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Ion Exchange in the $Cs_x[Ti_{2-\frac{x}{2}}Mg_{\frac{x}{2}}]O_4$ Structure

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The corrugated layer structure of $Cs_{0.7}[Ti_{1.65}Mg_{0.35}]O_4$ shows a variety of ion-exchange reactions of the Cs^+ ion with both aqueous and molten Li^+, Na^+, K^+, NH_4^+, and H_3O^+ ion-exchange salts. Chemical analysis of the products shows almost complete exchange in most cases, but with the extent of water sorption increasing in the order NH_4^+, $K^+ < Na^+$, $H^+ < Li^+$. Structure analysis of powder X-ray data is in agreement with the analytical findings. The $[Ti_{1.65}Mg_{0.35}]O_4$ framework is retained on exchange; an expansion perpendicular to the corrugated layers depends on the exchange ion and its state of hydration. The exchange times are compatible with the measured ionic conductivities.

I. Introduction

The purpose of this paper is to extend our investigation of ion-exchange reactions in mixed oxides (*1*) and to explore its relation to transport properties. In this paper we investigate exchange phenomena between corrugated layers of the $Cs_x[Ti_{2-\frac{x}{2}}Mg_{\frac{x}{2}}]O_4$ structural type (*2*, *3*) (Fig. 1).

The structure consists of corrugated $[Ti_{2-\frac{x}{2}}Mg_{\frac{x}{2}}]^{x-}$ layers of edge and corner shared octahedra which are stacked so that the large Cs^+ ions occupy eight-coordinate interstices sharing rectangular faces. The Cs^+ layer contains $(1 - x)$ vacant sites, which makes possible extrinsic diffusion for $0 < x < 1$. The fully oxidized, high temperature phase $Cs_{0.7}[Ti_{1.65}Mg_{0.35}]O_4$, which we abbreviate throughout to $Cs_{0.7}M_2O_4$, has been chosen as a good model system for this type of study; it exhibits an intricate series of ion-exchange reactions. Simpler compounds containing the same corrugated sheets, but displaced with respect to the interleaved cations, are γ-FeOOH (*4*), FeOCl (*5*), and β-$NaMnO_2$ (*6*).

II. Preparation and Characterization

$Cs_{0.7}M_2O_4$ was prepared by reacting Cs_2CO_3, MgO, and TiO_2 in the stoichiometric proportions at 1000°C overnight in a platinum crucible. An X-ray diffractogram indicated pure $Cs_{0.7}M_2O_4$ with refined orthorhombic lattice parameters $a = 3.827(2)$ Å, $b = 17.03(1)$ Å, $c = 2.981(3)$ Å, in agreement with published values (*3*). Thermogravimetric analysis, on a Stanton Redcroft TG 770 thermobalance, showed no weight loss to 1000°C which implies negligible sorption of water despite the presence of large, vacant interlayer sites.

Aqueous solutions and molten salts were used as the source of exchanging ions. Separations were achieved by centrifuging and

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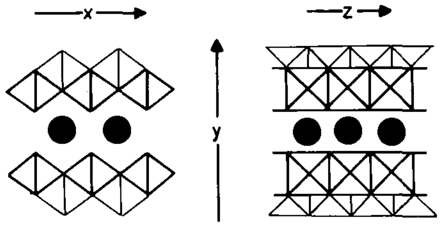

FIG. 1. Idealized $Cs_x[Ti_{2-\frac{x}{2}}Mg_{\frac{x}{2}}]O_4$ structure; filled circles, Cs^+.

