Ion-exchange Reaction of Rubidium Ion in $Rb_8Nb_{22}O_{59}$

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Rubidium ion in $Rb_8Nb_{22}O_{59}$ with a tunnel structure was ion-exchanged with alkaline ions and proton. The ion-exchange with proton was almost complete to yield $H_{7.71}Rb_{0.29}Nb_{22}O_{59}\cdot 8.9H_2O$. The degree of ion-exchange with alkaline ions was 79.1%(Na^+), 41.8%(K^+) and 2.5%(Cs^+), and the chemical compositions for the ion-exchanged compounds were $Rb_{1.27}Na_{6.33}H_{0.40}Nb_{22}O_{59}\cdot 6.1H_2O$, $Rb_{3.06}K_{3.34}H_{1.60}Nb_{22}O_{59}\cdot 5.1H_2O$ and $Rb_{6.22}Cs_{0.20}H_{1.58}Nb_{22}O_{59}\cdot 1.9H_2O$. The ion-exchange of $H_{7.71}Rb_{0.29}Nb_{22}O_{59}\cdot 8.9H_2O$ with alkaline ions was also attempted.

The rubidium niobium oxide, $Rb_8Nb_{22}O_{59}$,[1] has a tunnel structure built up by corner-sharing of NbO_6 octahedra as shown in Figure 1. The Rb^+ ions located in the tunnel seem to be ion-exchangeable because some of pyrochlore type compounds with similar tunnel structure exhibit ion-exchange of monovalent cations in the tunnel.[2-5]

The starting material, $Rb_8Nb_{22}O_{59}$, was prepared by heating a stoichiometric mixture of Rb_2CO_3 and Nb_2O_5 at 900 °C for 12 h. The X-ray powder pattern was indexed in the hexagonal system with the lattice parameters of a=7.511(1) and c=43.13 (1)Å which agreed with the published values (a=7.53(1) and c=43.39(6)Å).[1] Ion-exchange reactions were performed with 0.1M alkaline chlorides and HCl solutions. The reaction temperature was 90 °C and the reaction duration was 1-14 days. The solid products were separated by centrifuging, washed with distilled water and dried at 50 °C. The products were identified by X-ray powder diffraction using Ni-filtered CuKα radiation. Ion-exchanged compounds were completely dissolved by mixed acid of HF and HNO_3 at 90 °C. The solution was completely evaporated to obtain a white precipitation, and then HNO_3 solution was added. After filtration, the amount of alkaline ions in the solution was analyzed by atomic absorption spectroscopy. The amount of water molecules was calculated by subtraction of the weight loss caused by release of proton from the total weight loss. Lattice parameters were determined by using silicon as an internal standard. The thermal stability was investigated by TG-DTA with a heating rate of 10°/min in air.

Figure 2 shows time dependence of uptake amount of ion-exchange reaction with alkaline ions and proton. The ion-exchange reaction attains equilibrium in 7 days and no uptake of Li^+ ion was observed. The Rb^+ ion in $Rb_8Nb_{22}O_{59}$ is maximally ion-exchanged with proton to yield $H_{7.71}Rb_{0.29}Nb_{22}O_{59}\cdot 8.9H_2O$. The uptake amount decreases in the order of Na^+, K^+ and Cs^+ ions. The X-ray powder patterns for the ion-exchanged compounds could be indexed with the hexagonal system similar to the starting material, indicating that the crystal structure remains intact during the ion-exchange reactions. Also the color of the samples and the profile of the X-ray powder patterns did not change during the ion-exchange reactions. The chemical composition and lattice parameters for the ion-exchanged compounds are listed in Table 1. In the ion-exchange with alkaline ions the total amount of the incorporated alkaline ion and the unreacted Rb^+ ion in the ion-exchanged compound is less than the amount of Rb^+ ion in the starting compound, therefore it is considered that proton is incorporated into the ion-exchanged compounds in order to maintain the charge neutrality. The a- and c-axes for the ion-exchanged compound with K^+ ion are the largest values among ion-exchanged compounds. Probably this is caused by the fact that large alkaline ions, K^+ and Rb^+ ions, are hydrated in the ion-exchanged

