Sodium Intercalation into the Defect Garnets $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$

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Sodium has been reversibly intercalated into the defect garnets $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$, yielding two new compounds, $Na_2Fe_2(MoO_4)_3$ and $Na_2Fe_2(WO_4)_3$, which retain the monoclinic symmetry of the parent compounds but with expanded unit cells. The lattice parameters for $Na_2Fe_2(MoO_4)_3$ are $a = 16.09$ Å, $b = 9.507$ Å, $c = 18.64$ Å, $\beta = 125.27°$ and for $Na_2Fe_2(WO_4)_3$ $a = 16.16$ Å, $b = 9.582$ Å, $c = 18.80$ Å, $\beta = 125.56°$. At low sodium contents a narrow solid solution range is evident for both the tungstate and the molybdate, the structure of which is based on the parent compound. © 1990 Academic Press, Inc.

Introduction

To date, investigations of sodium intercalation and deintercalation have concentrated mainly on layered sulfide and oxide hosts (*1, 2*). However, hosts which possess a three-dimensional framework structure and do not confine guest ions to diffuse in only one or two dimensions are now receiving greater attention for the intercalation of a variety of guest species, including sodium. This arises in part because of the absence of solvent cointercalation when inserting guest ions from an electrolyte in an electrochemical cell, and also because of the absence of staging. It is on sodium intercalation into such three-dimensional framework hosts which we concentrate in this paper.

It is evident from studies of ion transport in solid electrolytes that Li^+ ions, with a radius in an octahedral oxide environment of 0.76 Å (*3*), are highly mobile within a

close-packed anion framework such as that in LISICON and its isostructural compounds (*4*). Whereas the larger Na^+ ion, with a radius of 1.02 Å in a similar environment (*3*), exhibits its greatest mobility in an open framework of anions with channels of large diameter such as in the NASICON structure (*5*). We may conclude that hosts optimized for sodium intercalation must possess at least two features: first, an open framework structure with wide channels for guest ion diffusion, and second, the framework must be capable of accepting electrons. Sodium has already been intercalated into a NASICON framework, $NaTi_2(PO_4)_3$ (*6*). A group of compounds known as the defect garnets and possessing the general formula $M_2(XO_4)_3$ bear a structural resemblance to NASICON in that they consist of corner sharing MO_6 octahedra and XO_4 tetrahedra. Two such compounds, $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$, have been shown to act as intercalation hosts for lithium (*7–10*). Nadiri *et al.* (*10*) have also re-

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ported on sodium intercalation into $Fe_2(MoO_4)_3$; they identify two phases with composition ranges $0.3 \leq x \leq 1.0$ and $1.10 \leq x \leq 1.60$. In this paper we report on sodium intercalation into both $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$: our results for the former compound differ from that in Ref. (*10*), and to our knowledge, this is the first report of sodium intercalation into ferric tungstate.

Experimental

Both the ferric molybdate and the ferric tungstate were prepared by a solution-based technique. In the case of the former compound a procedure based on that reported by Rapposh *et al.* (*11*) was followed. An appropriate proportion of an aqueous solution of $Fe(NO_3)_3$ (BDH, 98%) was added slowly to a stirred solution of Na_2MoO_4 (Aldrich, 99%) in water, the acidity of which was adjusted to a pH of 1.8 by the addition of nitric acid. The resulting precipitate was aged at 90°C for 24 hr then filtered and washed with dilute nitric acid. The solid was then dried at 100°C, ground to a fine powder, and transferred to a gold crucible which was heated in air, first at 480°C for 15 hr then at 600°C for 24 hr. The grinding and heating procedures were repeated until no further improvement in crystallinity was observed by X-ray diffraction. $Fe_2(WO_4)_3$ was prepared similarly following a procedure reported by Harrison *et al.* (*12*). Aqueous solutions of $Fe(NO_3)_3$ and Na_2WO_4 (Aldrich, 99%) were combined such that the resulting mixture contained an iron to tungsten ratio of $2:3$. The solution and precipitate were stirred for 30 min, then heated to dryness. The dried solid was then ground to a fine powder, washed in a Büchner funnel, and dried. The resulting powder was heated in air in a gold crucible at 475°C for 8 hr.

Sodium intercalation was carried out using sodium napthalide, which was prepared by the addition of sodium metal (Alfa, 99.995%) to napthalene (Aldrich, 99%) in dry THF (Aldrich, 99.9% anhydrous) under argon (*13*). The sodium concentration of the resulting solution was determined by titration to be 1.5 moles dm^{-3}. This was carried out by first adding water to the napthalide solution and then titrating the resulting NaOH against an aqueous solution of HCl. The sodium napthalide solution was added under an inert argon atmosphere to several grams of the defect garnet. A sufficient quantity of the napthalide solution was added such that the sodium content of the mixture was approximately 10% in excess of the desired composition of the intercalate. The mixture was stirred continuously for 3 days under argon, vacuum filtered, and washed with anhydrous THF.