TABLE I

X-RAY POWDER DATA FOR Li^+-EXCHANGED $Cs_{0.7}M_2O_4$

h k l	d_{obs}	d_{calc}	I_{obs}
0 2 0	8.715	8.714	m
0 4 0	4.353	4.357	m
1 3 0	3.187	3.176	vs
0 1 1	2.950	2.957	w
0 6 0	2.903	2.905	mw
0 3 1	2.660	2.666	w
1 5 0	2.571	2.566	vvw
1 0 1	2.353	2.353	vvw
1 2 1	2.271	2.272	s
1 4 1	2.080	2.071	w
0 7 1	1.914	1.916	w
2 0 0	1.895	1.896	m
2 2 0	1.852	1.853	vw
1 6 1	1.827	1.828	vw
0 10 0	1.743	1.743	w
1 9 0	1.728	1.725	w
1 8 1	1.599	1.599	m
2 1 1	1.593	1.596	mw
2 3 1	1.544	1.545	w
0 0 2	1.497	1.500	w
0 2 2	1.475	1.479	w
2 5 1	1.457	1.456	mw

washing. The degree of exchange was followed by determining the quantity of Cs released into solution with the photometric method of Huey and Hargis (7). The weight change was also used as a check on the extent of exchange; in certain cases characteristic X-ray emission analysis was utilized. The latter was achieved with a Link System Ltd. X-ray analyzer on a JEOL Temscan 100CX electron microscope with the sample and calibrants supported on a copper grid. Thermogravimetric (TGA) and differential thermal analysis (DTA) were also used to study the temperature stability of the products; C/H/N analysis was performed on a Hewlett–Packard 185 analyzer.

1. Li^+ ion exchange. Reaction of $Cs_{0.7}M_2O_4$ with molten $LiNO_3$ at ≈300°C gave a product whose X-ray pattern could not be identified. This suggested the decomposition of a metastable ion-exchange product. Treatment of $Cs_{0.7}M_2O_4$ with excess, well-stirred, aqueous 3.5 *M* $LiNO_3$ at 80°C for 4 days resulted in 47 (±0.5)% of the Cs being replaced by Li, according to Cs analysis on duplicate runs. TGA of the product showed one sharp loss of weight at 100°C and no further loss to 1000°C. The analyses were consistent with the reaction scheme

$$0.33Li^+ + yH_2O + Cs_{0.7}M_2O_4 = Li_{0.33}Cs_{0.37}M_2O_4 \cdot yH_2O + 0.33Cs^+$$

with $y \approx 0.72$. The X-ray diffraction pattern ($CuK\alpha$) of the ion-exchanged product (Table I) confirmed retention of structure since it could be indexed on a $Cs_{0.7}M_2O_4$ cell with $a = 3.792(2)$, $b = 17.43(1)$, $c = 3.001(2)$ Å. The cell expansion is compatible with the TGA evidence for water sorption.

2. Na^+ ion exchange. Exchange was carried out under two sets of conditions: molten $NaNO_3$ and aqueous NaCl solution. For the molten salt exchanges, approximately 120 mg of $Cs_{0.7}M_2O_4$ was treated with 10 g of $NaNO_3$ (Analar) at 380°C for 60 hr in an alumina crucible. The solid matter was separated by washing, centrifuging, and drying at 70°C. Analysis of the caesium collected in the washings showed that complete exchange had occurred.

For the aqueous exchange, about 120 mg of $Cs_{0.7}M_2O_4$ was treated with 250 ml of well stirred 4 *M* NaCl for different time periods and temperatures. There was 30% ex-

