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New Metal Oxides of the Family $A_m[(TO)_q]$: $A\mathrm{LiMn_3O_4}$ and $A\mathrm{LiZn_3O_4}$ (A = K, Rb)*

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The new compounds $\mathrm{KLiMn_3O_4}$ (**I**), $\mathrm{RbLiMn_3O_4}$ (**II**), $\mathrm{KLiZn_3O_4}$ (**III**) and $\mathrm{RbLiZn_3O_4}$ (**IV**) have been prepared by solid state reaction of $A_2\mathrm{O}$ (A = K, Rb), $\mathrm{Li_2O}$, and $M\mathrm{O}$ (M = Mn, Zn). The isomorphous compounds are tetragonal, space group $I4/m$, $Z = 2$, with lattice constants a = 838.32(4) pm, c = 341.88(3) pm for **I**; a = 840.66(8) pm, c = 344.85(4) pm for **II**; a = 819.27(9) pm, c = 334.20(7) pm for **III**, a = 823.62(9) pm, c = 339.73(7) pm for **IV**, as determined from Guinier X-ray powder patterns. The orange-colored manganates and colorless zincates are sensitive to moisture. The crystal structures of **II** and **III** have been determined by single-crystal X-ray techniques and refined to $R = 0.09$ (**II**) and $R = 0.06$ (**III**). The structure is built up from chains of face-shared cubes, $^1_\infty[A\mathrm{O}_{8/2}]$ (A = K, Rb), running parallel to the c axis. These are connected by $\mathrm{Li^+}$ and M^{2+} (M = Mn, Zn), statistically distributed on tetrahedral positions between the chains. © 1988 Academic Press, Inc.

Introduction

The zeolites as a subgroup of metal oxides with the formula $A_m[(T\mathrm{O}_2)_n]$ (T = tetrahedrally coordinated metal or Si, A = a "big" cation) are well known as stuffed derivatives of possible modifications or forms of $\mathrm{SiO_2}$. With $\mathrm{KNaZnO_2} = \mathrm{K[(NaZn)O_2]}$ ($m = 1$, $q = 2$) (*1*) as well as with KNaO ($m = 1$, $q = 1$) (*2*), we noticed the existence of a new series of metal oxides, the general formula being $A_m[(T\mathrm{O})_q]$. In addition, with $\mathrm{Rb_2Li_2SiO_4}$ and $\mathrm{Rb_2Li_2GeO_4}$ (*3*) we found two representatives of another series with the general formula $A_m[(T\mathrm{O}_2)_n(T\mathrm{O})_q]$ formally connecting both series mentioned above.

Table I summarizes further examples. Following this point of view, we attempted to prepare other examples of the type $A_m[(T\mathrm{O})_q]$ with, e.g., $m = 1$ and $q \geq 2$. We wanted to find structural resemblances between corresponding oxides of manganese and zinc.

Experimental

Starting materials. $\mathrm{Li_2O}$ was prepared by dehydration of LiOH (*11*), $\mathrm{K_2O}$, and $\mathrm{Rb_2O}$ by oxidation of the metals (*12*). Gray-greenish, very "active" MnO was obtained by thermal decomposition (vacuum) of $\mathrm{MnC_2O_4 \cdot 2H_2O}$. ZnO was purchased from Merck and dried at 350°C (5 hr, vacuum).

Preparation. Appropriate quantities of the binary oxides (with a 5% by weight excess of alkali metal oxides) were ground