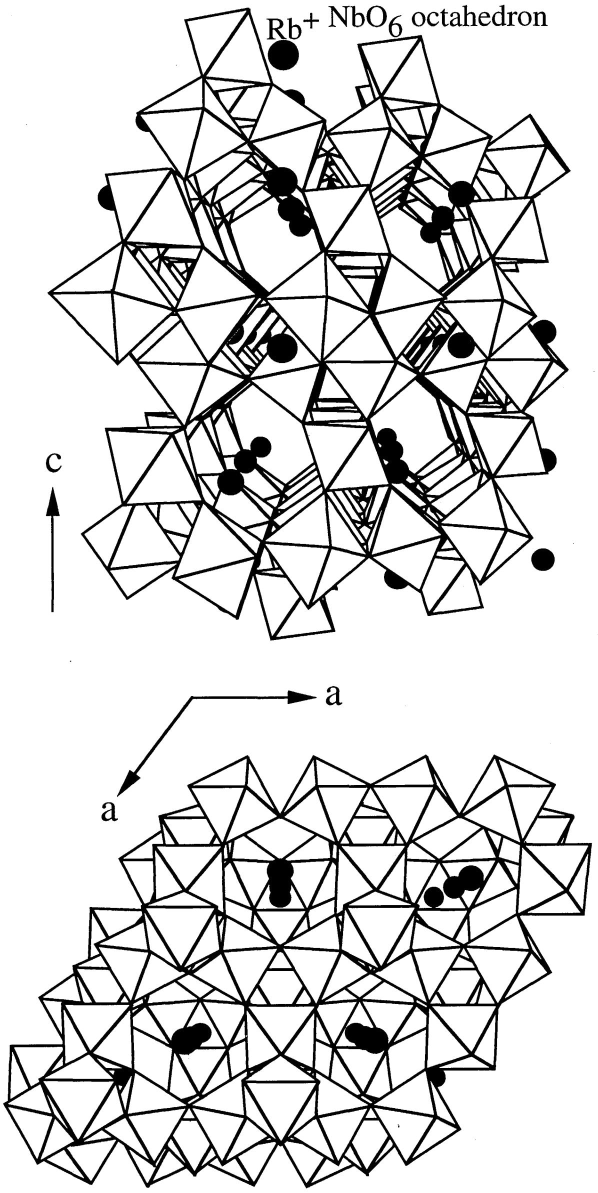

Figure 1. Projection of $Rb_8Nb_{22}O_{59}$ along the a-axis (upper) and the c-axis (lower).

Table 1. The chemical composition and lattice parameters for the ion-exchanged compounds

Chemical composition	a(Å)	c(Å)
$Rb_8Nb_{22}O_{59}$	7.511(1)	43.13(1)
$Rb_{0.29}H_{7.71}Nb_{22}O_{59}\cdot 8.9H_2O$	7.534(2)	43.06(3)
$Rb_{1.27}Na_{6.33}H_{0.40}Nb_{22}O_{59}\cdot 6.1H_2O$	7.514(1)	43.13(1)
$Rb_{3.06}K_{3.34}H_{1.60}Nb_{22}O_{59}\cdot 5.1H_2O$	7.534(4)	43.30(1)
$Rb_{6.22}Cs_{0.20}H_{1.58}Nb_{22}O_{59}\cdot 1.9H_2O$	7.511(1)	43.15(3)

compound with K^+ ion. Figure 3 shows the TG curves for the ion-exchanged compounds. Gradual weight losses observed up to 500 °C are considered to be caused by release of two kinds of water molecules; one is incorporated into a tunnel during ion-exchange reaction and another is formed by protons and oxygen atoms of the host lattice on the course of pyrolysis.

Ion-exchange reaction of $H_{7.71}Rb_{0.29}Nb_{22}O_{59}\cdot 8.9H_2O$ with alkaline ions was also performed using alkaline chloride solutions at 90 °C. The trend of ion-exchange reaction of the protonated compound was similar to that of $Rb_8Nb_{22}O_{59}$; the maximal uptake was observed for Na^+ ion and the uptake amount decreases in the order of Na^+, K^+, Rb^+ and Cs^+ ions. No uptake of Li^+ ion was also observed.