TABLE II

X-RAY POWDER DATA FOR HYDROUS AND ANHYDROUS Na^+-EXCHANGED $Cs_{0.7}M_2O_4$

	A. Hydrous			B. Anhydrous		
h k l	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}
0 2 0	8.934	8.917	vs	8.080	8.070	vs
0 4 0	4.484	4.458	w			
1 1 0	3.708	3.695	mw	3.666	3.672	m
1 3 0	3.198	3.188	vs	3.089	3.088	ms
0 1 1	2.978	2.964	mw			
0 6 0				2.685	2.690	w
0 3 1	2.683	2.682	m	2.616	2.613	mw
1 5 0	2.592	2.593	vw			
1 0 1	2.356	2.352	vw			
0 5 1	2.298	2.298	ms	2.196	2.193	mw
1 2 1	2.276	2.274	w	2.262	2.250	mw
0 7 1	1.945	1.943	m			
2 0 0	1.890	1.888	m	1.885	1.885	ms
2 2 0	1.847	1.847	m	1.834	1.836	m
1 6 1				1.765	1.767	vvw
0 10 0	1.783	1.783	w			
1 8 1	1.618	1.618	m	1.529	1.529	m
2 1 1	1.593	1.592	vw			
2 3 1	1.544	1.544	w			
0 0 2	1.503	1.503	w	1.494	1.495	m
2 5 1	1.484	1.482	mw			
0 2 2	1.459	1.459	w			
1 10 1	1.421	1.421	vw			
1 1 2	1.393	1.392	vw			
1 3 2	1.356	1.359	w			

change after 15 hr at 40°C and 74% exchange after 15 hr at 60°C; complete exchange took place after 4 days at 80°C. The X-ray data (Table IIA) for the fully exchanged material again showed large changes in the intensities and lattice parameters from the unexchanged material. TGA studies showed that the products from both molten salt and aqueous exchange were hydrated. One sharp weight loss occurred at 100°C, with no further weight loss to 1000°C; a composition of $Na_{0.7}M_2O_4 \cdot 0.7H_2O$ was deduced with lattice parameters $a = 3.776(2)$, $b = 17.83(1)$, $c = 3.005(1)$ Å.

A Debye–Scherrer photograph was taken in a Lindemann tube immediately after the weight loss at 100°C was complete in order to determine whether the original structure is retained on the loss of water. The resultant pattern could be indexed on an orthorhombic cell similar to the hydrated form, but with a much reduced b parameter (perpendicular to the MO_2 layers) (Table IIB). Refined lattice parameters for the dehydrated phase were $a = 3.771(3)$, $b = 16.14(2)$, $c = 2.990(2)$ Å.

Partial exchange occurs at lower exchange medium: $Cs_{0.7}M_2O_4$ ratios with a corresponding reduction in water content and *b* lattice parameter. A typical composition, deduced from X-ray emission and TGA analysis, was $Na_{0.59}Cs_{0.11}M_2O_4 \cdot (H_2O)_{0.4}$. A Cs elemental map showed an even distribution of residual Cs atoms, in keeping with an equilibrated product.

A dried sample of the Na^+-exchanged material was observed to rehydrate rapidly in air, which explains the origin of water in the molten salt exchange product. A sample heated to 1000°C gave a completely different X-ray pattern, implying that the anhydrous exchange product is metastable. The pattern of the stable dehydrated phase could be mainly indexed on the basis of a Na_xTiO_2 type cell (*8*). Refined lattice parameters of $a = 12.36(2)$, $b = 3.807(1)$, $c = 6.467(3)$ Å, $\beta = 106.92(2)°$ were obtained, which may be compared with the known phase $Na_{0.5}[Sc_{0.5}Ti_{1.5}]O_4$ ($a = 12.442$, $b = 3.845$, $c = 6.578$ Å, $\beta = 107.49°$) (*8*). X-Ray intensity data were also collected and analyzed for $Na_{0.7}M_2O_4 \cdot (H_2O)_{0.7}$ and are discussed in Section III.

3. K^+ ion exchange. A 400-mg sample of $Cs_{0.7}M_2O_4$ was treated with ≈4 g of molten KNO_3 for 12 hr; the weight change was compatible with almost complete exchange of K^+ for Cs^+ ions. Since K^+ interferes with the photometric method of Cs^+ analysis, X-ray emission analysis for Cs^+ was performed on the ion-exchanged samples. This analysis, together with TGA data, implied a composition $K_{0.67}Cs_{0.03}M_2O_4 \cdot nH_2O$.

