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Cation-Exchange Characteristics of $K_2W_4O_{13}$ in Molten Nitrate Salts

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The cation-exchange characteristics of $K_2W_4O_{13}$, with its tunnel framework structure, for univalent cations in molten nitrate salts just above their melting points have been investigated. From the results, K^+ ions in the tunnels were found be topotactically exchanged for Li^+, Na^+, Rb^+, and Ag^+, and the exchange ratios were found to follow the order; $Rb^+ < Li^+ < Na^+ < Ag^+$. It was found that the host–guest reactions on $K_2W_4O_{13}$ produce new materials with this tunnel structure that cannot be prepared by the ordinary synthetic method. © 1991 Academic Press, Inc.

Introduction

Alkali-metal polytungstates form crystals with various three-dimensional framework or layer structures, dependent on alkali-metal ions and the polymarization of $W_n O_{3n+1}^{2-}$ anions. Alkali-metal ions are located in framework or interlayer tunnels. $K_2W_4O_{13}$, which is one of the stable phases in the K_2WO_4–WO_3 system (*1*), crystallizes in the trigonal space group $P\bar{3}$, with lattice constants of $a = 15.526$ and $c = 3.840$ Å, and has two kinds of framework tunnels running along the c axis, as is seen in Fig. 1 (*2*). One is a hexagonal tunnel formed by stacking six-membered rings of WO_6 octahedra, and the other is a pentagonal tunnel formed by strings of WO_6 octahedra connecting the hexagonal tunnels. Potassium ions are located in both tunnels and weakly bonded to the host lattice. Potassium ions were, therefore, expected to be topotactically exchangeable with external guest cations. The host–guest reaction can create isomorphic or polymorphic forms that cannot be prepared by the ordinary synthetic methods, i.e., solid state reaction, fusion, and hydrothermal techniques.

In this paper, we report the cation-exchange charateristics of $K_2W_4O_{13}$ for Li^+, Na^+, Rb^+, and Ag^+ ions in molten nitrates just above melting points.

Experimental

$K_2W_4O_{13}$ was prepared by a solid state reaction at 750°C for 72 hr, using fully mixed K_2CO_3 and WO_3 with a molar ratio of 1 : 4 as starting materials. The obtained specimens, which are pale yellow needles, were ground, washed with distilled water to remove the impurities, and then dried at 80°C under vacuum. They were characterized by powder X-ray diffraction (XRD), using a Shimazu X-ray diffractometer XD-3 with Cu$K\alpha$ radiation.

A total of 0.5 g synthetic $K_2W_4O_{13}$ was

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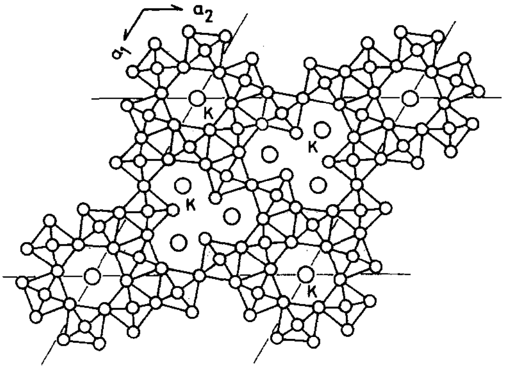

FIG. 1. Crystal structure of $K_2W_4O_{13}$ viewed along the *c* axia (*2*).

allowed to react with 1 g molten RNO_3 (R = Li, Na, Rb, and Ag) just above melting point. The reaction temperatures were 270, 350, 330, and 220°C for $LiNO_3$, $NaNO_3$, $RbNO_3$, and $AgNO_3$, respectively. After the treatment within fixed times, the nitrate salts were dissoved in deionized water. The solid and solution phases were separated by centrifugation, and an aliquot of supernatant was collected for chemical analyses. The solids were dried at 80°C under vacuum and then characterized by XRD and by thermal gravimetric analytical techniques (TG-DTA), using a Rigaku TG-DTA instrument. The solutions were analyzed for K by atomic absorption spectroscopy, using a Hitachi 180-30 instrument, and also for W by inductively coupled plasma emission spectroscopy (ICP), using a Shimazu ICPS-500 instrument. The ionic conductivity of original and some treated samples were measured up to 400°C by the complex impedance method in the frequency region from 5 Hz to 13 MHz, using Yokogawa Hewlett–Packard LCZ meters. The samples employed for the measurements were prepared by coating Ag paste on the surfaces of pressed disks.