Powder X-ray diffraction of the parent host and the intercalated compounds was carried out in sealed capillaries with copper $K\alpha$ radiation and a Stöe Guinier camera in transmission mode. The sodium content of the various intercalated materials was determined by atomic absorption analysis using a Pye-Unicam SP9 spectrometer. The solids were first dissolved in concentrated HCl then diluted to pH 2. Solutions of NaCl were used as standards.

The materials used in the construction of the electrochemical cells for ocv (open circuit voltage) measurements are sensitive to air and therefore the cells were constructed in a high integrity argon-filled Mbraun glove box, in which the argon is constantly cycled over molecular sieves and oxygen catalyst, thus maintaining levels of less than 1 ppm for both O_2 and H_2O. The cathode consisted of either the pure host compound or a chemically intercalated material. Five to ten milligrams of the appropriate powder was mixed with 20% (v/v) acetylene black and pressed onto a stainless steel grid. The sodium anode was cut from an ingot of the metal and rolled flat to form a thin disk. A Whatman low porosity, GF/F pad was placed next to the cathode and two higher porosity GF/E pads were inserted between this and the anode.

The pads were soaked in a solution of 1 M $NaClO_4$ (Aldrich, 99 + %) in propylene carbonate (Aldrich, 99 + %). The salt was first dried at 170°C for 24 hr and the propylene carbonate was carefully distilled under vacuum at 80°C using a 1-m column packed with glass beads. The entire assembly was placed in a Teflon-bodied cell between two stainless steel end pieces and compressed axially until a stable potential was obtained. By transferring the cell to a gas-tight container it could then be removed from the glove box for the electrochemical measurements. The container was fitted with electrical breakthroughs and a thermocouple. All measurements were carried out at 25°C. In most instances the composition of the electrode was modified *in situ,* by charging or discharging the cell at a constant current of 10 μA cm^{-2} using a Schlumberger–Solartron 1286 potentiostat/galvanostat. The high input impedance DVM incorporated into the 1286 was used for open circuit voltage measurements. Potentials were recorded when a change of less than 2 mV in 24 hr was observed.

Results and Discussion

The results of open circuit voltage measurements made as a function of the sodium content in $Fe_2(MoO_4)_3$ and $Fe_2(WO_4)_3$ are presented in Fig. 1. The trends are similar for both materials. Initially, the potential drops continuously over a limited composition range, indicating continuous intercalation of sodium into the host structure. At higher sodium contents a plateau is observed extending up to a composition of two sodiums per formula unit and indicating the presence of two phases for $0 < x < 2$. Powder X-ray diffraction patterns confirm the presence of two phases in both the ferric molybdate and the ferric tungstate systems. One phase possesses the structure of the parent compound, and the other is a new phase with a composition $Na_2Fe_2(XO_4)_3$

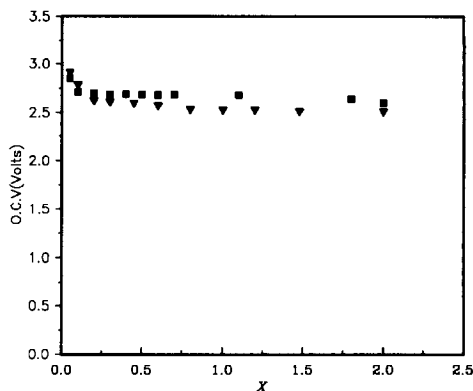

Fig. 1. Variation of open circuit voltage, with respect to a sodium metal electrode, as a function of the sodium content, x; $Na_xFe_2(MoO_4)_3$ (■) and $Na_xFe_2(WO_4)_3$ (▼).

where X = Mo or W. All of the sodium may be extracted from these new phases thus recovering the original ferric molybdate and tungstate, by the action of a solution of Br in dry acetonitrile on the solids.

Sodium contents in excess of two per formula unit may be obtained. However, no new crystalline phases appear on the X-ray powder patterns, and no shift in the positions of the lines is observed which would have indicated a continuous range of solid solutions. An increase in the background of the powder profile at low angles was evident, suggesting the formation of an as yet unidentified amorphous phase at compositions beyond $Na_2Fe_2(XO_4)_3$, X = Mo or W.

The X-ray powder data for the two new crystalline phases are presented in Table I. Both powder diffraction patterns could be indexed in the same monoclinic space group, $P2_{1/a}$, as that of their parent compounds. The unit cell parameters were refined using the program POWREF. The cell parameters for the parent compounds have been reported previously and are in the case of $Fe_2(MoO_4)_3$, a = 15.707 Å, b = 9.231 Å, c = 18.204 Å, β = 125.25°, and for $Fe_2(WO_4)_3$, a = 15.95 Å, b = 9.32 Å, c = 18.47 Å, β = 125.7° (8, 9). Comparing the