TABLE III

X-RAY POWDER DATA FOR HYDROUS AND ANHYDROUS K^+-EXCHANGED $Cs_{0.7}M_2O_4$

	A. Hydrous			B. Anhydrous		
h k l	d_{obs}	d_{calc}	I_{obs}	d_{obs}	d_{calc}	I_{obs}
0 2 0	8.672	8.693	m	7.918	7.899	s
1 1 0	3.696	3.701	m	3.696	3.693	w
1 3 0	3.164	3.171	m	3.082	3.081	s
0 1 1				2.784	2.784	w
0 6 0				2.644	2.633	m
0 3 1	2.652	2.654	mw			
1 0 1	2.266	2.265	w	2.269	2.269	m
0 5 1						
0 8 0				1.973	1.975	vw
2 0 0	1.894	1.894	m	1.899	1.899	ms
2 2 0	1.850	1.850	w			
0 9 1	1.627	1.621	vw			
2 5 0				1.626	1.628	m
2 6 0				1.543	1.540	w
2 2 1					1.546	
2 3 1	1.542	1.541	vw			
0 0 2	1.488	1.493	m			
1 8 1				1.485	1.490	m

The X-ray patterns of the K^+-exchanged material were indexable on the basis of two orthorhombic cells, each similar to $Cs_{0.7}M_2O_4$ except with different lattice constants (Table III). Depending on the drying conditions, one or both of the orthorhombic phases would be present. We attribute the phase with smaller *b* lattice constant (a = 3.798(2), b = 15.80(1), c = 2.829(3) Å) to an essentially dehydrated $K_{0.67}Cs_{0.03}M_2O_4$, and the phase with larger constants (a = 3.787(1), b = 17.38(2), c = 2.985(3) Å) to a fully hydrated product. The hydration equilibrium was not studied in detail, but TGA confirmed the presence of H_2O (loss at 100°C) in one of the mixed phase samples; the weight loss corresponded to an overall composition $K_{0.67}Cs_{0.03}M_2O_4 \cdot 0.4H_2O$.

4. H_3O^+ ion exchange. Reid *et al.* (*3*) speculated on the possibility that compounds might be prepared in which both H^+ and Cs^+ ions were present between M_2O_4 corrugated layers. No results along these lines were subsequently published.

A preliminary experiment showed that 25% HCl at 60°C dissolved $Cs_{0.7}M_2O_4$ rapidly. More dilute acids and a lower temperature were necessary for ion exchange without complete dissolution. With 10% HCl at 20°C overnight, a 40% dissolution occurred. Cs^+ analysis of the washings indicated that 92% of the remaining solid had been exchanged. X-Ray diffraction showed that large changes in *d* spacings and intensities had taken place, consistent with essentially complete exchange (Table IV). These results substantiate the reaction

$$Cs_{0.7}M_2O_4 + 0.65H^+(aq) + yH_2O$$
$$= Cs_{0.05}H_{0.65}M_2O_4 \cdot yH_2O + 0.65Cs^+(aq)$$

TGA on the acid exchanged compound showed weight loss in two overlapping steps around 100°C; and DTA on the same material showed that two peaks were present, indicating that two dehydration processes were occurring. It was possible to extract the weight loss for the two processes by taking the TGA weight loss after the first DTA peak was complete. A reasonable reaction scheme, substantiated by C/H/N analysis, is

$$H_{0.65}Cs_{0.05}M_2O_4(H_2O)_{0.7}$$
$$\xlongequal{20\text{–}175^\circ C} H_{0.65}Cs_{0.05}M_2O_4 + 0.7H_2O$$
$$\xlongequal{175\text{–}600^\circ C} 0.325H_2O + \text{oxides}$$

TABLE IV

X-RAY POWDER DATA FOR ACID-EXCHANGED $Cs_{0.7}M_2O_4$

h k l	d_{obs}	d_{calc}	I_{obs}
0 2 0	8.630	8.806	s
1 1 0	3.723	3.700	vw
1 3 0	3.184	3.181	s
0 1 1	2.940	2.939	vw
0 3 1	2.659	2.657	vw
0 5 1	2.273	2.275	s
2 0 0	1.892	1.892	s
2 2 0	1.850	1.850	vw
1 8 1	1.604	1.604	vw
0 0 2	1.492	1.490	vw

Note. a = 3.784(1) Å, b = 17.61(1) Å, c = 2.980(1) Å.

