Ion Exchange of $K_4Nb_6O_{17}\cdot 3H_2O$

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Ion exchange of the layered compound $K_4Nb_6O_{17}\cdot 3H_2O$ with mono- and bi-valent cations (Li^+, Na^+, Ca^{2+}, and Ni^{2+}) has been carried out in the aqueous chloride solutions at 90 °C. Only Na^+ was found to attain to complete exchange. For exchange with Li^+, almost all the K^+ ions in the interlayers seemed to be replaced, although partial decomposition was observed. The degrees of exchange with the bivalent cations were found to be $< 50\%$. The interlayer spacings of interlayers I (hydrated) and II (not hydrated) in $K_4Nb_6O_{17}\cdot nH_2O$ and derivatives were determined from electron-density projections along the *b* axes. From the change in interlayer spacings, it is considered that K^+ ions in interlayer II are only substituted by monovalent cations whereas both mono- and bi-valent cations exchange for K^+ in interlayer I. By exchanging K^+ in interlayer II with Li^+ or Na^+, this interlayer becomes hydrated.

The niobates $A_4Nb_6O_{17}\cdot nH_2O$ (A = K, Rb, or Cs) are known layered compounds[1] and K^+ ions have been found to be replaced by organic cations.[2] Recently, Gasperin and Le Bihan[3,4] have solved the structures of some of these compounds. According to their results, corrugated niobate sheets are stacked along the *b* axis of an orthorhombic unit cell and form four interlayer spaces which are classified into two types.[3] Alkali ions are distributed in these spaces. The first interlayer space (denoted as interlayer I hereafter) can take up water molecules, but the second layer (interlayer II) is not hydrated. For $K_4Nb_6O_{17}\cdot nH_2O$, two hydrated states with $n = 3$ or 4.5 have been reported, that with $n = 3$ being stable under ambient conditions.[1] Results of ion exchange obtained before the structural analyses must now be reviewed, since they were derived without knowing the existence of the two types of interlayer spaces.

Ion-exchange reactions of $K_4Nb_6O_{17}\cdot nH_2O$ with Li^+, Na^+, Ca^{2+}, and Ni^{2+} ions are reported herein.

Experimental

Preparation of $K_4Nb_6O_{17}\cdot 3H_2O$.—Powders of K_2CO_3 and Nb_2O_5 were mixed in a molar ratio of 2.1:3.0 and heated at 1 100 °C overnight in a platinum crucible. The product was washed with distilled water and dried in air. An *X*-ray powder diffraction pattern of this material corresponded to that of $K_4Nb_6O_{17}\cdot 3H_2O$ reported by Nassau *et al.*[1]

Cation-exchange Reactions.—Two types of starting material were used for the ion-exchange reactions, one was a ground powder and the other, flakes of *ca.* 0.2 × 0.5 × 1.5 mm. The reactions were carried out in 1 mol dm^{-3} chloride solution at 90 °C. The duration ranged from several minutes to 3 weeks. Separation was achieved by centrifuging and washing with distilled water. Samples were then dried at 60 °C and kept under ambient conditions. By treating samples in such a way, no change in basal spacing was observed. Using different starting materials did not give inconsistent results, although the flakes needed a longer time to attain a certain degree of exchange than the powdered sample.

Characterization.—The degree of exchange was determined by analysing the quantity of K^+ released into solution using atomic absorption methods. The basal spacing (length of the *b* axis) was calculated by using high-order 0*k*0 reflections of the *X*-ray powder powder pattern for orientated samples taken using Cu-K_α radiation. One-dimensional Fourier synthesis was performed after corrections for Lorentz-polarization factors and for thickness. Intensities were collected for 7—16 reflections by using orientated samples and orientation was achieved by arranging flakes carefully. Differential thermal analysis (d.t.a.) and thermal gravimetric analysis (t.g.a.) were carried out to estimate the amount of water and thermal stability.

