before etching, after etching for 40 s, and after etching for 80 s.

Although the Nb(3d) peak did not change, the O(1s) peak changed during the ion etching. The O(1s) peak at 531.2 eV immediately decreased after etching for 40 s, and only one peak at 529.5 eV was observed after etching for 80 s. Taking into account the etching rate (ca. 100 \AA min^{-1}), it is considered that the chemical state of oxygen assigned to 531.2 eV would exist only at the external surface of the thin film.

Ion Exchange of the Thin Films. If the thin film of $\text{K}_4\text{Nb}_6\text{O}_{17}$ has ion-exchange properties like those of the original powder,^{10,12–14} the modified thin film would find application in many fields and functional materials. Therefore, we investigated the ion-exchange properties of the thin film for Li^+ , Na^+ , Ca^{2+} , and Ni^{2+} ions, which had been already studied by Kinomura et al. for the powder one.¹⁰ Additionally, the H^+ exchange was also investigated from the standpoint of photocatalysis² and the precursor of further intercalation of various molecules.^{15,16} The XRD patterns of H^+ , Ni^{2+} , Ca^{2+} , Na^+ , and Li^+ -exchanged thin films with the original one are shown in Figure 8. The d values of the (040) diffraction and the extent of ion exchange of the thin films are also shown. It was observed that the d values of the thin films remarkably changed with cation exchange from K^+ to others. The extents of ion exchange of H^+ , Ca^{2+} , Ni^{2+} , Na^+ , and Li^+ were estimated by the decrease of K^+ to be ca. 75%, 37%, 23%, 77%, and 75%, respectively. As reported by Kinomura et al., the extent of exchange with the divalent cations had been found to be < 50% for the powder one, because the exchange with divalent cations occurs only at the interlayer I.¹⁰ Similar results were obtained for the thin film, where the extents of exchange with Ca^{2+} and Ni^{2+} were found to be < 50%, while those of H^+ , Li^+ , and Na^+ were all found to be

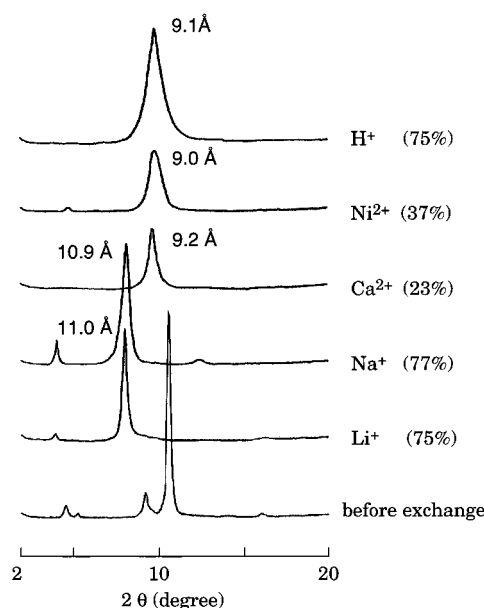


Figure 8. The XRD patterns of the ion-exchanged thin films with H^+ , Ni^{2+} , Ca^{2+} , Na^+ , and Li^+ , and the approximate extents of the ion exchange.

> 50%. This indicates that the ion exchange proceeds in the thin film as well as in the original power $\text{K}_4\text{Nb}_6\text{O}_{17}$. These results encourage us to do further modification of the thin films. For example, the reduction of the intercalated transition metal cation such as Ni^{2+} and $\text{Pt}(\text{NH}_3)_4^{2+}$ could produce ultrafine metal particles at the interlayer space, and the ultrafine particles of transition metals in restricted spaces would exhibit interesting magnetic properties. Furthermore, some organic and inorganic functional (photoactive) species such as $\text{Ru}(\text{bpy})_3^{2+}$ or methyl viologen could be immobilized in the interlayer of $\text{K}_4\text{Nb}_6\text{O}_{17}$. The obtained $\text{K}_4\text{Nb}_6\text{O}_{17}$ thin film would have an advantage in that the properties of immobilized species can be discussed on the basis of their more defined structures than in the powder one. The electronic and magnetic properties as well as the optical properties of these modified thin films are now under investigation.

Conclusion

A thin film having a layered structure was obtained from ultrafine particles of $\text{K}_4\text{Nb}_6\text{O}_{17}$. The ultrafine particles crystallized by calcination at 1073 K, and a flat thin film in submicron order was obtained. The calcined thin films had ion-exchange capabilities as were demonstrated by H^+ , Li^+ , Na^+ , Ca^{2+} , and Ni^{2+} ions.

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