A sample of partially dehydrated material at 170°C was allowed to cool in a sealed Lindemann tube and analyzed by X-ray diffraction. The resulting pattern had very broad lines, but a diminution in the *b* axis had occurred. The (020) peak had changed from $d = 8.35$ to 6.55 Å, corresponding to a change in *b* from 16.7 to 13.1 Å; this value of *b* is similar to that for γ-AlOOH (12.23 Å), which suggests that the layer structure may be maintained without the presence of interlayer water molecules.

5. NH_4^+ ion exchange. Exchange was carried out in two ways: by treating $Cs_{0.7}M_2O_4$ with 1 *M* NH_4Cl solution and with a concentrated NH_3 solution. Samples were treated twice, each treatment being of 48 hr duration at 80°C. As NH_4^+ also interferes with Cs^+ analysis, the Cs^+ lost was not directly obtainable.

H/C/N analysis showed that both NH_4^+ and H_3O^+ ions were incorporated with significantly more NH_4^+ using NH_3(aq) than with NH_4Cl(aq). This is in accordance with the relative concentrations of NH_4^+ and H_3O^+ in the two solutions. The analytical data suggested a formula $(NH_4)_{0.32}(H)_{0.38}M_2O_4 \cdot 0.68H_2O$ for the NH_3(aq) exchange assuming an essentially complete reaction (as demonstrated by the X-ray analysis in Section III). This formula is compatible with the overall observed weight loss during exchange of 28 (±1)% (calculated = 30%) and with the lattice expansion indicated by the X-ray data shown in Table V. TGA on the sample showed two sharp peaks at 100 and 400°C. The weight losses were compatible with the reactions

$$(NH_4)_{0.32}(H)_{0.38}M_2O_4 \cdot 0.68H_2O \overset{100^\circ C}{=\!=} (NH_4)_{0.32}(H)_{0.38}M_2O_4 \overset{400^\circ C}{=\!=} \text{oxides}$$

TABLE V

X-RAY POWDER DATE FOR NH_4^+-EXCHANGED $Cs_{0.7}M_2O_4$

h k l	d_{obs}	d_{calc}
0 2 0	8.723	8.980
0 4 0	4.491	4.490
1 1 0	3.708	3.704
1 3 0	3.202	3.199
0 1 1	2.958	2.954
0 3 1	2.679	2.678
1 5 0	2.603	2.605
1 0 1	2.349	2.349
0 5 1	2.299	2.300
1 2 1	2.273	2.272
1 4 1	2.080	2.081
0 7 1	1.948	1.948
2 0 0	1.893	1.893
2 2 0	1.849	1.852
1 6 1		1.848
0 10 0	1.792	1.796
1 8 1	1.622	1.623
2 3 1	1.546	1.546
1 11 0	1.497	1.499
0 0 2		1.497
0 12 0		1.497
0 2 2	1.478	1.477
2 5 1	1.462	1.461
0 11 1	1.435	1.434
1 10 1	1.426	1.427
1 1 2	1.388	1.388
2 7 1	1.357	1.358
1 3 2		1.356
2 10 0	1.299	1.303
1 5 2		1.298

Note. $a = 3.785(1)$ Å, $b = 17.96(1)$ Å, $c = 2.995(1)$ Å.

III. Structure Refinements

X-Ray structural work was performed to attempt to confirm the degree of exchange implied by chemical analysis and to verify the existence of sorbed water in the structure. Single crystal material is not readily synthesized as $Cs_{0.7}M_2O_4$ decomposes below its melting point.

X-Ray powder intensities were obtained on a Philips PW 1051 diffractometer with a focussing graphite monochromator. A slow scan speed was used, and intensities were determined by cutting and weighing peaks. This procedure introduces a negligible error compared with the inherent systematic errors. Atom parameters were refined by a full-matrix intensity least squares program written by one of us (*9*), and a $\sqrt{I}$ weighting scheme was used. Final atom positions were compatible with the low intensity of the peaks omitted from the refinement.