TABLE Ia

$Na_2Fe_2(MoO_4)_3$

$a = 16.09(1)$ Å $b = 9.507(3)$ Å $c = 18.64(1)$ Å $\beta = 125.27(4)°$

Space group $P2_{1/a}$

hkl	d_{calc} (Å)	d_{obs} (Å)	I_{obs}
200	6.568	6.583	v.w.
012	5.941	5.926	m
21$\bar{2}$	5.933		
112	4.679	4.681	w
31$\bar{2}$	4.671		
120	4.476	4.470	v.s.
21$\bar{4}$	4.185	4.189	v.s.
32$\bar{2}$	4.032	4.029	v.s.
22$\bar{2}$	4.029		
11$\bar{4}$	3.990	3.990	v.s.
31$\bar{4}$	3.985		
202	3.966	3.964	v.s.
40$\bar{2}$	3.959		
220	3.851	3.849	v.w.
212	3.661	3.654	m
41$\bar{2}$	3.655		
122	3.561	3.556	v.s.
32$\bar{2}$	3.557		
22$\bar{4}$	3.328	3.326	s
400	3.284	3.286	w
222	3.045	3.039	m
42$\bar{2}$	3.042		
024	2.970	2.977	m
42$\bar{4}$	2.966		
032	2.926	2.924	m
23$\bar{2}$	2.924		
132	2.730	2.734	m
33$\bar{2}$	2.728		
420	2.702	2.699	m

TABLE Ib

$Na_2Fe_2(WO_4)_3$

$a = 16.16(1)$ Å $b = 9.582(3)$ Å $c = 18.80(1)$ Å $\beta = 125.56(5)°$

Space group $P2_{1/a}$

hkl	d_{calc} (Å)	d_{obs} (Å)	I_{obs}
200	6.573	6.559	w
012	5.976	5.981	m
21$\bar{2}$	5.976		
120	4.561	4.502	v.s.
21$\bar{4}$	4.219	4.218	v.s.
40$\bar{2}$	3.971	3.969	v.s.
202	3.971		
004	3.823	3.821	v.w.
40$\bar{4}$	3.822		
212	3.669	3.669	w
41$\bar{2}$	3.669		
122	3.580	3.570	v.s.
32$\bar{2}$	3.580		
22$\bar{4}$	3.355	3.347	m
400	3.286	3.293	w
12$\bar{4}$	3.251	3.246	w
32$\bar{4}$	3.250		
024	2.988	2.983	m
42$\bar{4}$	2.988		
032	2.947	2.937	m
23$\bar{2}$	2.947		
132	2.747	2.739	w
33$\bar{2}$	2.747		
11$\bar{6}$	2.712	2.709	s
51$\bar{6}$	2.712		
420	2.710		

host parameters with those of the corresponding intercalated compound, it is evident that the β angle changes little upon the insertion of sodium whereas all three dimensions increase significantly.

The structure of $Fe_2(MoO_4)_3$ has been determined (14) by single crystal X-ray diffraction and the structure of $Fe_2(WO_4)_3$ has been shown (12) to be analogous by powder X-ray methods. The structure, Fig. 2, is based on Fe^{3+} ions in an octahedral oxygen environment which are linked by sharing all six corners with tetrahedrally coordinated Mo^{6+} or W^{6+}. On the basis of the mechanism of lithium intercalation, insertion of sodium is accompanied by reduction of the Fe^{3+} to Fe^{2+}. This is consistent with the very similar open circuit voltages obtained for both the compounds, Fig. 1. The Na^+ ions diffuse down the open channels, which are very evident in Fig. 2. The location of the sodium ions within this open framework must await future detailed structure determinations.

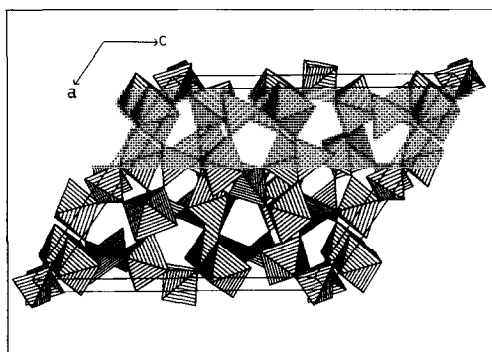The studies of lithium intercalation into

FIG. 2. The structure of ferric molybdate or tungstate generated from the data given in Ref. (14).

ferric tungstate and molybdate also indicate the existence of new phases containing two guest ions per formula unit, $Li_2Fe_2(XO_4)_3$ where $X =$ Mo or W, with two phase regions present at lower lithium concentrations. However, the new lithium phases possess the orthorhombic symmetry of the high temperature polymorph of $Fe_2(MoO_4)_3$, space group *Pbcn* (8), in contrast to the retention of monoclinic symmetry in the case of sodium intercalation. The initial studies of sodium intercalation into $Fe_2(MoO_4)_3$ (10) had suggested the existence of two solid solution ranges, $Na_xFe_2(MoO_4)_3$, $0.30 \leq x < 1.00$ and $1.10 \leq x \leq 1.60$. We can find no evidence for such solid solutions in our work. The reason for this difference is unclear; it may be due to some difference in the materials or in the method of intercalation. On the basis of the potential drop observed on applying a constant current pulse to the electrochemical cells when the cathode composition is within the two phase region, intercalation is slow; this is consistent with the two phase nature of the intercalation process.

Acknowledgments

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