Results and Discussion

XRD showed that the samples treated with molten RNO_3 were single phases and isostructural with the original $K_2W_4O_{13}$, as shown in Fig. 2. The positions of XRD peaks shifted toward higher diffraction angle sides in the reaction with $NaNO_3$ and $AgNO_3$, while they shifted toward lower diffraction angle sides in the reaction with $LiNO_3$ and $RbNO_3$. The W atoms in the aqueous nitrate solutions could not be detected by ICP. The results mean that K^+ ions in the tunnel along the *c* axis were exchanged with Li^+, Na^+, Rb^+, and Ag^+ ions without destroying the skeletal structure; $R_xK_{2-x}W_4O_{13}$ with tunnel framework structures were produced. The structure of $K_2W_4O_{13}$ was, however, destroyed by the reaction with molten $CsNO_3$.

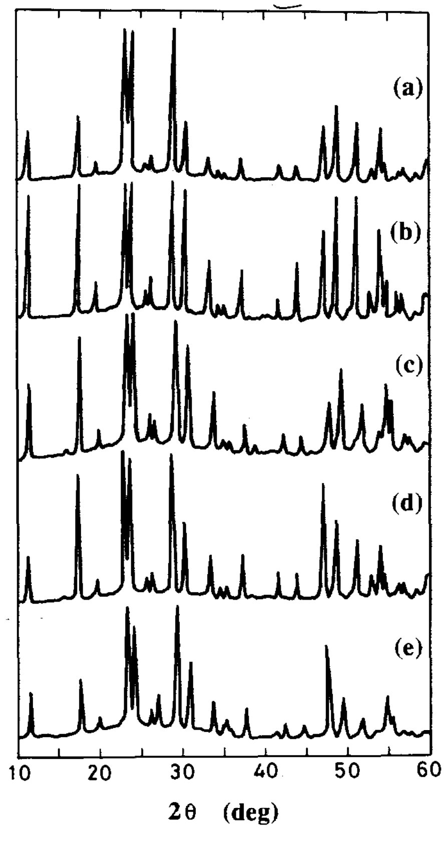

FIG. 2. X-ray diffractograms of $K_2W_4O_{13}$ and its reaction products. (a) Original; (b) treatment with molten $LiNO_3$; (c) treatment with molten $NaNO_3$; (d) treatment with molten $RbNO_3$; and (e) treatment with molten $AgNO_3$.

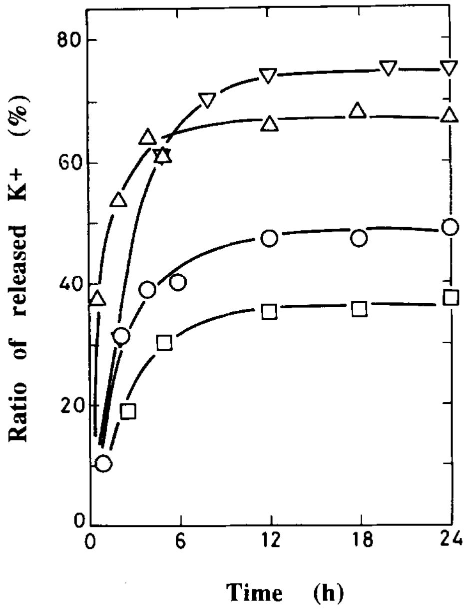

FIG. 3. Time dependence of cation-exchange reactions on $K_2W_4O_{13}$ with molten $LiNO_3$ (○), $NaNO_3$ (△), $RbNO_3$ (□), and $AgNO_3$ (▽).

This was considered to be the result of the far larger radius of the Cs^+ ion compared with that of the K^+ ion, and the melting point of $CsNO_3$, which was higher than those of the others (i.e., mp = 414°C for $CsNO_3$).

The time dependence of the ratio of K^+ ions released from $K_2W_4O_{13}$ in the cation-exchange reactions is shown in Fig. 3. Na^+ and Ag^+ ions are very reactive with $K_2W_4O_{13}$, and the order of the exchange ratios for univalent cations in molten nitrate salts was found to be $Rb^+ < Li^+ < Na^+ < Ag^+$. From the results, the exchange behavior for univalent cations was considered to be promoted by the conditions in which the ionic radius of the exchanging ion is smaller than that of K^+ ion; moreover, the difference between ionic radii is small, i.e., 0.60 Å for Li^+, 0.95 Å for Na^+, 1.33 Å for K^+, 1.48 Å for Rb^+, and 1.26 Å for Ag^+ (*3*). Although all the cation-exchange reactions that occurred attained steady states within 12 hr, they remained incomplete.