Reid *et al.* (*3*) refined the crystal structure of $Cs_{0.7}M_2O_4$ from powder diffractometer data (Fig. 2). The corrugated M_2O_4 layers contain *M* atoms coordinated to two O(1) atoms on the outside of the layers and four O(2) atoms in the middle of the layers. The large Cs^+ ions are coordinated to eight O(1) atoms in a rectangular prism, four at 3.40 Å, and four at 3.12 Å due to off-center displacement of the Cs^+ ions. These prism sites are randomly occupied by 0.7 Cs^+ ions per site. Although the *Imm*2 space group of $Cs_{0.7}M_2O_4$ is noncentric, only the Cs atoms do not obey centrosymmetry. If the Cs atoms were centric, then the space group would be *Immm*. The analyses were performed as follows.

1. $Na_{0.7}(H_2O)_{0.7}M_2O_4$. It was assumed that the M_2O_4 positions of $Cs_{0.7}M_2O_4$ provided a good starting model. The large increase in the *b* parameter on exchange suggests the incorporation of both Na and H_2O between the layers. In order to keep the number of parameters at a reasonable level compared to the number of observations, it was assumed that Na and H_2O were randomly distributed over the same set of positions and could be represented by identical scattering factors. Isotropic temperature factors were fixed at 1.0 for all atoms, and neutral atomic scattering factors were used.

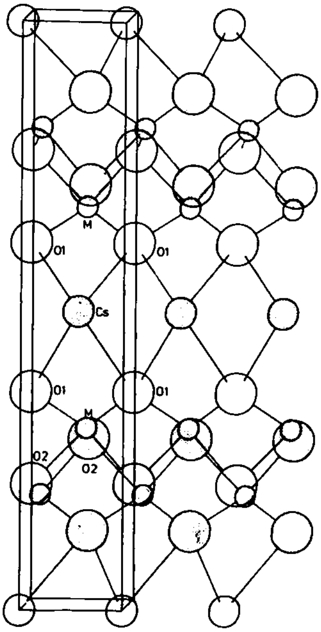

FIG. 2. (100) section of $Cs_{0.7}[Ti_{1.65}Mg_{0.35}]O_4$; open circles $x = 0$ and 1; stippled circles, $x = \frac{1}{2}$.

Refinements in the space group *Immm*, even with statistical displacements of Na/H_2O on the special position (0, 0, 0), gave a minimum R_I value of 28%. However, in the special position (0, *y*, 0) of space group *Imm*2, with $y = 0.051$, a satisfactory R_I factor of 14.6% was obtained. This corresponds to a realistic $Na^+{-}OH_2$ unit in the Cs^+ interlayer cavity with the Na–O axis parallel to the *b* axis (Fig. 3). Observed and calculated intensities are given in Table VI and refined atomic parameters in Table VIIB. An important aspect of the analysis is that the data are very sensitive to the scattering power of the interlayer atoms. Incorporation of residual Cs^+ ions in the refinements leads to a dramatic increase in the R_I value.

As in the case of $Cs_{0.7}M_2O_4$, the M_2O_4 framework remains centric within experimental error. The *M*–O bond distances are little changed with values ranging from 1.97–2.06 Å. The entire lengthening of the *b* axis is therefore caused by the replacement of Cs by Na/H_2O in the interlayer interstices. The O(1)–Na/H_2O distance of 2.2 Å

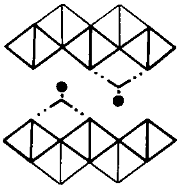

FIG. 3. Proposed structure of $Na_{0.7}[Ti_{1.65}Mg_{0.35}]O_4 \cdot 0.7H_2O$; filled circles, Na^+; angled units, H_2O.