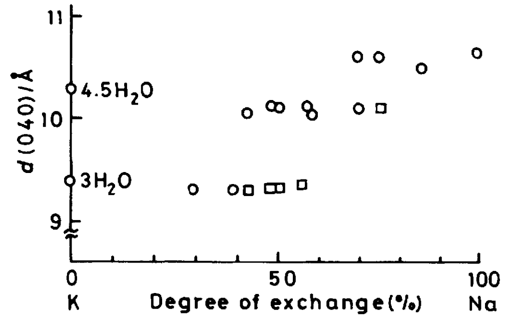

Figure 1. Spacings of the 040 reflection *versus* degree of exchange for the Na^+ derivative: ○ main phase, □ secondary phase

Results

Li^+ *Ion Exchange.*—The length of the *b* axis increased stepwise on exchange; *b* was 36.8 at the initial stage, 39.2 at the middle stage, and 40.9 Å at the final stage. These values correspond to the range of exchanged amounts of K^+ of 30—50, 50—70, and 70—100%, respectively. Weight losses for the products at the three stages were *ca.* 5.3, 9.0, and 20% respectively. The ion exchange appeared to be complete. However, as the degree of exchange increased, the solutions lost their clarity and the products included hygroscopic substances; this indicated that decomposition was proceeding as well as exchange. The degree of exchange was thus ambiguous and the number of water molecules in the interlayer spaces was not determined in this case.

Na^+ *Ion Exchange.*—In Figure 1, spacings of the 040 reflection are plotted against the degree of exchange. As can be seen, the basal spacings increase stepwise like those of the Li^+ derivative. The exchange of K^+ with Na^+ was complete and decomposition was not observed. In a reverse reaction in KCl solution, $K_4Nb_6O_{17}\cdot 3H_2O$ could be reformed at any of the stages of Na^+ exchange. T.g.a. for the completely exchanged

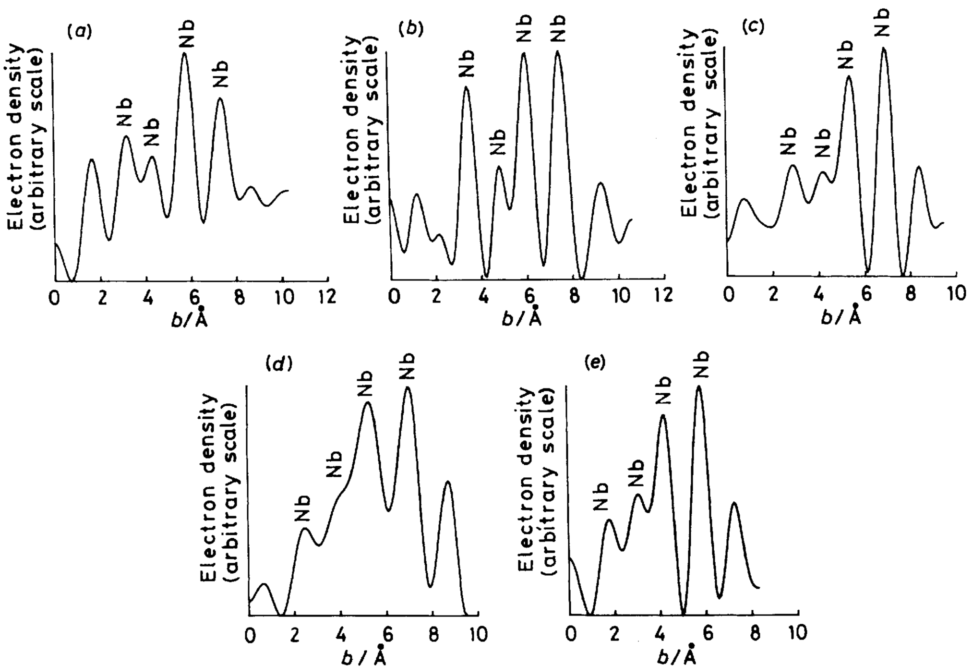

Figure 2. One-dimensional Fourier synthesis along the *b* axis (one quarter of the *b* axis is shown) for (*a*) Li^+ derivative, (*b*) Na^+ derivative, (*c*) $K_4Nb_6O_{17}{\cdot}3H_2O$, (*d*) Ca^{2+} derivative, and (*e*) Ni^{2+} derivative