The lattice constants of cation-exchanged $R_xK_{2-x}W_4O_{13}$ as a function of x are shown in Fig. 4. In the exchange reactions with Na^+ and Ag^+, the a axis drastically decreased with an increasing amount of exchanging ions, while the c axis slightly decreased. This corresponds to the fact that the tunnel framework structure is parallel to the c axis. K^+ ions of 68 and 75% were exchanged with Na^+ and Ag^+ ions in the reaction for 24 hr; $Na_{1.4}K_{0.6}W_4O_{13}$ with a = 15.301(2) and c = 3.786(1) Å and $Ag_{1.5}K_{0.5}W_4O_{13}$ with a = 15.289(5) and c = 3.819(4) Å were produced, respectively. The structure of $Na_2W_4O_{13}$, synthesized by a solid state reaction at high temperature, is quite different from that of $K_2W_4O_{13}$; namely, the former structure consists of the layers formed by $(W_4O_{13}^{2-})_\infty$ anion groups (*4*). $Ag_{1.5}K_{0.5}W_4O_{13}$ showed a different XRD pattern from that of $Ag_2W_4O_{13}$, as reported by Faurie (*5*). On the other hand, Gatehouse and Leverett reported that $Ag_2W_4O_{13}$ did not appear in the Ag_2WO_4–WO_3 system (*6*). Either way, the results obtained here suggest

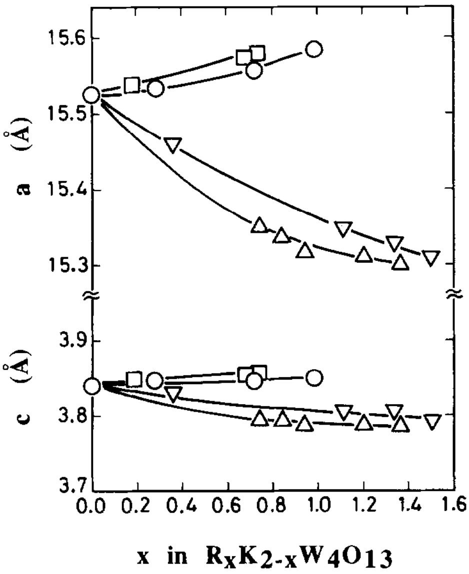

FIG. 4. Lattice constants of cation-exchanged $R_xK_{2-x}W_4O_{13}$ [R = Li (○), Na (△), Rb (□), and Ag (▽)] as a function of x.

the possibility of syntheses of new $Na_2W_4O_{13}$ and $Ag_2W_4O_{13}$ with tunnel framework structures by using the cation-exchange reactions.

K^+ ions of 49 and 37% in $K_2W_4O_{13}$ were exchanged with Li^+ and Rb^+ ions in the reaction for 24 hr; $LiKW_4O_{13}$ with a = 15.585(5) and c = 3.848(2) Å and $Rb_{0.7}K_{1.3}W_4O_{13}$ with a = 15.576(3) and c = 3.849(1) Å were produced, respectively. In spite of the smaller radius of the Li^+ ion compared with that of the K^+ ion, the a axis increased with an increase in the exchange ratio in the reaction with Li^+ ions, as is seen in Fig. 4. The result was against our expectations. Moreover, TG-DTA showed no weight loss due to leakage of water molecules up to 600°C. Li^+ ions were, therefore, guessed to deviate from the centers of pentagonal and hexagonal tunnels to a location in the vicinity of the WO_6 octahedra, because of the small radius of the Li^+ ion.

A significant difference between the ionic conductivities of the cation-exchange and the original samples could not be observed; e.g., $\log \sigma = -4.0, -5.4, -4.8$, and -4.9 Ω^{-1} cm^{-1} at 400°C for $Na_{1.4}K_{0.6}W_4O_{13}$, $Ag_{1.5}K_{0.5}W_4O_{13}$, $LiKW_4O_{13}$, and $K_2W_4O_{13}$, respectively. This was considered to be a result of K^+ ions surviving in the tunnels which disturbed the conductivity of the exchanged cations.

The ion-exchange soft reaction of $K_2W_4O_{13}$ was concluded to be available for creating new materials with the tunnel framework structure that cannot be prepared by the ordinary synthetic method.

Acknowledgments

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References

1. L. L. Y. Chang, *J. Am. Ceram. Soc.* **58,** 267 (1975).
2. K. Okada, F. Marumo, and S. Iwai, *Acta Crystallogr. Sect. B* **34,** 3193 (1978).
3. R. D. Shanon and C. T. Prewitt, *Acta Crystallogr. Sect B* **25,** 925 (1969).
4. K. Viswanathan, *J. Chem. Soc. Dalton Trans.*, 2170 (1974).
5. J. P. Faurie, *Bull. Soc. Chim. Fr.* **4,** 1170 (1971).
6. B. M. Gatehouse and P. Leverett, *J. Chem. Soc. Dalton Trans.*, 1316 (1976).