TABLE VI

OBSERVED AND CALCULATED INTENSITIES FOR $Na_{0.7}M_2O_4 \cdot 0.7H_2O$

h k l	I_{obs}	I_{calc}
0 2 0	100	96
0 4 0	9	7
1 1 0	18	0
1 3 0	80	82
0 1 1 0 6 0	16	18
0 3 1	36	34
1 5 0	4	4
1 0 1	9	11
0 5 1	49	48
1 2 1	10	9
1 4 1	1	4
0 7 1	19	9
2 0 0	22	26
2 2 0 1 6 1	15	14
0 10 0	7	1
1 8 1	28	27
2 6 0 2 1 1	3	3
2 3 1	11	9
0 0 2	7	4
0 12 0 0 2 2	8	10
2 5 1	15	16
0 4 2 1 10 1	4	3
1 1 2	3	5
1 3 2 2 7 1	12	7

is reasonable and is achieved by the departure from *Immm* symmetry. The calculated Na–O bond length of 1.8 Å for the Na–OH_2 unit is satisfactory considering the approximations made in the analysis. The precise arrangement of Na atoms and H_2O molecules is too complex to determine with powder X-ray data.

2. *$(NH_4)_{0.32}(H)_{0.38}M_2O_4 \cdot 0.68H_2O$.* In this case it is reasonable to assume that each H^+ ion is associated with water either as H_3O^+ or as an M–OH–OH_2 unit and that the remaining $0.3H_2O$ occupy interlayer sites. The corresponding structural formula is $(NH_4)_{0.32}(H_3O)_{0.38}(H_2O)_{0.3}M_2O_4$. The interlayer X-ray scattering is dominated by O and N, and a neutral atom scattering factor for N was used for both light atoms. The interlayer O and N atoms were randomized over the same set of positions. A satisfactory refinement was achieved with R_I = 18.3% in *Immm* with no significant improvement in *Imm*2. This agreement could only be achieved by increasing slightly the *A* atom scattering factor compatible with the present of ≈5% of unexchanged Cs. Observed and calculated intensities and refined atom parameters are given in Tables VIII and VIIC, respectively.

As before, the MO_2 layer has similar dimensions to those found in $Cs_{0.7}M_2O_4$ with M–O distances ranging from 1.88–1.97 Å. The $Na^+/H_3O^+/H_2O$ interlayer arrangement is necessarily imprecise although the N/O . . . O(1) bond length of 3.2 Å is reasonable.

TABLE VII

REFINED ATOMIC PARAMETERS

Atom	Equi-point	*x*	*y*	*z*
A. $Cs_{0.7}M_2O_4$ (from (*3*))				
Space group *Imm*2				
0.7Cs	2(*a*)	0	0	0
M	4(*d*)	0	0.312(4)[a]	0.64(3)
O(1)	4(*d*)	0	0.373(9)	0.10(11)
O(2)	4(*d*)	0	0.216(10)	0.11(12)
B. $Na_{0.7}M_2O_4 \cdot 0.7H_2O$				
Space Group *Imm*2				
0.7Na/O	4(*d*)	0	0.051(1)	0
M	4(*d*)	0	0.305(1)	0.83(2)
O(1)	4(*d*)	0	0.388(1)	0.352(1)
O(2)	4(*d*)	0	0.226(1)	0.32(6)
C. $(NH_4)_{0.32}(H)_{0.38}M_2O_4 \cdot 0.68H_2O$				
Space group *Immm*				
1.12(16)N/O	2(*a*)	0	0	0
M	4(*h*)	0	0.324(3)	0.5
O(1)	4(*g*)	0	0.387(7)	0
O(2)	4(*g*)	0	0.207(7)	0

[a] Estimated standard deviations in parentheses.