Na^+ derivative, $Na_4Nb_6O_{17}{\cdot}nH_2O$, showed a weight loss of 11.2% and *n* was evaluated to be 7.0. Above *ca.* 630 °C, the Na^+ derivative decomposed to a mixture of $NaNbO_3$ and $Na_2Nb_4O_{11}$ as shown by *X*-ray powder diffraction.[5,6]

Lengths of the *b* axes for the main phases at each stage of exchange seen in Figure 1 were calculated to be 37.6, 40.2 and 42.3 Å, respectively. The first value is similar to that of $K_4Nb_6O_{17}{\cdot}3H_2O$ (37.7 Å), and the second corresponds to that of $K_4Nb_6O_{17}{\cdot}4.5H_2O$ (41.09 Å).[1] The weight losses for the products at the first and second stages of ion exchange were *ca.* 5.2 and 7.5% respectively and the number of water molecules closely agree with the formulae $K_4Nb_6O_{17}{\cdot}3H_2O$ and $K_4Nb_6O_{17}{\cdot}4.5\ H_2O$. At the final stage of exchange with Na^+, the Na^+ derivative took up more water molecules into the interlayer spaces and had a longer *b* axis than $K_4Nb_6O_{17}{\cdot}4.5H_2O$. Whether interlayer I had swelled further or interlayer II had become hydrated remains unsolved.

Ca^{2+} *Ion Exchange*.—In this case, extensive exchange caused decomposition and an amorphous material was produced. A Ca^{2+} phase with b = 38.0 Å coexisted with the amorphous material before complete decomposition. This value is similar to the *b* axis of $K_4Nb_6O_{17}{\cdot}3H_2O$. The degree of exchange was determined to be 39.9% for a sample in which the amorphous material did not appear to coexist. The observed weight loss of 8.5% corresponded to five water molecules in the interlayer spaces.

Ni^{2+} *Ion Exchange*.—The maximum degree of exchange observed was 49.7% and the length of the *b* axis for this Ni^{2+} derivative was 34.1 Å. The number of water molecules was calculated to be *ca.* 4 from the weight loss of 7.0%, by assuming a chemical formula of $NiK_2Nb_6O_{17}{\cdot}nH_2O$. Decomposition was not observed in this case.

Fourier Synthesis.—To estimate the change in interlayer spacing, one-dimensional Fourier syntheses were carried out for orientated samples of the Li^+ derivative with b = 40.9 Å, the Na^+ derivative with b = 42.3 Å, the Ca^{2+} derivative, the Ni^{2+} derivative, and the niobate $K_4Nb_6O_{17}{\cdot}3H_2O$. The atomic parameters were based on those of $Rb_4Nb_6O_{17}{\cdot}3H_2O$[3] and a one-dimensional Patterson function for each derivative. By changing the atomic parameters, calculated intensities were fitted to observed values. In the cases of Li^+ and Na^+, parameters were varied considerably, but in other cases variations were small. The number of reflections used was 8 for Li^+, 16 for Na^+, 10 for K^+, 7 for Ca^{2+}, and 11 for Ni^{2+}. Results are shown in Figure 2, where one quarter of the *b* axis, from the centre of interlayer I to the centre of interlayer II, is shown.

Discussion

In (*a*)—(*e*) of Figure 2, four strong peaks are observed which are considered to indicate the positions of niobium along *b*. Because the niobate layers are corrugated it is difficult to estimate exactly the interlayer spacing and layer thickness. Distances between the strong peaks can be used to observe the changes in interlayer spacing and thickness on ion exchange. Hence, twice the distance between the origin and the left-hand peak indicates the spacing of interlayer I, the distance between the left-hand and right-hand peaks indicates the layer thickness, and twice the distance between the right-hand peak and the centre of interlayer II indicates the spacing of interlayer II. These values are listed in the Table.