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TABLE I

OXIDES OF THE GENERAL FORMULA $A_m[(TO)_q]$

$m = 1$	$q = 1$	K[NaO] (*2*)
$m = 1$	$q = 2$	K[$LiZnO_2$] (*4*); K[$LiMnO_2$] (*5*) Li_2MnO_2 = Mn[Li_2O_2] (*6*)
$m = 1$	$q = 3$	Rb[$LiZn_2O_3$] (*7*)
$m = 1$	$q = 4$	K[Li_3MO_4] (M = Si,Ge,Ti) (*8*)
$m = 2$	$q = 4$	K_2[Na_3TlO_4] (*9*)
$m = 2$	$q = 5$	Rb_2[$Li_2Cd_3O_5$] (*10*)

thoroughly and transferred to nickel or silver tubes, which after closing werre sealed under argon in quartz tubes. For $KLiZn_3O_4$ and $RbLiMn_3O_4$, the mixtures were heated slowly to 300°C and maintained at this temperature for 18 hr, and then the temperature was gradually increased to 940 or 640°C, respectively. After approximately 3 weeks of heating, single crystals were obtained.

Powder samples of $KLiZn_3O_4$, $RbLiZn_3O_4$, $KLiMn_3O_4$, and $RbLiMn_3O_4$ were prepared at 400–500°C (5 days). All powder samples as well as the single crystals are sensitive to moisture. The decomposition products of the colorless zincates are chalky powders. In the case of the orange-colored manganates we observed brown decomposition products.

For *crystal structure determination*, single crystals of $KLiZn_3O_4$ and $RbLiMn_3O_4$ were selected under dry argon and sealed in glass capillaries of 0.3-mm diameter. Preliminary Weissenberg and precession photographs suggested that the Laue group was $4/m$. Systematic absences were observed for *hkl* with $h + k + l \neq 2n$. The data were collected on a Philips PW1100 automated diffractometer, for details cf. Table II. The crystal structures were solved by direct methods. Least-squares refinement using the Shel-X program (*13*) led to R values of 0.06 (for 260 unique *hkl*) and 0.09 (261 *hkl*) for $KLiZn_3O_4$ and $RbLiMn_3O_4$, respectively. Final atomic

TABLE II

CRYSTAL AND REFINEMENT DATA FOR $KLiZn_3O_4$ AND $RbLiMn_3O_4$

	Formula	
	$KLiZn_3O_4$	$RbLiMn_3O_4$
Lattice constants	cf. Table IV	
Multiplicity	$Z = 2$	
Volume (pm^3)	224.3×10^6	243.7×10^6
Calculated density	4.533	4.376
Crystal color	Colorless	Orange
Crystal shape	Square prismatic	Needle-like
Radiation	Graphite monochromatized Ag$K\alpha$ (λ = 71.07 pm)	
Linear absorption coefficient (cm^{-1})	84.36	88.67
Data collection technique (Philips PW1100 diffractometer)	$\omega - 2\theta$ scan	ω scan
Scan width	2.1°	1.5°
Scan speed	0.07°/sec	0.05°/sec
Recorded reflections within a $3° \leqq \theta \leqq 26°$ half sphere ($\pm h + k \pm l$)	947	1042
Unique reflections	260	$261[\lvert F_o \rvert > 2\sigma(F_o)]$
R merging factor	0.06	0.04
Weighting scheme	$w = 1.032/(\sigma^2(F_o) + 0.007\lvert F_o \rvert^2)$	$w = 1.548/(\sigma^2(F_o) + 0.0003\lvert F_o \rvert^2)$
Residual values	$R = 0.061$, $R_w = 0.069$	$R = 0.090$, $R_w = 0.071$

TABLE III

POSITIONAL AND "ANISOTROPIC" THERMAL ($pm^2 \times 10^{-4}$)[a] PARAMETERS FOR $RbLiMn_3O_4$ AND $KLiZn_3O_4$

	Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	$U_{13} = U_{23}$
$RbLiMn_3O_4$	Rb	2*a*	0	0	0	0.0256(8)	0.0256(8)	0.0255(11)	0	0
	M^b	8*h*	0.6327(2)	0.8183(2)	0	0.0087(8)	0.0095(8)	0.0096(8)	−0.0015(5)	0
	0	8*h*	0.3991(7)	0.7663(8)	0	0.006(2)	0.013(3)	0.008(2)	−0.003(2)	0
$KLiZn_3O_4$	K	2*a*	0	0	0	0.0133(7)	0.0133(7)	0.0109(11)	0	0
	M^c	8*h*	0.6330(1)	0.8170(1)	0	0.0069(5)	0.0128(5)	0.0062(6)	−0.0018(3)	0
	0	8*h*	0.4018(5)	0.7700(6)	0	0.004(2)	0.015(2)	0.007(2)	−0.001(1)	0

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$.