TABLE VIII

OBSERVED AND CALCULATED INTENSITIES FOR $(NH_4)_{0.32}(H)_{0.38}M_2O_4 \cdot 0.68H_2O$

h k l	I_{obs}	I_{calc}
0 2 0	100	101
0 4 0	5	3
1 1 0	10	11
1 3 0	41	40
0 1 1	7	5
0 3 1	15	16
1 5 0	1	1
1 0 1	6	0
0 5 1	28	32
1 2 1	3	6
1 4 1	1	1
0 7 1	15	0
2 0 0	11	11
2 2 0 1 6 1	13	12
0 10 0	3	1
1 8 1	12	8
2 3 1	4	5
1 11 0 0 0 2 0 12 0	5	6
0 2 2	3	1
2 5 1	11	10
0 11 1	2	2
1 10 1	4	1
1 1 2	1	1
2 7 1 1 3 2	9	4
2 10 0 1 5 2	4	1

The relative X-ray intensities of the ion-exchanged products are seen to vary markedly from compound to compound, but the refinements indicate that major structural alterations only occur to the interlayer region. Satisfactory agreement is achieved only if models are used that correspond directly with the ion-exchange products suggested by chemical analysis.

IV. A.C. Conductivity Measurements

A.C. conductivity measurements were made on $Cs_{0.7}M_2O_4$ and its acid exchanged analog in order to determine the ionic conductivity of these materials.

A half-inch pellet of $Cs_{0.7}M_2O_4$ was fired at 1000°C for 3 days and sintered to 87% theoretical density. Evaporated gold electrodes were applied to the pellet, and A.C. measurements were made under a flowing nitrogen atmosphere. An 83% dense, 5-mm pellet of H_3O^+-exchanged $Cs_{0.7}M_2O_4$ was pressed at room temperature. Blocking indium amalgam electrodes were applied to the pellet, and room temperature measurements made.

Even at 378°C, a susceptance/conductance (B/G) plot of $Cs_{0.7}M_2O_4$ showed only a spur to the *G* axis. Similar behavior was found for the H_3O^+-exchanged analog at room temperature. It is impossible to determine the conductivity accurately in such cases; an upper limit of $\approx 10^{-8}$ ohm^{-1} cm^{-1} was estimated.

V. Discussion

The results clearly indicate that ion-exchange reactions are possible in the $Cs_{0.7}M_2O_4$ structure with both molten salt and aqueous exchangers. In this structural type, a substantial concentration of mobile cations in a partially filled set of equivalent sites are present; however, the measured ionic conductivities, and therefore the ionic diffusion coefficients, are not high. This is compatible with the bottleneck sizes computed from X-ray work. For example, Cs^+ ions, in $Cs_{0.7}M_2O_4$, must pass through an oxygen ion bounded rectangle with a center to corner distance of 2.89 Å (ideally this should be $\geq$3.10 Å). The observed exchange times are also in keeping with the transport measurements, as detailed elsewhere (*1*).

In general the exchange times were sufficient to establish an exchange equilibrium. However, the products were metastable; gross structural transformations were observed to occur at sufficiently high temperatures. Once again, the use of ion-exchange reactions to prepare at low temperatures new inorganic solids has been demonstrated.

Chemical analysis of the exchanged products revealed a much greater complexity than might have been anticipated. Incomplete exchange (e.g., with Li^+ and H_3O^+ exchange), substantial water sorption (e.g., with aqueous and molten Li^+, Na^+, and H_3O^+ exchange), and even exchange of unexpected ions (e.g., H_3O^+ ions in NH_4^+ exchange) was found. Lattice parameter and structural refinement from X-ray powder patterns provides a convincing corroborative technique for detecting concurrent solvent sorption.

The sorption was found to increase in the order $Cs^+ < NH_4^+$, $K^+ < Na^+$, $H^+ < Li^+$. This sequence, and the magnitude of the sorption effect, is dictated by the driving thermodynamic enthalpy factors of ionic hydration and ionic dilution. The opposing factors are the corresponding entropy terms and, predominantly, the free energy of expansion of the lattice. A high degree of sorption is anticipated for substantial concentrations of small interlayer cations in an easily expandable material (too large a concentration may clamp the structural fragments too firmly). The phenomena observed with the layered materials studied here find an exact parallel with the behavior of conventional ion exchangers and related materials (*10, 11*).

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