$Rb_8Nb_{22}O_{59}$ and its protonated compound have high selectivity for Na^+ ion and similar high selectivity for Na^+ ion was found in antimonic acid with the pyrochlore type structure.[4,5] Probably this is attributed to similarity of the tunnel structure between $Rb_8Nb_{22}O_{59}$ and the pyrochlore type compound; tunnels are formed by the hexagonal ring built up by corner-sharing of six octahedra in both structural types. This structural feature is considered to affect the ion-exchange behavior such as high selectivity for Na^+ ion and insensitivity for Li^+ ion.

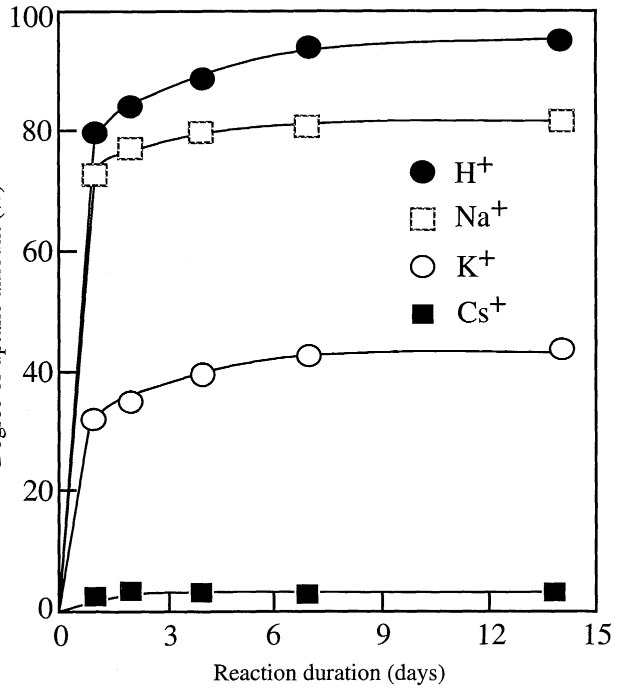

Figure 2. Time dependence of uptake amount of ion-exchange reaction of Rb^+ ion in $Rb_8Nb_{22}O_{59}$ with proton and alkaline ions.

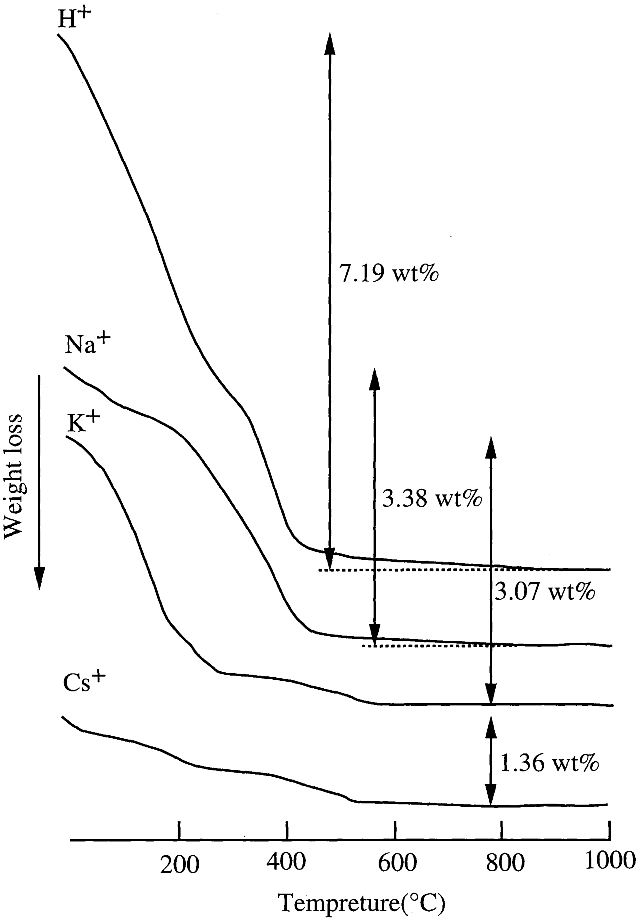

Figure 3. TG curves for the ion-exchanged compounds.

References and Notes

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