As can be seen from the Table, the layer thickness remains unchanged throughout all the derivatives. Considerable swelling was observed for interlayers I and II of the Li^+ and Na^+ derivatives; the remainder had almost the same spacings except for the Ni^{2+} derivative whose interlayer I spacing was much smaller than that of $K_4Nb_6O_{17}{\cdot}3H_2O$. Small changes in interlayer II of the Ca^{2+} and Ni^{2+} derivatives from that of $K_4Nb_6O_{17}{\cdot}3H_2O$ suggest that the K^+ ions in interlayer II were not exchanged with Ca^{2+} or Ni^{2+} (the final products showed degrees of exchange $<50\%$). If the K^+ ions in interlayer II had been exchanged with these bivalent ions, of smaller ionic radii than K^+, the interlayer spacing would have been reduced. The K^+ ions in interlayer I could be exchanged more easily than those in interlayer II, because interlayer I can be hydrated and

Table. Interlayer spacings and thicknesses of niobate layer (in Å). These distances almost correspond to Nb–Nb distances across interlayers or layers along the *b* axis

	Interlayer I	Layer	Interlayer II	Ref.
Rb^+	6.1	4.1	5.3	3
K^+	5.8	4.1	4.9	This work
Na^+	6.9	4.0	6.3	This work
Li^+	6.4	4.1	5.9	This work
Ca^{2+}	5.6	4.1	5.2	This work
Ni^{2+}	3.8	4.1	5.2	This work

shows swelling and shrinkage dependent upon the amount of water present.

The number of water molecules in the interlayer has been found to increase in the order $K^+ < Na^+ < Li^+$ in several layered compounds.[7–9] In particular, an increase in water molecules and then an increase in basal spacing were clearly seen in sulphides.[7,8] K^+ and Rb^+ derivatives of these sulphides have monolayers of water, but those of Li^+ and Na^+ have bilayers of water.

By replacing K^+ with Li^+ or Na^+, three states of hydration were observed under ambient conditions, depending on the degree of exchange. The derivatives at the first and second stages of exchange were considered to correspond to the K^+ niobates with $n = 3$ and 4.5 from their basal spacings and weight losses. Replacement of K^+ in interlayer II by Li^+ or Na^+ increases the number of water molecules in this interlayer and stabilizes the hydration state $n > 3$ under ambient conditions, whereas the hydration state $n = 3$ is stable under ambient conditions for $K_4Nb_6O_{17}\cdot nH_2O$. At the final stage of exchange with Li^+ or Na^+ the number of water molecules in the interlayers increases further. The swelling of interlayer II, as mentioned above, indicates that water molecules are taken up into this interlayer as well as interlayer I. Peaks which were considered to be due to water were seen at the centre of interlayer II in Figure 2(*a*) and (*b*). Interlayer II becomes hydrated with increasing amounts of Li^+ or Na^+ present, since K^+ in this interlayer has been substituted by Li^+ and Na^+ which hydrate more easily than K^+, as mentioned above.

Changes in interlayer spacings accompanied by monolayer water formation are reported to be *ca.* 3 Å for layered sulphides[8,9] and *ca.* 2 Å for α-zirconium phosphate.[10,11] An increase of 3.68 Å was proposed for clay minerals.[12] Changes in interlayer spacings on going from the first to the second stage of exchange for the Li^+ and Na^+ derivatives are 1.2 and 1.3 Å, respectively. These values are smaller than those mentioned above, but agree with the value of 1.6 Å for $K_2Rb_2Nb_6O_{17}\cdot nH_2O$ from $n = 3$ to 5 (ref. 4) and for $K_4Nb_6O_{17}\cdot nH_2O$ from $n = 3$ to 4.5.[1] These values are also comparable with the increase in interlayer II spacings by hydration: 0.6 Å for Li^+ and 1.2 Å for the Na^+ derivative. The value of 0.6 Å for the Li^+ derivative seems to be too small. However, if the difference in size of the small Li^+ and large K^+ ions is taken into account, the value can be considered reasonable.

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