[b] Site statistically occupied by 2 Li^+ and 6 Mn^{2+}. Refinement (only Mn^{2+} considered) yielded the site occupation factor $k(M)$ = 0.77(1) (expected value 0.759).

[c] Site statistically occupied by 2 Li^+ and 6 Zn^{2+}. Refinement (only Zn^{2+} considered) yielded the site occupation factor $k(M)$ = 0.75(1) (expected value 0.759).

parameters based on the centrosymmetric space group *I*4/*m* are listed in Table III.

The refinement showed that in both oxides 2 Li^+ and 6 Zn^{2+} (Mn^{2+}) are statistically distributed on an eightfold position (denoted *M*). Refinement of the site occupancy factors $k(M)$ yielded site occupancies, which are in good agreement to the expected values (Table III).

The powder diffraction patterns of $RbLiZn_3O_4$ and $KLiMn_3O_4$ indicate that these oxides are isostructural with their respective K or Rb analogs. Table IV gives the lattice constants calculated from powder data (Guinier–Simon photographs (*14*), Cu*Kα*).

Results

$KLiZn_3O_4$ and $RbLiMn_3O_4$ are isostructural. Since Li^+, Zn^{2+}, and Mn^{2+} are tetrahedrally coordinated and K^+ and Rb^+ are 8-coordinated, these oxides are members of the $A_m[TO)_q]$ family, according to, e.g., $K[\{(Li_{1/4}, Zn_{3/4})O\}_4]$. The coordination polyhedron (*CP*) around O^{2-} is a distorted octahedron (4 *M* plus 2 *A* (*A* = K, Rb) with *A* in *cis* arrangement), see Fig. 3a). Details of the *CP* are presented in Figs. 1a–3a. Important interionic distances and the "motifs of mutual adjunction (*15*) are given in Table V.

$KLiZn_3O_4$ ($RbLiMn_3O_4$) contains linear chains of face-shared slightly distorted cubes KO_8 (RbO_8). These chains are arranged as shown in Fig. 4. This arrangement shows that Li^+ and Zn^{2+} (Mn^{2+}) are statistically distributed on tetrahedral vacancies between the $AO_{8/2}$ chains. Connection of the *CP* can be obtained from their Schlegel diagrams (*15*) (Figs. 1b–3b).

The Madelung Part of Lattice Energy (MAPLE (*16*))

In Table VI the MAPLE values of the binary constituents of $RbLiMn_3O_4$ and $KLiZn_3O_4$ are compared with (a) the results of the average-charge calculations ($M^{1.75+}$) and (b) the mean MAPLE values for ordered distribution of Li^+ and Mn^{2+}

TABLE IV

LATTICE CONSTANTS OF QUATERNARY OXIDES (DERIVED FROM GUINIER PHOTOGRAPHS, Cu*Kα*: λ = 154.18 pm)

Formula	*a* (pm)	*c* (pm)
$KLiZn_3O_4$	819.27(9)	334.20(7)
$RbLiZn_3O_4$	823.62(9)	339.73(7)
$KLiMn_3O_4$	838.32(4)	341.88(3)
$RbLiMn_3O_4$	840.66(8)	344.85(4)

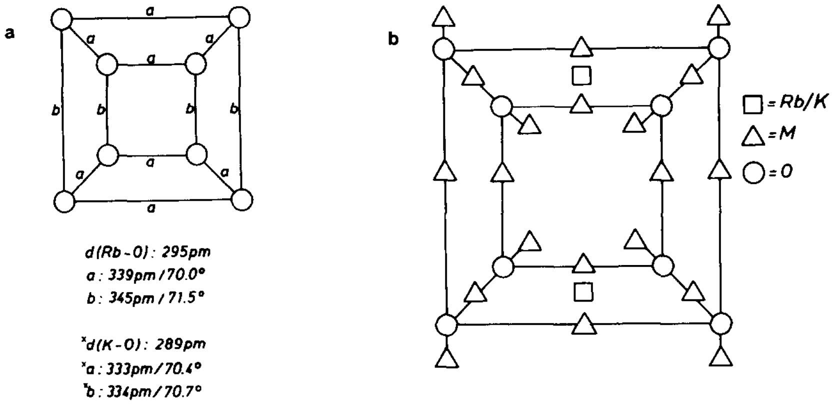

FIG. 1. (a) Schlegel projection of the $CP(\text{Rb}^+)$ in $\text{RbLiMn}_3\text{O}_4$ and $CP(\text{K}^+)$ in KLiZn_3O_4. Interionic distances and angles are listed below (values for the zincate are marked). (b) Schlegel diagram, corresponding to the Schlegel projection.

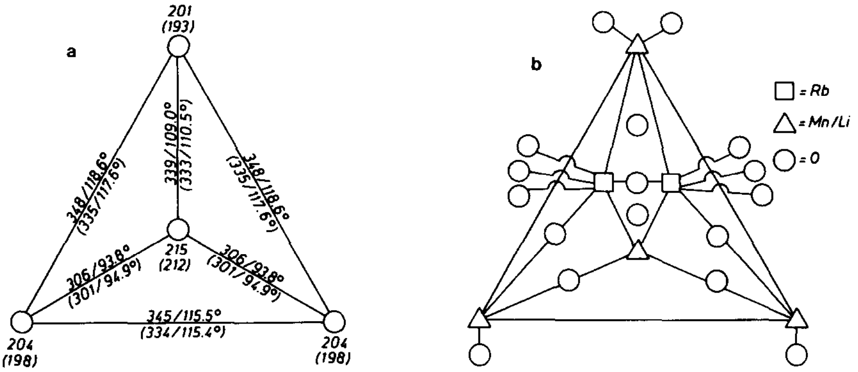

FIG. 2. (1) Schlegel projection of the $CP(M)$ in $\text{RbLiMn}_3\text{O}_4$ (M = Li,Mn) and KLiZn_3O_4 (M = Li, Zn). Distances and angles for the zincate are given in parentheses. (b) Schlegel diagram, corresponding to the Schlegel projection.

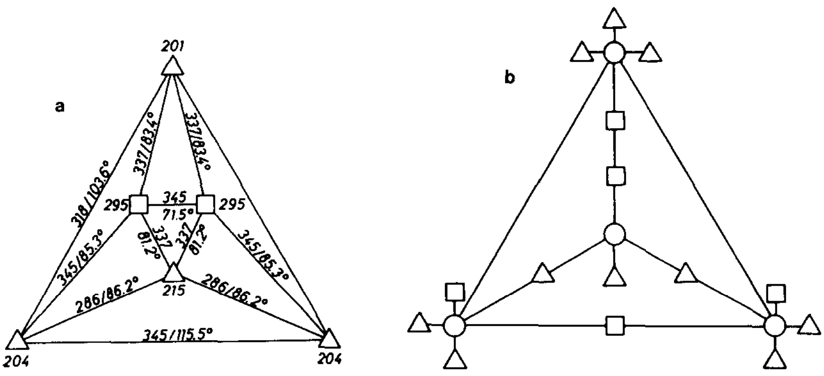

FIG. 3. (a) Schlegel projection and (b) Schlegel diagram of the $CP(\text{O})$ in $\text{RbLiMn}_3\text{O}_4$.

TABLE V

MOTIFS OF MUTUAL ADJUNCTIONS AND INTERATOMIC DISTANCES (pm) OF $RbLiMn_3O_4$ AND $KLiZn_3O_4$ (IN PARENTHESES)

	4 O	CN	ECoN	MEFIR
1 Rb (K)	8/2 295.0 (288.6)	8	8.2(8.2)	155(150)
4 M	1/1 + 2/2 + 1/1 201.2 203.8 214.5 (193.3 197.7 211.5)	4	3.9(3.8)	66(60)
CN	6	$M = 1\ Li^+ + 3\ Mn^{2+}$ ($RbLiMn_3O_4$)		
ECoN	5.9(5.9)	$= 1\ Li^+ + 3\ Zn^{2+}$ ($KLiZn_3O_4$)		
MEFIR	140(139)			

Note. CN, coordination number; ECoN, effective coordination number (*15*); MEFIR, mean fictive ionic radii (*15*) (calculated using ionic radii from Shannon (*20*)).

Further interatomic distances (A = K,Rb; M see above):

	A–2A	A–8M	M–2M	O–2O
$KLiZn_3O_4$	334.2	327.5	277.0	301.4
$RbLiMn_3O_4$	344.9	337.3	286.0	305.5

TABLE VI

THE MADELUNG PART OF LATTICE ENERGY (MAPLE) FOR $KLiZn_3O_4$ AND $RbLiMn_3O_4$ (kcal/mole)

Model I: Calculation by use of an average charge (1.75+) for disordered ions (Li^+, Zn^{2+} or Li^+, Mn^{2+} respectively)

Model II: Mean of the MAPLE values for the seven possible ordered arrangements of Li^+ and Zn^{2+}(Mn^{2+}) in the unit cell

		Binary	Model I	Model II			Binary	Model I	Model II
K	1×	104.9[a]	108.4	108.4	Rb	1×	100.2[a]	110.0	110.0
Li	1×	146.2[a]	428.9	215.6	Li	1×	146.2[a]	414.4	207.8
Zn	3×	550.9[a]	428.9	509.9	Mn	3×	521.8[a]	414.4	492.8
O	4×	529.9[b]	528.3	528.3	O	4×	505.9[c]	512.3	512.3
Σ		4023.3	3937.2	3966.9	Σ		3835.4	3816.8	3845.4
Deviation			−2.1%	−1.4%	Deviation			−0.5%	+0.2%

[a] From K_2O, Rb_2O, Li_2O, ZnO, respectively, and MnO.

[b] Corresponding value from K_2O, Li_2O, and ZnO.

[c] Corresponding value from Rb_2O, Li_2O, and MnO.

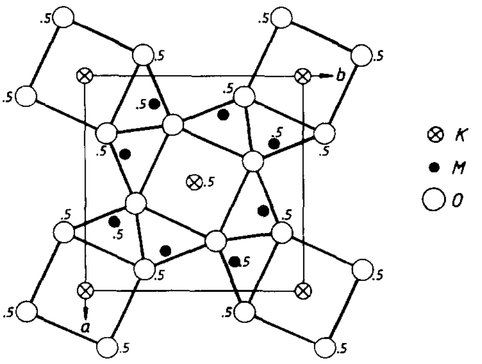

FIG. 4. Projection of the structure of $KLiZn_3O_4$ down the c axis (heights $x = 0$ are omitted).

(Zn^{2+}). The discrepancy between corresponding values can be regarded as acceptable.

Closing Remarks

Like in $KLiZnO_2$ (*4*) and $KLiMnO_2$ (*5*) the similarity between the zinc and manganese oxides is striking. In the case of other oxides of the type $ANaM_3O_4$ (with A = K, Rb, Cs and M = Mn, Zn) we find principally the same structural features, but in every case there is an unsolved superstructure observed. Other members of this family are the tetragonal oxides $NaLi_3SiO_4$ and $NaLi_3GeO_4$ (*17*), the triclinic compounds KLi_3MO_4 (M = Si, Ge, Ti) (*8*) and $CsNa_3PbO_4$ (*18*), and surprisingly KLi_3PbO_4 (*19*).

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